Redistribution of Adsorbed VOCs in Activated Carbon under Electrothermal Desorption

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Electrothermal desorption is an electricity-promoted desorption technology developed only in the last decade. It is extremely efficient and straightforward when the adsorbent is electrically conductive, since heating can be achieved by the Joule effect. The volatile organic compound (VOC) vapors desorbing from micropores might redistribute and condense in mesopores with high concentration, which is possible since no dilution occurs. To study this problem, benzene and activated carbon were used as the working system, and a theoretical analysis was developed. In a wide temperature range up to 400°C, no VOC vapor could be condensed in mesopores with the strong micropore adsorption effect. With the weak micropore adsorption effect, however, mesopore condensation will occur, but it only takes place in mesopores smaller than 3 nm in diameter, and the amount is generally negligible. To prevent any possible condensation, the desorption temperature should at least equal the liquid boiling point calculated in a 2-nm capillary tube.

Introduction

As an established technology, adsorption has found wide applications in purification and separation of gas mixtures. For removal and recovery of the volatile organic compound (VOC) components, adsorption on activated carbon (A.C.) is most commonly used since the nonpolar substances have a relatively high affinity for the hydrophobic carbons. The adsorption capacity of VOC in A.C. is usually appreciable, for example, on the order of 0.4 to 0.5 mL/g, due to the highly developed porous structure. As an example of an industrial application, a VOC recovery facility with a capacity of 125 kg/h in methylene chloride, 2.7 kg/h in carbon monoxide, and traces of methanol, formaldehyde, and dichloromethyl ether, has been installed in a company that produces herbicides (Thermatrix Inc., 2001). Nevertheless, the present adsorption technology is still subject to some engineering problems, for example, the long operation time and high energy required for the desorption operation, and in addition, recovery of the VOC is still a difficult task. To develop a novel compact plug-in adsorption device (CPAD), electrothermal desorption should be considered as a good candidate.

Electrothermal desorption shows some distinctive advantages over the conventional steam-heated method. In the latter process, steam is introduced into the system and then comes in contact with the adsorbent. In spite of its high heat-transfer efficiency, the negative effects are obvious (Erpelding and Bart, 1998). Since the steam is in contact with the cold adsorbent, water condensation will frequently occur on the external and internal surfaces of the adsorbent. This may seriously decrease the mass-transfer rate of VOCs from the adsorbent to the gas phase or may even destroy the structure of the adsorbent. Moreover, contamination of water by VOCs would give rise to some additional environmental pollution.

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Electrothermal desorption is a promising new solution to such desorption problems when electricity is employed instead of steam (Petkovska et al., 1991; Bonnissel et al., 1998). However, one should keep in mind that VOC may be condensed in the mesopores when it is removed from the micropores. Because VOC is not diluted under electrical heating, and its concentration can be much higher than the typical relative pressure of 0.35, which has been considered as the condition of condensation in the mesopore. The purpose of this article is thus to provide an analysis of the possibility of condensation of VOC in the mesopores when it is released from the micropores during electrothermal desorption.

Theoretical Establishment

To establish the theoretical background for the electrothermal desorption of VOC from the adsorbent, a working system composed of benzene and activated carbon may be considered for illustration.

Phase equilibria within the micro- and mesopores

Because the VOC molecules and the micropores are similar in size, adsorption of gases within micropores usually follows a pore-filling process rather than a surface adsorption mechanism as described by the Langmuir or BET equations. Instead, the Dubinin equations, especially the Dubinin–Astakhov (DA) equation, are often employed (Dubinin, 1989; Do, 1998)

$$W = W_0 \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \qquad (1)$$

where W_0 is the micropore volume; A is the chemical potential defined as $R_g T \ln(p_0/p)$; E_0 is the characteristic energy and is also a measure of the interaction between the adsorbate and adsorbent; n represents the reduction in freedom of the molecular movement due to the restriction by the pore wall; and β denotes the similarity of VOC with benzene, which is measured by the ratio of their molar liquid volumes.

