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 $T_a$ and that of the adsorbed gas $T_g$ substantially affects the adsorption process. Depending on the heat-exchange conditions, two different types of mechanisms may be operating in the experiments: quasi-isothermal intracrystalline diffusion (at $T_a > T_g$), and essentially nonisothermal mass transport (at $T_a < T_g$) [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 $T_a$. Immediately before the experiment the liquid thermostat containing the adsorption vessel was replaced by a thermostat at temperature $T_o$. Preliminary experiments showed that in a vacuum
Fig. 1. Kinetic adsorption curves for Xe on CaA zeolite obtained under the conditions \( T_0 = T_k = 295.8^\circ K \) (curve 1) and quasadiabatic conditions \( (T_k = 295.8, T_0 = 303^\circ K) \) (curve 2).

Fig. 2. Scheme for determining the role of heat and diffusion components in the kinetics of nonisothermal adsorption: 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 adsorption under nonisothermal (solid lines) and quasadiabatic (dashed lines) conditions.

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 \( M_1 \), 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]:

\[
M_1 = M_D + M_q
\]

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 represents 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...