KINETICS OF NONISOTHERMAL ADSORPTION BY BIPOROUS ADSORBENTS.

COMMUNICATION 7. ADSORPTION KINETICS UNDER QUASIADIABATIC CONDITIONS

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Analysis of experimental data on the kinetics of nonisothermal adsorption by microporous adsorbents has shown that in many cases thermal effects play an important role [1-6]. This led to the development of various theoretical models and the creation of new experimental techniques for studying the kinetics of nonisothermal adsorption. A model that has been analyzed in greater detail than others includes diffusion in the transport pores and a fixed rate of dispersion of the heat of adsorption from the surface of the adsorbent granules [2, 4-10]. Methods have been developed for determining the parameters of mass and thermal transport [4, 7, 8, 10], which make it possible to analyze experimental kinetic and temperature curves, and to determine the contribution of, and calculate the parameters for, various types of mass and thermal transport.

In analyzing the role of mass and thermal transport in the kinetics of nonisothermal adsorption another approach is possible, namely, selecting experimental conditions so as to exclude the effect of any type of transport, or to make it negligible. In [11, 12], it is shown that the difference between the temperature of the adsorbent T_0 and that of the adsorbed gas T_V substantially affects the adsorption process. Depending on the heat-exchange conditions, two different types of mechanisms may be operating in the experiments: quasiisothermal intracrystalline diffusion (at $T_0 > T_V$), and essentially nonisothermal mass transport (at $T_0 \leqslant T_V$) [11]. In the latter case the process is interpreted as transport over a heat barrier formed on the surface of the crystals by the evolution of the heat of adsorption. It is assumed that by minimizing the temperature of the adsorbate one can choose experimental conditions so that the coefficients of mass transport are the same as the coefficients of diffusion obtained by independent techniques, for example, by NMR. The observed effect can be used as direct experimental proof of the influence of the rate of heat dispersion on the kinetics of adsorption [11, 12], but it is not, apparently, suitable for quantitatively determining the role of the various types of mass and thermal transport. During the process of adsorption the adsorbent is warmed by the heat of adsorption and the subsequent heat exchange between the adsorbent, cooled by the adsorbate and the external medium (the thermostat), and pseudo-isothermal conditions may result by chance due to the off-setting effects of the different heat- and mass-transfer processes. However, a quantitative analysis of the overall process and its component parts is extremely difficult.

The method proposed here for assessing the role both mass and heat transfer play in the kinetics of adsorption is based on conducting experiments under quasiadiabatic conditions where the temperature of the thermostat is maintained equal to the temperature of the adsorbent, and heat exchange between the granule of the adsorbent and its surroundings does not occur. Since at present it is not considered possible to analyze the general case of the kinetics of adiabatic adsorption, we shall consider just the limiting cases, when the rate of the adsorption process is basically determined either by external heat exchange or by internal diffusion.

EXPERIMENTAL

The experiments were carried out on an automatic gravimetric apparatus used for adsorption kinetics studies [13]. Plates of CaA zeolite 0.18 cm thick were thermostatted at temperature T_k, and the adsorbate, Xe or n-butane, was thermostatted at temperature T_0. Immediately before the experiment the liquid thermostat containing the adsorption vessel was replaced by a thermostat at temperature T_0. Preliminary experiments showed that in a vacuum
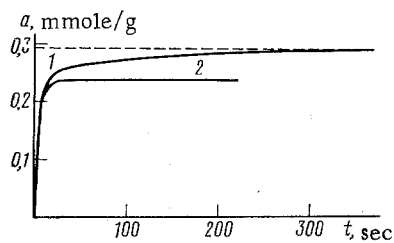
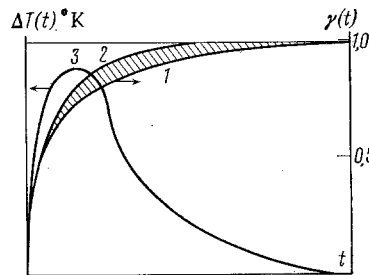Fig. 1   Fig. 2

Fig. 1. Kinetic adsorption curves for Xe on CaA zeolite
obtained under the conditions $T_0 = T_k = 295.8°K$ (curve 1)
and quasiadiabatic conditions $(T_k = 295.8, T_0 = 303°K)$
(curve 2).