For the purpose of this work, the following model parameters from Do (1998) are utilized

$$W_0 = 0.457\,\text{mL/g}, \qquad E_0 = 17.61\,\text{kJ/mol}, \qquad n = 1.46, \qquad \text{and} \qquad \beta = 1$$

The preceding parameter values are representative of benzene adsorption over the activated carbon, since the micropore volume of the activated carbon is normally between 0.25 and 0.5 mL/g, the characteristic energy is above 15 kJ/mol for the VOC, and n is from 1 to 3, depending on the relative magnitude of the adsorbate molecule diameter to the adsorbent pore size.

However, when the pore diameter is between 2 and 50 nm, and especially when the reduced pressure is greater than 0.35, the DA equation is no longer valid and should be replaced by a model in describing capillary condensation. The Kelvin equation is the theory used to describe the gas–liquid equilibrium within a capillary tube, but it is questionable when the pore size is only about 2–4 nm, since the pore wall potential field will influence the equilibrium. To account for the wall effect, the classic Kelvin equation should be modified (Yoshioka et al., 1997)

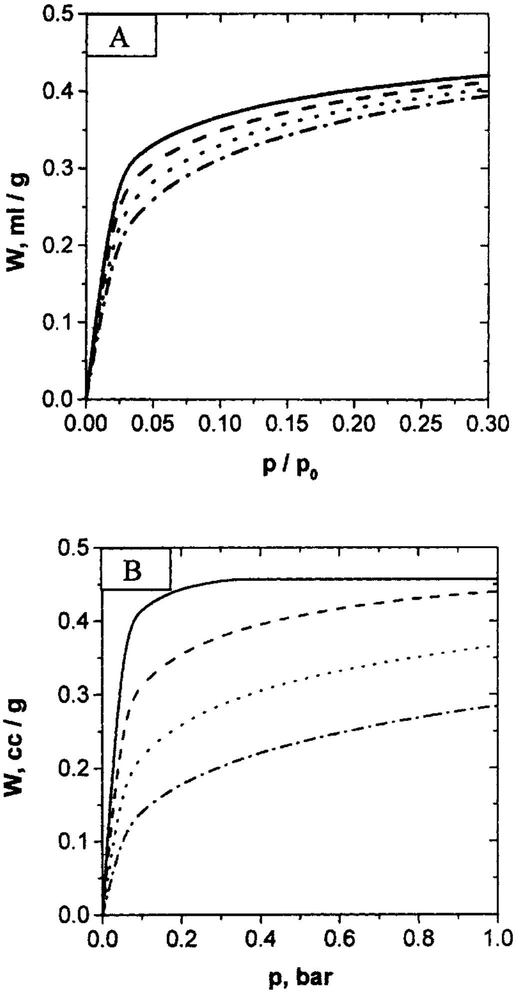

Figure 1. Isotherm for adsorption of VOC in the micropores.

(A) Temperature against the reduced pressure; (B) temperature against the absolute pressure. Temperature: —50°C; ----100°C; ····150°C; -·-·-200°C.

$$r_K = \frac{V_M \sigma \cos\theta}{R_g T \ln(p_0/p)} + t \qquad (2)$$

This correction is necessary, since the diameter of the benzene molecule is estimated to be 5.95 Å, which is not negligible when the pore diameter is only several nanometers.

For simplicity, the film thickness t in Eq. 2 may be taken as the molecular diameter of benzene, which implies that only one layer of molecules is adsorbed onto the pore wall prior to the capillary condensation.

