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Kinetics of spontaneous water-N_2 imbibition in carbon molecular sieves

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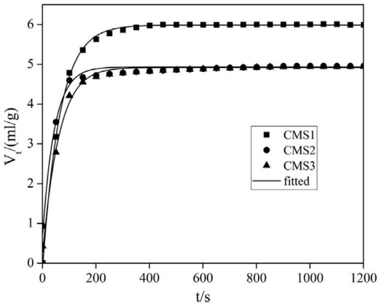
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a new kinetic model of spontaneous liquid-gas imbibition (SLGI) for microporous adsorbents has been developed. With three carbon molecular sieves (CMS) as adsorbents, N_2 as gas probe and water as liquid probe, the kinetics of spontaneous water-N_2 imbibition in CMS has been investigated at atmospheric pressure, and the applicability of the kinetic model to the SLGI has been assessed. The influences of the particle size of CMS and the experimental temperature in the range of 20–35 °C on the imbibition process have been analyzed based on the kinetic model. The relations between the kinetic parameters of the SLGI and the microporous parameters of the CMS obtained by CO_2 adsorption at 273 K have been elucidated. The results indicate that the imbibition process is controlled by the diffusion of the water molecules into and N_2 out of the micropores and the adsorption of the water on the pore surface of the CMS. The equilibrium gas recovery is positively related with the micropore volume, and the gas recovery rate depends mainly on the micropore size of the CMS.

1. Introduction

The porous materials with abundant micropores are widely used in catalysis, adsorption, separation and purification [1–4]. The characterization of micropores is, therefore, of great significance. N_2 adsorption at 77 K is the most common method for the characterization of micropores and mesopores [5–8]. However, it is invalid for the micropores comparable to the diameter of the adsorbate, such as those in carbon molecular sieves (CMS), because the diffusion of the adsorbate molecules in the micropores is limited and the adsorption is difficult to reach equilibrium at low temperature [9]. As an alternation, the method based on CO_2 adsorption at 273 or 298 K has been put forward. The kinetic energy of CO_2 molecules is large enough to enter into the micropores at these temperatures [10,11]. Yet high pressure is required for the CO_2 adsorption, because the critical pressure of CO_2 is as high as 7.39 MPa at room temperature [12].

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Spontaneous liquid-gas imbibition (SLGI) has been successfully to characterize the mesopores and macropores structure of cement stone, mortar and concrete by measuring the diffusion capacity and diffusion distance of liquid molecules in the pores [13,14]. In this process, the wetting phase, i.e., the liquid, spontaneously invades into the pores, and the unwetting phase, i.e., the gas in the pores, is driven off simultaneously. The SLGI process occurs also in micropores [15,16]. However, the fluid is in a special confined state in micropores, its properties are quite different from the macroscopic state, and the SLGI based on the capillarity is not available to the characterization of micropores [17–21]. Hence new methods are needed to describe the adsorption and diffusion of fluid in micropores [22–24].

The gas adsorbed in the micropores of molecular size level is in condensed state, and so that the gas driven off from the micropores during SLGI could be measured accurately [25,26]. In this sense, our group has developed a method based on SLGI by measuring the gas recovery kinetics and capacity to obtain the information of the pore structure of microporous materials. As a preliminary study, spontaneous water- N_2 imbibition at 293 K and 0.1 MPa was conducted [27]. The micropore size of CMS was assessed by comparing the apparent density of N_2 in the CMS evaluated by the gas recovery volume and that calculated by grand canonical simulation, which is in consistent with the result obtained by N_2 adsorption at ambient temperature. Based on molecular probing principle, the size-exclusion property of the CMS was estimated through comparing the N_2 gas recovery by imbibition of the liquid probes with various molecular dimensions. Furthermore, the changes in the pore structure of CMS during chemical vapor deposition treatment were revealed. In a recent work of our group [28], the kinetics of spontaneous water-gas imbibition with O_2 and N_2 as gas probe separately was measured. By fitting the linear driving force (LDF) model [29–31] and the pseudo-second-order (PSO) model [32–34], it was found that the rate-limiting steps of the spontaneous water-O_2/N_2 imbibition are mainly the surface adsorption of water and the diffusion of the gas through the micropore mouth or interior in CMS. Based on the kinetics, a new assessment method for O_2/N_2 separation performance of CMS in pressure swing adsorption was established.

In this study, a new kinetic model of SLGI in CMS has been developed. With three CMS as adsorbents, N_2 as gas probe and water as liquid probe, the applicability of kinetic model to the SLGI system has been assessed. Still the influences of the particle size of adsorbents and experimental temperature on the spontaneous water-N_2 imbibition process were analyzed based on the kinetic model.

2. Materials and methods

Three commercial CMS were used as adsorbents, the gas probe was N_2 and the liquid probe was deionized water. Before imbibition test, the adsorbents were crushed to 0.90–1.70 mm, 0.45–0.90 mm, 0.28–0.45 mm and 0–0.28 mm fraction. Then the selected fraction was washed three times with distilled water, and dried overnight in the vacuum drying oven at 423 K.

The experimental setup and procedure of SLGI have been described in detail in previous publication [28]. Briefly, the pretreated adsorbents and the water were firstly saturated with the gas probe, then the adsorbents were immersed in the water and the SLGI process took place. The pressure of the sample chamber P_t (kPa) with time in SLGI process was measured, and then converted to the volume V_t (ml·g^{-1}) of gas recovered by the water imbibition in standard condition (T_0 = 273.2 K, P_0=101.325 kPa) by the equation

$$V_\mathrm{t} = \frac{(P_t - P_{t=0})(V_s - V_l)T_0}{P_0 T} \quad (1)$$

Table 1
Micropore parameters of CMS from CO_2 adsorption at 273 K.

Adsorbent	V_{mic}/cm^3•g^{-1}	D_{mic}/nm	S_{mic}/m^2•g^{-1}
CMS1	0.2107	0.5760	731.7
CMS2	0.2023	0.6226	649.8
CMS3	0.1974	0.6136	643.1

where V_t (ml·g^{-1}) is the gas recovery volume at time t, P_t (kPa) is the pressure at time t, $P_{t=0}$ (kPa) is the initial pressure in the sample chamber, V_s (ml) is the volume of the sample chamber, V_l (ml) is the volume of the water, and T (K) is the experiment temperature.

The gas recovery coefficient η obtained by the Eq. (2) was introduced to calculate the net gas recovery volume by subtracting the volume occupied by the liquid vapor in the evolved gas. Here P_s (kPa) is the saturated vapor pressure of water at the given temperature.

$$\eta = \frac{P_0 - P_S}{P_S} \quad (2)$$

Based on the method raised by Cazorla-Amorós D [10,11], the CO_2 adsorption isotherms of CMS obtained at 273 K and 0–100 kPa were measured on a JW-BK112W static volumetric absorption apparatus and analyzed by the Dubinin-Radushkevich (DR) equation. The obtained micropore parameters, i.e. the micropore volume V_{mic} (mL•g^{-1}), micropore mean pore size D_{mic} (nm) and micropore specific surface area S_{mic} (m^2•g^{-1}), are shown in Table 1.

3. Result and discussion

3.1. Kinetic model for SLGI

The SLGI process consists of several steps, i.e., the diffusion of the liquid probe from the bulk fluid to the external surface of the adsorbent and enters into the pores of it, the adsorption of the liquid probe and simultaneous desorption of the pre-adsorbed gas probe on the internal surface of the adsorbent, and the diffusion of the desorbed gas through the pores and further through the liquid film on the external surface of the adsorbent [28]. The limiting step of the kinetics of SLGI depends on the pore structure and surface property of the adsorbent, and the molecular size, shape and polarity of the gas and liquid probes. In specific experimental condition, where the effect of the external diffusion of liquid and gas molecules through the liquid film could be excluded as in the case of this study, the dominating kinetic resistances in SLGI process could be attributed to the diffusion of liquid molecules into and gas molecules out of the pores and the surface adsorption of liquid molecules in the pores.

To get the kinetic model of SLGI, the following assumptions are proposed: (1) The gas molecules exist in a confined state in the micropores, and its density is greater than that of the gas in the bulk, but not greater than that in liquid state; (2) The diffusion of liquid molecules in the microporous adsorbent occurs spontaneously; (3) The liquid molecules enter into the microporous adsorbent at a certain rate and the gas molecules are discharged at the same rate; (4) The diffusion rate of the liquid probes into and the gas probes out of the pores and the surface adsorption rate are constant, and they depend only on temperature. In this case, the diffusion rate of liquid into or gas out of the pores is essentially proportional to the difference between equilibrium gas recovery volume and the gas recovery volume at any time:

$$\frac{dV_1}{dt} = m(V_e - V_t) \quad (3)$$