Fig. 2. Scheme for determining the role of heat and dif-
fusion components in the kinetics of nonisothermal adsorp-
tion: 1) overall kinetic curve; 2) hypothetical kinetic
curve under isothermal conditions; 3) temperature curve.
The hatched area represents the contribution of the heat
component M_q to the overall first moment of the kinetic
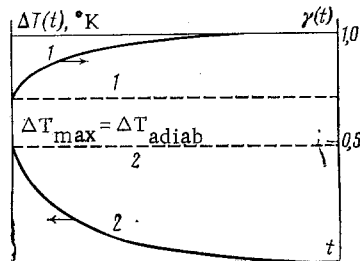curve.

Fig. 3. The kinetic (1) and temperature (2)
curves of a two-stage nonisothermal adsorp-
tion under nonisothermal (solid lines) and
quasiadiabatic (dashed lines) conditions.

heat exchange between the adsorbent plate and the walls of the thermostat proceeds very
slowly, and upon changing the thermostat the temperature of the plate remains, to all in-
tents and purposes, unchanged and equal to T_k. The temperature T_k was selected such that
the adsorbent temperature would remain close to T_0 as it was heated by the heat of adsorp-
tion. After the adsorbate was admitted, the change in weight of the adsorbent was recorded
as a kinetic curve.

Figure 1 shows kinetic adsorption curves for xenon on a plate of CaA zeolite obtained
under the usual nonisothermal conditions at $T_0 = T_k$ (curve 1) and under pseudoadiabatic
conditions (curve 2).

RESULTS AND DISCUSSION

For the model of nonisothermal adsorption kinetics that takes into account diffusion
in the transport pores and the dissipation of the heat of adsorption from the surface of
the granule, the first moment of the kinetic curve M, can be considered to be constant with
respect to time and equal to the sum of the diffusional component M_D and the dissipation of
the heat of adsorption M_q, also constant with respect to time [7, 8]:

$$M_1 = M_D + M_q \tag{1}$$

The principle used to estimate the role of the diffusional and the thermal components
in nonisothermal adsorption kinetics is represented schematically in Fig. 2. Line 1 repre-
sents the overall kinetic curve; line 2 is the hypothetical kinetic curve under isothermal
conditions, for which the first statistical moment is equal to the diffusional component M_D.
The difference between the first statistical moments of kinetic curves 1 and 2 represents

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the contribution of the thermal component M_q. The thermal component of the first moment can be determined from independent measurements of the temperature curve (cf. Fig. 2, curve 3) [7, 8]:

$$M_q = \mu_0 \lambda / \Delta a_\infty \tag{2}$$

where μ_0 is the zero moment of the temperature curve; $\Delta a_\infty = (a_\infty - a_0)$; a_∞ is the equilibrium concentration of adsorbate; and a_0 is the concentration of the adsorbate at the initial moment of time.

If diffusion proceeds at an appreciably faster rate than heat exchange, adsorption is a two-stage process (Fig. 3). Initially there is a rapid coverage of the adsorbent under quasiadiabatic conditions which is accompanied by the heating of the granule to the maximum temperature T_{max}. The amount of adsorption at this time and later is an equilibrium quantity for the pressure of the adsorbate and the temperature of the adsorbent. During the second stage of the process the adsorbent slowly cools to the temperature of the thermostat T_0, thereby increasing the amount of adsorption. If the temperature of the thermostat is equal to T_{max} at the end of the first stage, cooling of the granule will not occur and the further course of the adsorption process will correspond to the kinetic and temperature curves represented in Fig. 3 by dashed lines. In this case the thermal component of the kinetic curves associated with the finite rate of the dissipation of the heat of adsorption is lacking, since there is no thermal emission from the granule to its surroundings.