The equilibrium relationships of pore filling and condensation are quite different as compared in Figures 1 and 2. In Figure 1, which is based on the pore-filling mechanism by Eq. 1, we see that the adsorption in the micropore is insensitive

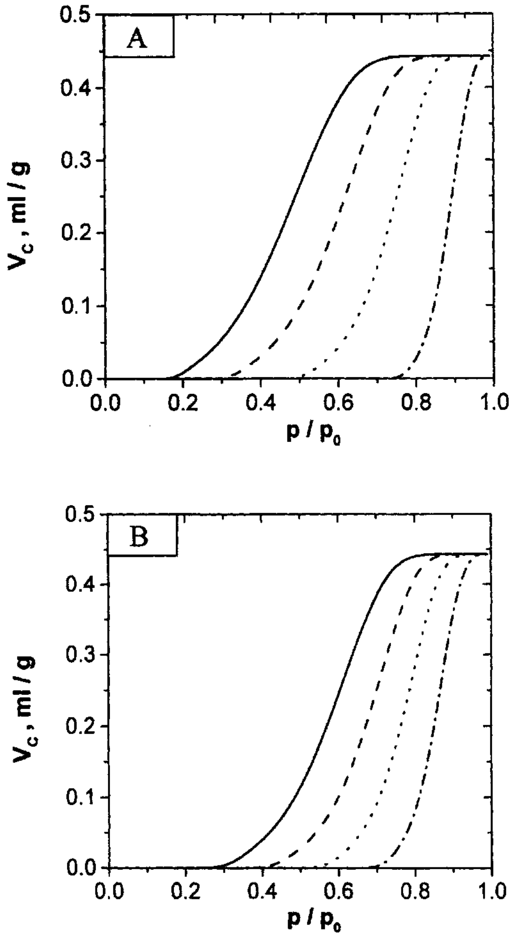

Figure 2. Thermodynamic condition for phase transition of VOC in the mesopore.

(A) Evaporation; (B) condensation. Temperature: — 50°C; ----100°C; ····150°C; —·—·—200°C.

to the pressure of VOC, but is sensitive to the temperature. On the contrary, in Figure 2A, which is obtained by Eq. 2, we see that adsorption due to condensation varies considerably with the gas-phase pressure, and the mesopore may be completely filled when the reduced pressure is over 0.95, even if the temperature is as high as 150°C. In Figure 2B, the desorption process is not simply the reverse of the adsorption, but shows a hysteresis phenomenon. We should point out that once the VOC condensate is produced in the capillary tube, the evaporation will be very slow because the desorption will be controlled by the vapor-phase diffusion. As an illustration, the evaporation rate of benzene from a Stefan tube to a flowing air stream is 4.3 mm/day (Do, 1998), which means the desorption time spent on evaporation will be on the order of 5 to 6 h, if the carbon pellet diameter is about 1.0 mm.

Since the VOC storage in the micropore can be as high as 40% of the weight of the adsorbent, condensation will be possible in the case of electrothermal desorption. To give an accurate prediction, we need to make a theoretical analysis based on the adsorbent structure as well as the adsorption thermodynamics.

Definition of the adsorbent pore structure

To simulate the phase transition and redistribution of the VOC components within the activated carbon, physical properties of this adsorbent should be first given.

Since the macropore only acts as a transportation channel rather than the effective adsorption site, a description of its pore-size distribution is not necessary in the practical approach; therefore, a double-gamma distribution will give a satisfactory description of the joint distribution of the micro- and mesopores

$$f(r) = V_{S,1}\frac{\alpha_1^{P_1+1}}{\Gamma(P_1+1)}r^{P_1}e^{-\alpha_1 r} + V_{S,2}\frac{\alpha_2^{P_2+1}}{\Gamma(P_2+1)}r^{P_2}e^{-\alpha_2 r} \quad (3)$$

where $f(r)$ is the pore-size distribution density at radius r, and the model parameters used are defined as $V_{S,1} = V_{S,2} = 0.45$ mL/g, $P_1 = 7$, $P_2 = 6$, $\alpha_1 = 15$ nm^{-1}, and $\alpha_2 = 3$ nm^{-1}.

The preceding parameters are regressed by fitting Eq. 3 to the experimental data of Paulsen et al. (1999) and Mazyck and Cannon (2000), and can be regarded as a good representative for a wide variety of activated carbons.

The average pore radius and the mean variance of the pore-size distribution are obtained according to

$$\bar{r} = \frac{P+1}{\alpha} \quad (4)$$

$$\delta = \frac{\sqrt{P+1}}{\alpha} \quad (5)$$

The overall pore-size distribution given by this relation is plotted in Figure 3, while the accumulative pore-volume distribution is shown in Figure 4. The total volume for pore diameters less than 2 nm is 0.457 mL/g, which is used as the value for W_0 in the DA equation.

Definition of the boundary between micro- and mesopores

To evaluate the respective volumes occupied by the micropores and the mesopores, it is important to determine the boundary between them. It should be noted that the definition given by the IUPAC is only specific to nitrogen at 77.34 K, and thus cannot be applied simply to the present system.

It is known that the transition from micropore to mesopore is characterized by the occurrence of capillary condensation when the chemical potential is reduced to a relatively low value. Considering that the pore-size boundary is related to the change in the adsorption mechanism, the type of the pore can be determined from the terminal point in the adsorption–desorption hysteresis loop. Eiden and Schlünder (1990) studied this phenomenon and introduced a new parameter, A_{Gr}, to denote the chemical potential at this phase transition point. According to their study, A_{Gr} was found to depend only on the molecular size of the adsorbate, but was independent of the adsorbent property. The boundary radius from the micropore to mesopore is therefore obtained from a

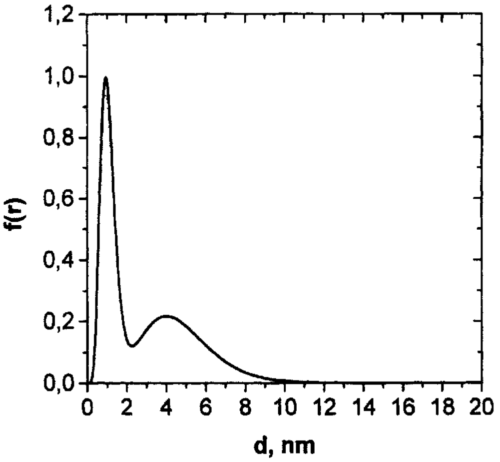

Figure 3. Double-gamma pore-size distribution.

modified Kelvin equation

$$r_{Gr} = \frac{2\sigma V_M}{A_{Gr}} \cos\theta + d_M \qquad (6)$$

where d_M is the molecular diameter of the adsorbate.

The prediction from Eq. 6 for benzene is plotted in Figure 5, where it is found that the r_{Gr} value decreases with an increase in temperature. This can be explained by the fact that under the same chemical potential, the VOC is easier to condense under lower temperatures, and thus the critical pore size should be correspondingly increased. It is also found that 2 nm is not the exclusive upper limit for the micropore. For example, from 50°C to 200°C, this critical diameter changes from 3.8 nm to 1.9 nm. This could be explained by the definition by IUPAC, for instance, the molecular diameter of nitrogen is 3.0 Å, while that for benzene is 5.95 Å, and correspondingly the upper limits of the micropore for these two adsorbates are 2 nm and 3.8 nm in diameter, respectively.

For the same reason, the upper limit of the mesopore domain is not 50 nm either, as defined by the IUPAC. Figure 6 shows the upper limit of mesopores in the meaning of capillary condensation denoted by the Kelvin radius, r_K, evaluated from Eq. 2 for temperatures from 50°C to 200°C.

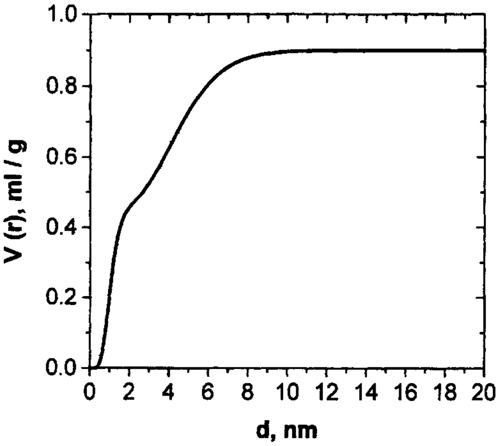

Figure 4. Integrated pore-volume distribution.

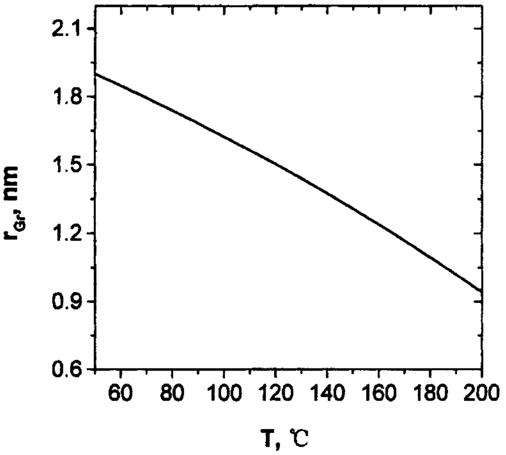

Figure 5. Upper limit of the micropore as a function of temperature.

Since the mesopore volume is the volume contained between r_{Gr} and r_K, it can be calculated by the following equations

$$V_{\text{meso}} = V(r_K) - V(r_{Gr}) \qquad (7)$$

where

$$V(r) = V_{S,1}\frac{\Gamma(P_1+1,\alpha_1 r)}{\Gamma(P_1+1)} + V_{S,2}\frac{\Gamma(P_2+1,\alpha_2 r)}{\Gamma(P_2+1)} \qquad (8)$$

and

$$\Gamma(a,b) = \int_0^b x^{a-1} e^{-x}\, dx \qquad (9)$$

Because r_{Gr} and r_K are not constants, the volume of VOC condensed in the mesopores not only depends on the porous

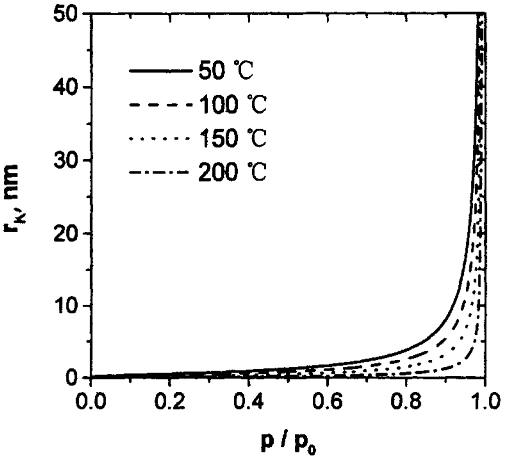

Figure 6. Upper limit of the mesopore as a function of temperature.

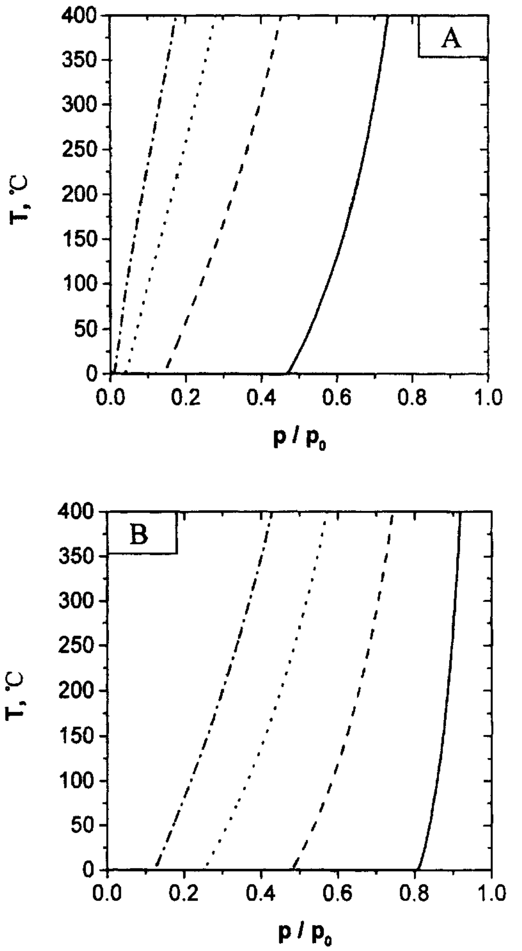

Figure 7. Phase equilibrium between the gas and the adsorbent.

Parameters in the DA equation: (A) $W_0 = 0.457$ mL/g; $E_0 = 17.61$ kJ/mol; $n = 1.46$; (B) $W_0 = 0.457$ mL/g; $E_0 = 10.40$ kJ/mol; $n = 1.10$. Adsorbent condition (mL VOC/gA.C.): — 0.442; --- 0.40; ···· 0.35; -·-·- 0.30.

structure of the adsorbent, but also on the temperature and on the specific isotherm shown in Figure 2.

Results and Discussion

Redistribution of VOC among different phases

In most of the adsorption applications, the VOC concentration in the gas phase to be purified is relatively low. Under this condition, there will be no capillary condensation in the mesopore, and only the micropore is involved for adsorption, as can be seen in Figure 2. When the adsorbent is saturated, it is believed the VOC in the gas phase is in equilibrium with the adsorbed VOC in the solid phase. To give an illustration, we assume the adsorption is performed at 20°C and under a VOC partial pressure of 0.05 bar. From Eq. 1 with the relevant parameters assumed, the adsorbed VOC amount will be 0.442 mL/g, which is only a little less than the saturated value of 0.457 mL/g.

As the adsorbent temperature is increased for desorption, a certain amount of VOC will leave the micropores, that is, from the adsorbent phase to the gas phase, and a new gas–solid equilibrium will be established at this elevated desorption temperature. Simultaneously, a gas–liquid equilibrium will also be implicitly established between the gas and liquid condensed in the mesopores. Since the Dubinin equation is intrinsically different from the Kelvin equation, there may be an overlap between them in the phase diagram. If this occurs, the gas phase will not only be in equilibrium with the adsorbent phase in the micropore, but also in equilibrium with the liquid phase in the mesopore.

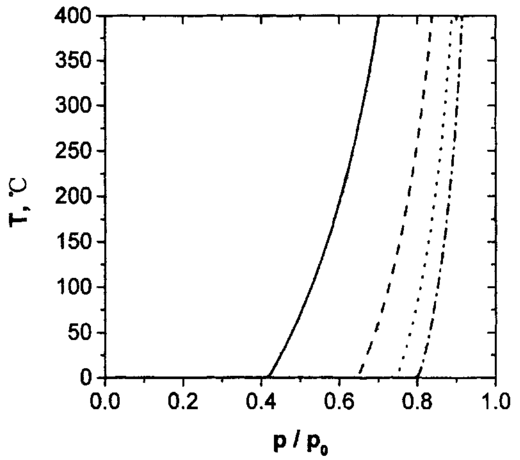

Figure 8. Phase equilibrium between the gas and condensed liquid residing in the mesopore of different sizes.

Pore diameters (nm); — 2; --- 4; ···· 6; -·-·- 8.

In order to know the influence of the adsorption energy on the redistribution of VOC between micropores and mesopores during the electrothermal desorption, two kinds of activated carbons are investigated. It is found that the gas–solid equilibrium is related to the adsorbent property, as can be observed from a comparison of Figure 7A and Figure 7B. Obviously, the activated carbon used in Figure 7A has a stronger adsorption effect, which is characterized by a higher characteristic energy, E_0, and a larger adsorption exponent, n.

Figure 8 shows the relationship between the thermodynamic condition and the maximum critical pore diameter available for the inception of capillary condensation. Since the upper limit for the micropore is approximately 2 nm in diameter, there will be no condensation below this pore diameter, and hence the condensation is only possible in the region right to the 2-nm profile shown in Figure 8.

Figure 9 shows the corresponding relationship between the temperature and relative pressure of VOC vapor under a certain amount of VOC adsorbed in the adsorbent. In Figure 9A, the solid line indicated by the Dubinin equation means 0.442 mL VOC/g A.C. can be adsorbed in the micropore if the temperature and pressure are located on the Dubinin line. However, any decrease in pressure or increase in temperature will make the VOC desorbed from the micropore space, as can be deduced from Figure 7. The dashed line indicated by the Kelvin equation gives the temperature and pressure conditions of VOC necessary for condensation in the mesopore of 2 nm in diameter. Since 2 nm is the lower limit for the mesopore, any increase in temperature or decrease in pressure from the Kelvin line will make the VOC condensa-

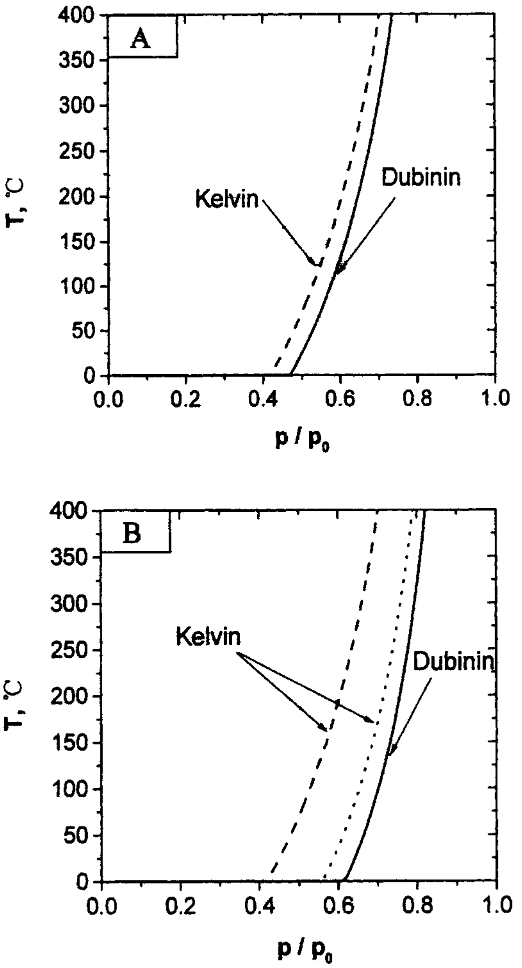

Figure 9. Equilibrium distribution of VOC between micropore and mesopore.

(A) — VOC in the micropores, $W = 0.442$ cc/g. The DA equation parameters: $W_0 = 0.457$ cc/g; $E_0 = 17.61$ kJ/mol; $n = 1.46$; ---- VOC in the mesopores, the largest condensation diameter d = 2 nm. (B) VOC in the micropores, $W = 0.40$ cc/g. The DA equation parameters: $W_0 = 0.457$ cc/g; $E_0 = 10.40$ kJ/mol; $n = 1.10$; ---- VOC in the mesopores. The largest condensation diameter $d = 2$ nm. ···· VOC in the mesopores. The largest condensation diameter $d = 3$ nm.

tion impossible. Therefore, no VOC will be condensed for this kind of adsorbent. However, when a "weak" adsorbent is employed (Eiden and Schlünder, 1990), a somewhat different result is obtained. As shown in Figure 9b, the condition indicated by the Dubinin equation under an adsorption amount of 0.40 mL VOC/g A.C. is equivalent to the Kelvin equation at a pore diameter of 3 nm. Since 3 nm is above the lower boundary of the mesopore, it is important to know whether the VOC vapor released from the micropore can be condensed by the mesopores between 2 and 3 nm. It can be calculated from Figure 4 that the integral pore volume in this range is 0.069 mL/g, which is larger than the volume of 0.042 mL/g that could be released from the micropores. Therefore, there will be 0.042 mL/g VOC condensed in the mesopore during the electrothermal desorption. However, it just accounts for 10% of 0.442 mL/g, which is the totally adsorbed amount.

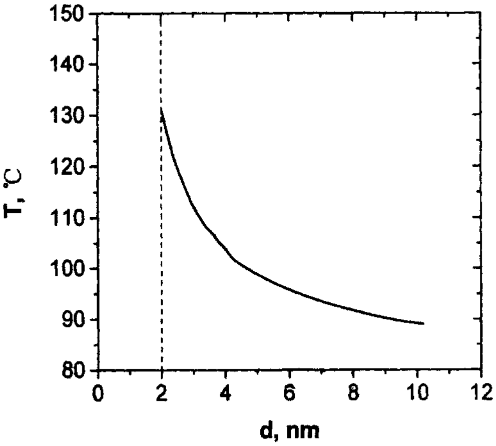

Figure 10. Relationship between pore diameter and evaporation temperature.

Minimum desorption temperature

To prevent any possible capillary condensation of the VOC species inside of the mesopore, the boiling point of liquid phase should be selected as the minimum desorption temperature.

The shape of the gas-liquid interface inside of a capillary depends on whether the outside vapor is condensed or the inside liquid is evaporated. Since the desorption process follows a similar mechanism to evaporation, the liquid boiling point should be predicted according to the Cohan equation rather than the Kelvin equation (Cheng et al., 2001).

$$\frac{p}{p_0} = \exp\left(-\frac{\sigma V_M}{R_g T}\cdot\frac{1}{r}\right) \tag{10}$$

The relationsip between boiling point and the capillary size is shown in Figure 10. As is expected, the boiling point increases rapidly when the pore diameter is decreased to 2 nm. Obviously, the boiling point of 131°C corresponding to the 2-nm tube will be the minimum desorption temperature so as to avoid any possible condensation of benzene under an operation pressure of 1.0 bar.

Conclusions

As a new kind of temperature swing adsorption (TSA) technology, which has been developed only in the last decade, electrothermal desorption shows distinct advantages over the traditional methods. Based on a phase-equilibrium analysis, the present work has established a method for evaluating the possible redistribution of VOC in different scales of porosities. Because of the strong interaction between the VOC vapor and the micropore as described by the Dubinin equation, the VOC vapor can hardly condense in the mesopore under the desorption temperature. It can be considered that this kind of electrically based operation can greatly intensify the VOC desorption, and the operation can also benefit from the high concentration of VOC and zero pollution to the environment.

Acknowledgment

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Notation

A = chemical potential, $R_gT\ln(p_0/p)$
A_{Gr} = chemical potential at the transition point from adsorption to condensation
d = pore diameter, m
d_M = diameter of a molecule, m
E_0 = characteristic energy, J/mol
f = pore volume distribution density function
n = adsorption exponent in the Dubinin equation
p = gas pressure, bar
p_0 = saturated gas pressure, bar
P = parameter in Eqs. 4 and 5
P_1, P_2 = parameters in Eq. 3
r = pore radius, m
$\tilde{r}$ = average pore radius, m
R_g = universal gas constant, J/mol·K
r_K = the Kelvin radius, m
t = thickness of adsorbed layer, m
T = temperature, K
V_M = molar liquid volume, mL/g
V_{meso} = mesopore volume, mL/g
$V_{S,1}$, $V_{S,2}$ = parameters in Eq. 3
W = amount adsorbed, mL/g
W_0 = limiting pore volume, mL/g

Greek letters

α = parameter in Eqs. 4 and 5
α_1, α_2 = parameters in Eq. 3
β = similarity factor in Eq. 1
δ = distribution variance, m
Γ = gamma function
θ = angle of contact
σ = surface tension, N/m

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