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Estimation of a Potential Contribution of Bed-Structure Regularization to Adsorber Downsizing in Adsorption Gas Separation

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Abstract—Five similarity criteria for adsorption systems have been formulated as follows: (1) the ratio of the adsorber length to the thickness of the front; (2) the adsorber output; (3) the relative molar density of the adsorbate at the adsorber inlet; (4) the ratio of the grain saturation time to the residence time of a grain in the front zone; and (5) the Peclet number, composed of the filtration rate, specific size of the filtration area (grain radius or half-width of gaps between sheets), and molecular diffusion coefficient. The values of these criteria change with modification of the tortuosity of transport nanopores. Simple mathematical analysis has shown that the adsorber volume decreases in proportion to the decrease in the nanopore tortuosity induced by bed-structure regularization. The pressure drop through the adsorber, as well as power consumption, will remain unchanged.

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The main indicators of gas separation are the product purity, output, power consumption per unit product, and adsorber size. The utilization efficiency of the adsorbent volume is also relevant: this parameter characterizes the accessibility of the inner surface of adsorbent grains. The accessibility depends on the structure of the transport pore system and the arrangement of adsorption-active particles (crystallites) in the bulk of grains. The effect of structure regularization at the adsorbent grain level was analyzed for a model separation of active and inert components by the frontal displacement of the latter by a two-component gas from the adsorber packed with a particulate zeolite adsorbent.

Zeolites are microporous materials. Pores, united into a regular spatial structure of voids and necks between them, have subnanometer sizes [1]. Adsorption on such materials occurs via bulk filling, i.e., avoids formation of polymolecular layers and capillary condensation [2]. The characteristic grain sizes for adsorbents based on NaX or CaA zeolites produced in Russia range from split millimeter to several millimeters. As a rule, adsorbent grains are formed of zeolite crystallites (20–50 nm) and a binder, usually kaolinite or bentonite, in a proportion of 16–20 to 100 (wt/wt). Crystallites are grouped into clusters, which are randomly distributed over the binder phase (Fig. 1).

This representation implies that pores in a zeolite adsorbent grain form a hierarchic structure of three interpenetrating substructures:

(1) inside each grain, there is a unimodal regular micropore network, constituted by voids and necks between them with characteristic sizes of $\rho_{mi} \leq 1$ nm.

(2) Inside a cluster, which is a random pack of crystallites, there is a virtually unimodal nanopore structure formed by intercrystallite spaces; the characteristic sizes of these intercrystallite spaces, ρ_n, are on the order of an individual crystallite size, i.e., 20–50 nm.

(3) The binder is penetrated by a random polymodal mesopore structure, with ρ_{me} on the order of several

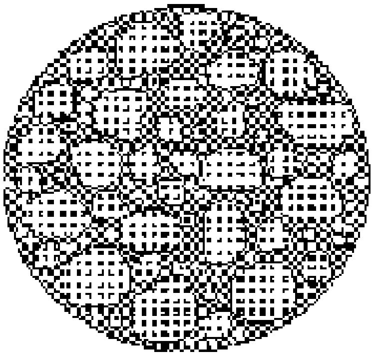

Fig. 1. Schematic of a zeolite adsorbent grain. Crystallite clusters (areas with uneven edges and white inclusions) are distributed over the bulk of the binder (shown in gray).

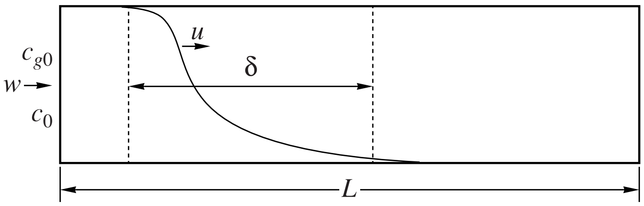

Fig. 2. Schematic of the adsorption front.

hundreds of nanometers, which is generated by annealing of zeolite plus binder blends. The following inequality holds:

$$\rho_{mi} \ll \rho_n \ll \rho_{me}.$$

Adsorbent grains form a random system of channels (macropores) that penetrate the adsorbent bed. The gas mixture to be separated is filtered through this system. Channel sizes are on the order of absorbent grain sizes, i.e., far greater than the intragrain pore sizes. The adsorptive concentration field for the gas mixture traveling through the bed obeys the convective diffusion equation with the longitudinal dispersion coefficient D. A natural assumption is that mass exchange between the gas mixture filtering through the bed and adsorbent grains is virtually never a rate-controlling stage. Therefore, the utilization efficiency of the adsorption capacity of a whole grain is controlled by the ability of gas molecules to overcome the in-grain diffusion drag.

The mesopore system of the binder and the nanopore system inside clusters play the role of the transport channels through which the adsorptive comes to crystallite surfaces in a zeolite grain. The structure of these interpenetrating systems is randomly formed during adsorbent preparation; it has a considerable inhomogeneity, which negatively influences the gas separation selectivity. Then, let us assume that

(1) transport of adsorptive molecules through the mesopore system of the binder is molecular diffusion with the effective molecular diffusion coefficient D_m;

(2) transport of adsorptive molecules through the nanopore system inside clusters is mixed (molecular plus Knudsen) diffusion with the effective molecular diffusion coefficient D_n;

(3) transport of adsorptive components through the micropore system in the bulk of crystallites, accompanied by adsorption proper, is activated diffusion.

A transition region is generated in the bed during adsorption, thin compared to the adsorber length L. The molar concentration of the active component in the gas flow in this transition region, c_g, varies from near zero to values close to the active component concentration at the adsorber inlet, c_{g0} (Fig. 2). This region is referred to as the adsorption front [3]. For equilibrium adsorption with a linear isotherm, an exact solution was obtained for the front shape problem [4]. From this solution, relationships for the front propagation rate u, the front thickness δ, and the residence time of an adsorbent grain in the adsorption front area τ_f are derived as below:

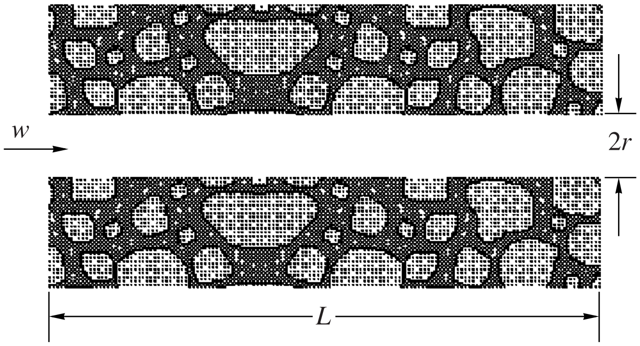

Fig. 3. Schematics of macroregular (planar) packing of adsorbent sheets in an adsorber. Gas is filtered between sheets in the Poiseuille flow.

$$u = w/(1-\varepsilon)k, \quad \tau_f = \frac{\delta}{u} = \frac{8(1-\varepsilon)kD}{\alpha w^2}, \quad \delta = 8D/w\alpha. \tag{1}$$

Here, ε is the volume density of voids in the bed (bed porosity), k is the Henry constant, $c_s = kc_g$ (c_s is the molar density of the active component in the adsorbent phase), w is the reduced gas velocity at the adsorber inlet, and $\alpha = c_{g0}/c_0$ (c_0 is the molar gas density at the adsorber inlet). The natural inequality $k(1-\varepsilon) \gg \varepsilon$ was used in the derivation of relationships (1). This inequality means that the weight of the active component in the gas phase can be ignored compared to its weight in the adsorbent phase. In derivation of the expression for the front thickness δ, in addition, it was taken for certainty that the relative densities of the active component at front boundaries, c_g/c_{g0}, are e^{-4} (~0.018) and $1 - e^{-4}$ (~0.982), respectively. The similarity parameters for an adsorption system are

$$A = L/\delta, \quad Q = Sw, \quad \alpha, \tag{2}$$

where S is the cross-sectional area of the adsorbent.

MACROREGULARIZATION

The regularization of grain packing is a way to improve the utilization efficiency of the adsorbent volume, as proposed in [5] for catalytic beds. Such regularization decreases the tortuosity of gas channels and enhances the decrease in the longitudinal dispersion for gas filtration through the bed, making the front more acute. Let us consider planar adsorbent packing in the bed, where adsorbent particles are biporous zeolite sorbent sheets lying at a distance of $2r$ from one another parallel to the adsorbent axis, to exemplify the limiting bed regularization (Fig. 3). For the filtration of a gas flow through planar slot channels, the longitudinal dispersion is represented as [6]

$$D = D_m + \frac{w^2 r^2}{48\varepsilon^2 D_m}, \tag{3}$$

where the second term is Taylor diffusion [7]. Let us compose the Peclet number from the reduced filtration velocity, half-width of the gap, and molecular diffusion coefficient, as follows:

$$Pe = wr/\varepsilon D_m. \tag{4}$$

If $Pe \ll 1$ (which occurs with decreasing gaps between adsorbent sheets), the second term in Eq. (3) should be ignored; therefore, molecular diffusion remains the only contributor into the longitudinal dispersion. Let us compare the residence time of an element of an adsorbent sheet in the adsorption area, τ_f, with the saturation time of a particle with an adsorbate, τ_s. Setting that the arrival of adsorptive molecules to the outer surface of zeolite crystallites through nanopores inside clusters is the rate-controlling stage, we can demonstrate that $\tau_s = kr_s^2/D_n$, where D_n is the diffusion coefficient in nanopores and r_s is the characteristic cluster size; from general considerations, $r_s \ll r$. Let us compose the relationship

$$\frac{\tau_s}{\tau_f} = \frac{\alpha r^2 w^2}{8(1-\varepsilon)D_n D_m}. \tag{5}$$

This relationship, together with the Peclet number (4), should be added to the similarity parameters (2). If the equilibrium adsorption model is used, the strong inequality $\tau_s/\tau_f \ll 1$ should hold; i.e., adsorption equilibrium should be acquired while clusters reside in the front area.

MICROREGULARIZATION

A way to improve the utilization efficiency of the adsorbent-grain volume is to regularize the nanopore system, i.e., to direct the synthesis to the generation of the nanopore system with the minimum dispersion of the pore-size distribution. Let us assume that crystallites, previously distributed chaotically, now form a regular structure (Fig. 4) in the bulk of a sorbent particle. The nanopore tortuosity will substantially decrease, and the diffusion coefficient in nanopores, D_n, will increase by a factor of β (the literature data indicate that the tortuosity factor ranges within $1.5 \le \beta \approx 3$ [6]).

For equality (5) to hold, it is necessary that the velocity change as $w \longrightarrow w\sqrt{\beta}$ with changing tortuosity. From expression (1), the adsorption front thickness in this case should change as $\delta \longrightarrow \delta/\sqrt{\beta}$. Next, in order for criterion A (Eq. (2)) to retain its value, the bed length should change as $L \longrightarrow L/\sqrt{\beta}$; and for criterion Q (2) to retain its value, the bed cross section should change as $S \longrightarrow S/\sqrt{\beta}$. Thus, the adsorber volume should change as $SL \longrightarrow SL/\beta$, i.e., should decrease in β times in response to the regularization of the nanopore system. Inasmuch as the Poiseuille flow occurs in gaps between adsorbent sheets (for which the pressure drop along the length L is $\Delta p \approx wL/r^2$), then for a fixed r (adsorbent particle packing step), the pressure drop remains unchanged.

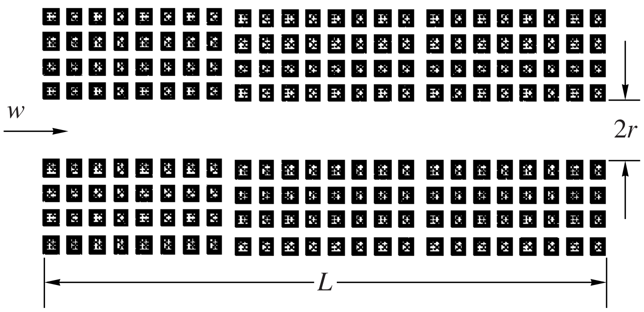

Fig. 4. Schematics of macro- and microregular adsorbent packing in a sheet. Squares, zeolite crystallite; gaps between squares, transport nanopore system. Gas is filtered between sheets in the Poiseuille flow.

CONCLUSIONS

Five similarity criteria for an adsorption system have been considered to characterize product quality and adsorber output, as follows: (1) the ratio of the adsorber length to the thickness of the front; (2) the adsorber output; (3) the relative molar density of the adsorbate at the adsorber inlet; (4) the ratio of the grain saturation time to the residence time of a grain in the front zone; and (5) the Peclet number, composed on the basis of the filtration rate, the specific size of the filtration area (grain radius or gap half-width), and the molecular diffusion coefficient. The values of these criteria are shown to change with modification of the tortuosity of transport nanopores. If the complete regularization of transport nanopores is provided during adsorbent synthesis, the diffusion coefficient of the adsorptive in nanopores will increase about twofold. But it is necessary that all five similarity criteria of the adsorption system retain their previous values, i.e., that the product quality and adsorber output be retained. Simple mathematical analysis has shown that the adsorber volume decreases in proportion to the decrease in the nanopore tortuosity induced by bed structure regularization. The pressure drop in the adsorber, as well as power consumption, will remain unchanged.

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