In the limiting case, when diffusion occurs practically instantaneously ($M_D \ll M_q$), in order to create quasiadiabatic conditions for adsorption the adsorbent must be at the temperature T_k before the experiment begins. This temperature, T_k, is less than the temperature at which the experiment is run T_0 by the amount ΔT_{adiab}, which is determined from the heat balance equation:

$$\Delta T_{adiab} = T_0 - T_k = q \Delta a_\infty / c_k \tag{3}$$

where q is the heat of adsorption and c_k is the heat capacity of the adsorbent. It is assumed that the heat generated upon adsorption is consumed in warming the adsorbent, and that the heat capacity of the adsorbate can be ignored. Since the temperature of the adsorbent rises to exactly that of the thermostat, there is no heat exchange between the granule and its surroundings.

It can be seen from Fig. 1 that the adsorption of Xe onto plates of finely crystalline CaA zeolite under nonisothermal conditions is a two-stage process. It was for this reason that temperature T_k was selected on the basis of Eq. (3). The first statistical moment of the kinetic curve obtained under quasiadiabatic conditions ($M_1 = 4$ sec), is substantially lower than the first statistical moment of the nonisothermal kinetic curve ($M_1 = 22$ sec). For this reason it can be asserted that for the Xe—CaA zeolite adsorption system the rate of the process is basically controlled by the external heat exchange between the adsorbent and its surroundings. When the method described is applied to the n-butane—CaA zeolite system, the shape and the first moment of the kinetic curve remain practically unchanged. Evidently, in this case the influence of thermal effects on the kinetics of adsorption can be ignored, and the adsorption process can be defined by the rate of internal diffusion transport.

CONCLUSIONS

1. A method is proposed for studying the kinetics of nonisothermal adsorption under quasiadiabatic conditions that enables the role of mass and thermal transport in the overall adsorption process to be evaluated.

2. For the adsorption of xenon on CaA zeolite the process is basically controlled by the dissipation of the heat of adsorption, while for the adsorption of n-butane by a plate of CaA zeolite 0.18 cm thick, heat effects can be ignored at low surface coverages.

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CAPILLARY CONDENSATION AND THE POROUS STRUCTURE OF ADSORBENTS

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The pore volume distribution as a function of radius as calculated from isotherms of sorbed vapors is widely used to characterize and describe the structures of adsorbents and catalysts. The common methods of analyzing the pore volume distribution on the basis of experimental data on the capillary condensation of vapors are described in [1]. In later works attention was focused primarily on substantially improving the precision of the calculations for the cylindrical pore model [2], as well as accounting for the thickness of the adsorbed layer [3, 4] as a function of surface tension due to the curvature of the meniscus [5-9].

These studies were based on the theory of capillary condensation, in which porosity is described as a system of noninterconnected capillaries. Applying the methods of percolation theory makes it possible to model processes in porous media as occurring in three-dimensional lattices formed by these pores [10].

In the present paper the pore volume distribution as a function of radius is calculated by the percolation theory model, and the results are compared with data obtained by the Kelvin and Dubinin methods.

MSK silica gel with a specific surface area $S_{BET}^{N_2}$ = 218 m²/g was used as the adsorbent. A gravimetric apparatus was used to obtain the adsorption isotherm of n-pentane on this silica gel at 20°C (Fig. 1; a is the amount adsorbed, in mmoles/g; p/p_s is the relative equilibrium pressure).

On the basis of this isotherm the pore volume distribution as a function of radius has been calculated by three methods: I) one based on Kelvin's equation; II) the method of Dubinin accounting for the thickness of the adsorbed layer; III) a method based on percolation theory. In all cases the cylindrical pore model was employed in the calculations.

I. The classic method for calculating the pore volume distribution as a function of radius for capillary emptying of cylindrical pores is based on Kelvin's equation: