Investigation of the mechanism of water transfer in catalysts and adsorbents

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Abstract

Drying is a key stage in numerous technological processes in the preparation of adsorbents and catalysts. A very efficient method preserving the quality of dried material is adsorption-contact drying (ACD). To calculate the rate of the mass transfer in the process of the ACD, it is necessary to have the data on the ratio between the gas-phase and liquid-phase transfer of moisture. A method to determine the rates for gas-phase and liquid-phase transfer of moisture in the process of mass transfer in porous materials is suggested. The data obtained agree well with the existing theoretical concepts about the liquid-phase transfer of moisture under the mechanical contact of two porous bodies. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Drying is a key stage in numerous technological processes in the preparation of adsorbents and catalysts. Conditions of drying may exert significant influence on characteristics of resulting catalytic materials. A very efficient method preserving the quality of dried material is adsorption-contact drying (ACD). ACD is based on the water transfer from a wet material (donor) to an adsorbent-drier (acceptor) at contact with following separation and regeneration of the acceptor at high temperatures in a special reactor. Such method allows a rapid drying of vari-ous porous materials (5–20 min) under mild conditions (down to 0°C).

To calculate the rate of the mass transfer in the process of ACD of a wet material contacting with a dry adsorbent, it is necessary to have the data on the ratio between the gas-phase and liquid-phase transfer of moisture, respectively. At present, the above ratio during the contact of porous bodies is determined via the method utilizing isotopically traced high-concentration salt solution [1]. Hence, it is difficult on the base of the experimental data to determine accurately the contributions of the gas-phase and liquid-phase transfers to the overall transfer of moisture. Here we suggest the method to determine the effect of geometrical sizes and pore structures of contacting bodies on the moisture transfer with application of the stable imidazo-

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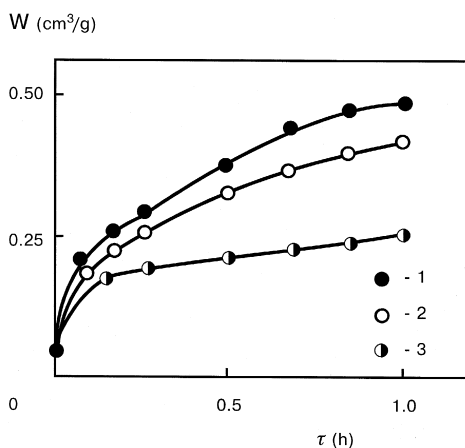[*] Corresponding author.

W (cm³/g)

Fig. 1. Wetness of the porous acceptor (W) as a function of time (t) of the mechanical contact with the porous donor. 1 — $R_d = \infty$, $R_a = 1.25$ mm; 2 — $R_d = 3.5$ mm, $R_a = 1.25$ mm; 3 — $R_d = 1.25$ mm, $R_a = 1.25$ mm.

line nitroxyl radicals, which permits to use pure solvents, including organic substances.

2. Experimental

The grains of Al_2O_3 2–3 mm in diameter with the total volume of pores $V = 0.82$ cm³/g and $S_{BET} = 200$ m²/g were used as a model porous acceptor. The same grains and porous corundum 7 mm in diameter with $S_{BET} = 1$ m²/g and $V = 0.14$ cm³/g were applied as a donor.

The acceptor was impregnated by a water solution to deposit the stable imidazoline nitroxyl radical (its concentration in the solution was 10^{-3} M/l) on its internal surface. Then the impregnated acceptor was dried in air at room temperature until the residual wetness of $W = 0.048$ g H_2O/g Al_2O_3. Then we placed in the quartz ampule a donor grain impregnated by water (wetness for corundum is 0.149 g H_2O/g, for alumina — 0.82 g H_2O/g) and an acceptor grain with the deposited radical. Experiments were carried out either with or without contact of the donor and acceptor. The intensity of ESR

spectra for the nitroxyl radical in the acceptor was recorded at different intervals of time. The amount of moisture transferred during the mass transfer was determined from the calibration curve for the intensity of the radical ESR signal vs. the wetness of the acceptor grains. The intensity of these signals was calculated as a product of the squared half-width for the utmost component of the spectrum by its height [2].

3. Results and discussion

The plotted dependences of the acceptor grain wetness on time for mass transfer with the donor are illustrated in Figs. 1 and 2 with their direct contact when both liquid-phase and gas-phase transfers take place (Fig. 1), and without contact when moisture is transferred only as vapor (Fig. 2). In the case of gas-phase transfer, the mass transfer is independent of the curvature of donor grains. During the contact of grains with increasing radii of the donor, moisture transfer to the acceptor is more intensive. This fact indicates the dependence of liquid-phase transfer of moisture on the geometrical size of contacting bodies. This phenomenon cannot be
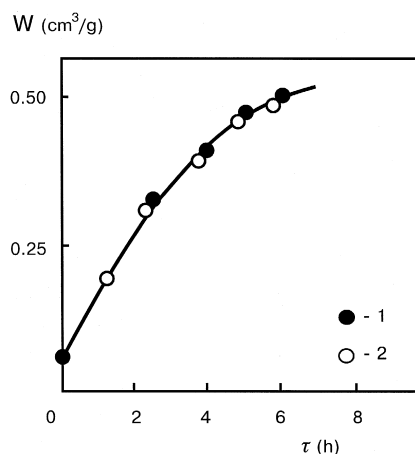
W (cm³/g)

Fig. 2. Wetness of the porous acceptor (W) as a function of time (t) of the mass transfer without contact with the porous donor. 1 — $R_d = \infty$, $R_a = 1.25$ mm; 2 — $R_d = 3.5$ mm, $R_a = 1.25$ mm.

Table 1
Calculated and experimental rates of the liquid transfer

A, cm^3/g h		B, cm^3/g h		Ratio of rates	
Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
0.336	661.5K_1	0.257	504.6K_1	1.30	1.31

interpreted in terms of the available concepts on contact moisture transferred.

For its interpretation we have suggested that the donor–acceptor contact produces a meniscus like in the case of capillary condensation in porous bodies [3,4]. Its size corresponds to the partial pressure of liquid vapors inside the donor grain, and the liquid-phase transfer is realized through the contact area formed by the meniscus on the acceptor grain. Using a model of a spherical meniscus [5,6], one can obtain the following expression for the contact area:

$$S_c = 2\pi R_a R_d r_d / (R_a + R_d) \tag{1}$$

where R_d and R_a are the radii for the donor and acceptor grains and r_d is the radius of the donor pores filled by water at given wetness.

Taking into account the dependence of the potentials for gas-phase and liquid-phase transfers on the pore structure of contacting bodies and the obtained expression for the contact area, the rates for the gas-phase and liquid-phase transfers of moisture can be written as:

$$j_g = K_g \Delta P_g \tag{2}$$

$$j_1 = K_1 \Delta P_1 R_a R_d r_d / (R_a + R_d). \tag{3}$$

Here ΔP_1 is the difference of capillary pressures for liquid in the donor and the acceptor

determined from the Laplace equation; ΔP_g is the difference of partial pressures of vapor in the donor and acceptor found from the Kelvin equation; $K_1(K_g)$ is the constant depending on the pore structure of acceptor and the physical properties of liquid (vapor).

Liquid-phase transfer rates during the contact of macroporous donor grains having various curvature radii, with the same acceptor, are listed in Table 1. These rates were calculated as a difference between the experimental total and gas-phase rates of moisture transfer (Table 2). Rates for the liquid-phase transfer of moisture were calculated from Eq. (3) using the Laplace equation for the ΔP_1 calculations at $W = 0.2$–0.3 cm^3/g. Radii for donor and acceptor filled by water were determined from the pore size distribution [7] and the material balance equations. As is seen, the ratio of the liquid-phase transfer rates agrees well with the calculated value, which makes it possible to determine K_1 typical for a given acceptor. In a similar way one can also calculate K_g for gas-phase transfer from the experimental data and ΔP_1.

A comparison of the total rate for moisture transfer in case C (Table 1), where a donor with a mesoporous structure was used, with the gas-phase transfer rate, e.g., in case A, shows that here, the gas-phase transfer of moisture is predominant. This agrees with the previous data

Table 2
Experimental rates of the moisture transfer under various mass transfer conditions

Moisture transfer rate	Value in cm^3/g h		
	A	B	C
j_{g+1}	0.4444	0.366	0.089
j_g	0.108	0.108	–

Table 3
The calculated transfer rate under contact of the acceptor with a mesoporous donor (case C, Table 2)

j_1 (cm^3/g h)	j_g (cm^3/g h)	j_{g+1} (cm^3/g h)
5.07×10	0.0866	0.0871

[1]. Calculation of the rates for the gas-phase and liquid-phase transfers of moisture using formulas 2 and 3 and the calculated values of K_l and K_g, confirms that in this case the former rate is higher than the latter (Table 3).

4. Conclusion

Our experiments with the nitroxyl radical demonstrate that the mass transfer at the contact of the wet and dry porous materials is affected by way of the liquid-phase and gas phase transfer of water. The method allows to define the ratio between the two mechanisms of the mass transfer. It was shown that the rate of the liquid-phase transfer depends on geometrical size and pore structure of the contacting materials.

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