Characteristics of \textit{n}-Hexane Adsorption over Heat-Treated Activated Carbon

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Abstract: To investigate quantitatively the effects of surface oxide complexes of activated carbon on \textit{n}-hexane adsorption, chromatographic analysis was performed using GC-TCD. Elution curves from the detector were analyzed by the moment method and adsorption parameters were calculated. The isosteric heat of adsorption was ca. -18.5 kcal/mol and the equilibrium adsorption constants were ca. 2500 – 3,000 cm$^3$/g. The diffusivities of \textit{n}-hexane in the macro and micropores of activated carbon were $10^{-2}$ cm$^2$/sec and $10^{-11}$ cm$^2$/sec, respectively. Heat treatment of the activated carbon did not affect these parameters. The variation of the adsorption parameters was within 10 %, which leads to the conclusion that an interaction between \textit{n}-hexane and the surface oxide complexes was not significant.

Keywords: adsorption, moment method, activated carbon, \textit{n}-hexane, heat treatment

Introduction

Much interests are focused on removing the volatile organic compounds (VOCs) that cause adverse effects on human health and photochemical smog. One of the most efficient ways to remove VOCs is through adsorption using carbonaceous materials. The physicochemical properties of activated carbon are important factors that determine its adsorptive capacity [1-4].

The surface chemistry of activated carbon is governed by a small number of heteroatoms that are responsible for the presence of acidic, neutral, or basic functionalities. When the activated carbons are treated with oxidizing agents, surface oxygen complexes are formed and can be classified into three types: acidic, basic, and neutral. It has been reported that acidic surface oxides increase the adsorptive capacity of activated carbon for polar molecules [5-8]. However, changes to the physical properties are inevitable when oxidizing chemicals are used to increase the number of surface oxides on activated carbon, because their use causes a reduction of the surface area and the pore size of activated carbon [6,9].

As a result, it becomes harder to discern each effect that the physical and chemical properties of activated carbon have on the adsorption characteristics. Therefore, it is necessary to perform more cautious analyses to determine the influences that surface functional groups have on the adsorption characteristics of activated carbon. As an alternative oxidizing method, heat treatment of activated carbon can be considered. This approach makes it possible to alter the concentration of surface functional groups without considerably changing the physical properties. Thus, in this study, we aimed to investigate quantitatively the pure effects of surface functional groups on the adsorption of \textit{n}-hexane.

Theoretical Background

Moment analysis of elution curves is a well known and effective tool for measuring the quantitative adsorption parameters of gas adsorbates [10,11]. A gas mixture containing a single adsorbable component flows through a bed of solid particles with a packing length $z$ under isothermal conditions at a constant superficial velocity. The concentration of adsorbate in the entering stream is $C$ and the following assumptions can be used:
1. Isothermal conditions of the column
2. Constant void fraction and interstitial velocity
3. Linear adsorption of adsorbate
4. Constant size of spherical particle
5. One-dimensional dispersed flow

The differential equation that describes \( c(t) \) in a packed bed can be derived as follows:

The material balance in the column is

\[
\frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial z} - \frac{3(1 - \varepsilon)}{\varepsilon R} N_0 = \frac{\partial C}{\partial t} \tag{1}
\]

The material balance at the external surface of particles is

\[
N_0 = k(c - C) |_{r=R} = D_{e} \frac{\partial C}{\partial r} |_{r=R} \tag{2}
\]

\( E_z \) = axial dispersion coefficient in the column
\( u_r \) = interstitial velocity of fluid
\( \varepsilon \) = void fraction in the bed

The material balance in a particle is

\[
D_{a} \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) - \frac{3(1 - v_a)}{v_a + 1 - v_a} N_i = \frac{\partial C}{\partial t} \tag{3}
\]

The material balance at the surface of micro-particles is

\[
N_i = D_i \frac{\partial q}{\partial r_i} \text{ at } r_i = a \tag{4}
\]

The adsorption, which is in equilibrium, at the surface of micro-particle is

\[
q = K \cdot c \tag{5}
\]

The material balance in the interior of a micro-particle is

\[
D_i \left( \frac{\partial^2 q}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial q}{\partial r_i} \right) = \frac{\partial q}{\partial t} \tag{6}
\]

The equations above are based on a model in which small micro-particles of radius \( a \) are pelletized to form a macro-particle of radius \( R \). As a result, inter micro-particle spaces remain as macropores and adsorption takes place at the surface of the micro-particles, which is followed by adsorption into micro-particles.

The Eqs. (1) ～ (6) have been solved in the Laplace domain to give the moments of the impulse response. The results are as follows:

\[
\varphi_1 = \frac{-\int_0^\infty C_e \cdot \varphi \, dt}{\int_0^\infty C_e \, dt} = \frac{(z/u)[1 + \delta_o]}{} \tag{7}
\]

\[
\varphi_2 = \frac{-\int_0^\infty C_e \cdot ... \, dt}{\int_0^\infty C_e \, dt} = \frac{(2z/u)[\delta_o + \delta_j + \delta_d + \delta_i]}{} \tag{8}
\]

where

\[
\delta_o = \left[ \frac{(1 - \varepsilon)}{\varepsilon} \right] (v_a + \rho I K_a) \tag{9}
\]

\[
\delta_x = \frac{E_z}{u_t} (1 + \delta_o)^2 \tag{10}
\]

\[
\delta_j = \frac{1 - \varepsilon}{\varepsilon \rho_i} \frac{R}{3k_i} (v_a + \rho I K_a)^2 \tag{11}
\]

\[
\delta_d = \frac{1 - \varepsilon}{\varepsilon \rho_i} \frac{R^2}{15D_i} (v_a + \rho I K_a)^2 \tag{12}
\]

\[
\delta_i = \frac{1 - \varepsilon}{\varepsilon \rho_i} \frac{\alpha v \mu K_a}{15D_i} \tag{13}
\]

When the output signal \( C_o(i) \) can be approximated by the normal distribution curve, the first absolute moment and the second central moment are readily related to the position and the width of the peak, respectively.

**Experimental**

The adsorbent used in this study was a bituminous coal particle-based activated carbon (Calgon Co. BPL 4×10 mm). To study the influence of the surface oxygen content, the activated carbon was heated in a tubular quartz reactor at various temperatures in a \( N_2 \) flow. After heat treatment of the activated carbon, the pellets were crushed, sieved, and then maintained in a desiccator. The physical properties of the activated carbon were measured using \( N_2 \) BET (ASAP 2020, micrometrics) and mercury porosimetry (Autopore IV 9500, Micrometritics) methods.

The surface functional groups were measured according to the method of Boehm [12]. It was assumed that the carboxyl groups would be neutralized in a solution of sodium bicarbonate; carboxyl and lactone groups would react with sodium carbonate; carboxyl, lactone, and phenolic groups could be determined in a solution of sodium hydroxide; and carboxyl, lactone, phenolic and carbonyl groups could be neutralized in a solution of sodium ethoxide. The activated carbon samples were...
Table 1. Characteristics of Packed Column and Experimental Conditions

<table>
<thead>
<tr>
<th>heat treatment conditions</th>
<th>packed length [m]</th>
<th>column I.D. [m]</th>
<th>particle size [mm]</th>
<th>adsorbent weight [g]</th>
<th>column porosity [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw material</td>
<td>0.07</td>
<td>3.86×10⁻³</td>
<td>0.34</td>
<td>0.5153</td>
<td>0.484</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.93</td>
<td>0.5002</td>
<td>0.539</td>
</tr>
<tr>
<td>500 °C-10 h</td>
<td>0.07</td>
<td>3.86×10⁻³</td>
<td>0.34</td>
<td>0.4927</td>
<td>0.507</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.93</td>
<td>0.4427</td>
<td>0.557</td>
</tr>
<tr>
<td>900 °C-10 h</td>
<td>0.07</td>
<td>3.86×10⁻³</td>
<td>0.34</td>
<td>0.5054</td>
<td>0.494</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.93</td>
<td>0.5054</td>
<td>0.539</td>
</tr>
<tr>
<td>Flow rate [cc/min]</td>
<td>30, 50, 70, 90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>240, 265, 290</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results and Discussion

Physicochemical Properties of Heat-Treated Activated Carbon

Physical properties of activated carbons were measured using N₂ BET and mercury porosimetry techniques, respectively; the results are summarized in Table 2 and shown in Figure 1. As can be seen from the Table, macro pores in the activated carbon were well developed; the Figure shows that the activated carbon had a bimodal distribution of pore sizes. The specific surface area and porosity were ca. 1000 m²/g and 0.4 g/cc, respectively; heat treatment did not affect the physical properties of the activated carbon. However, as shown in Table 3, an increased heat treatment temperature reduced the surface acidic complexes, among which the carboxyl concentration decreased greatly. This result suggests that heat treatment is a feasible approach to obtain a chemically stable activated carbon without a change of its physical properties.

To confirm the results in Table 3, which we obtained using the method of Boehm, TPD analysis of the activated carbon was performed; the analytical results are shown in Figure 2. When the raw material was heated, CO₂ and CO gas was evolved at ca. 200~300 °C, respectively. CO₂ evolution occurred mainly through de-
Table 3. Surface Oxide Functional Groups [meq/g]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total acidity</th>
<th>Carboxyls</th>
<th>Lactones</th>
<th>Phenols</th>
<th>Total basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>0.225</td>
<td>0.179</td>
<td>0.036</td>
<td>0.010</td>
<td>0.597</td>
</tr>
<tr>
<td>500 °C-10 h</td>
<td>0.195</td>
<td>0.129</td>
<td>0.051</td>
<td>0.015</td>
<td>0.582</td>
</tr>
<tr>
<td>900 °C-10 h</td>
<td>0.158</td>
<td>0.116</td>
<td>0.033</td>
<td>0.009</td>
<td>0.551</td>
</tr>
</tbody>
</table>

Figure 2. TPD analysis of activated carbon with respect to the degree of heat treatment.

Figure 3. Effect of z/u on the first absolute moment with respect to the adsorption temperature.

Figure 4. Effect of heat treatment of the activated carbon on the first absolute moment.

First Absolute Moment Analysis

The adsorption equilibrium constant ($K_a$) can be obtained using Eqs. (7) and (9); the plot of $\mu_1$ vs $z/u$ with respect to the particle size should be a straight line through the origin because $K_a$ is independent of the flow rate and the particle size. Such plots of the moment generated from the experimental curves are given in Figure 3. Variation of the particle size did not affect the value of the first absolute moment and the lines through the origin was straight. This result shows that the linearity requirement is fulfilled, which implies that the assumption of a linear isotherm is valid. Increasing the adsorption temperature decreased the slope of the line, which means that the quantity of $n$-hexane adsorbed decreased upon increasing the adsorption temperature [10,15,16]. To evaluate the effect of heat treatment of the activated carbon on the equilibrium adsorption constant of $n$-hexane, the first absolute moments of heat-treated samples are shown in Figure 4. The slopes of first absolute moment plot were not significantly different. This result means that the equilibrium adsorption constants decreased upon increasing the adsorption temperature, but they were not affected by the variation of composition of the carboxyl and lactone units, whereas CO evolution resulted from the presence of phenol, and carbonyl groups and basic complexes [13]. As can be seen in the figure, we found that heat treatment of activated carbon at 900 °C for 10 h reduced most of the acidic complexes.
Table 4. Equilibrium Adsorption Constants for n-Hexane on Activated Carbon [cm$^3$/g]  

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature</th>
<th>240 °C</th>
<th>265 °C</th>
<th>290 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>500 °C-10 h</td>
<td>12485.08</td>
<td>5328.90</td>
<td>2489.17</td>
</tr>
<tr>
<td></td>
<td>900 °C-10 h</td>
<td>13323.74</td>
<td>5659.90</td>
<td>2610.43</td>
</tr>
</tbody>
</table>

Figure 5. Van’t Hoff plots of equilibrium adsorption constants.

the heat treatment condition. The values of $K_a$ were obtained from the slopes of the lines; the results are summarized in Table 4. These results suggest that the adsorption of n-hexane was not affected by the presence of surface oxide complexes. This situation might be the result of the hydrophobicity and non-polarity of n-hexane.

The isosteric heat of adsorption can be obtained using the value of a slope of the Van’t Hoff plot, which is shown in Figure 5 along with data obtained by others. Isosteric heat of adsorption of n-hexane on activated carbon was -18.5 kcal/mol; it was not influenced by variation of the heat treatment conditions. Carrot and coworkers [3] reported that the isosteric heat of adsorption of hydrocarbons in MSC (molecular sieving carbon) was 2.6 times higher than that of liquefaction. The isosteric heat of adsorption in Figure 5 agrees with the results of Carrot and coworkers [3] because the heat of liquefaction of n-hexane is ca. -7.5 kcal/mol. The isosteric heats of adsorption are linearly proportional to the specific surface areas of carbonaceous materials. As can be seen in the Figure, R activated carbon [14] had a similar value to the one we obtained because the specific surface area of R activated carbon is similar to that of BPL carbon. However, the isosteric heat of adsorption of n-hexane in non-porous carbon was ca. -9.5 kcal/mol, which is lower than that of porous carbon. Therefore, we conclude that the isosteric heat of adsorption of n-hexane on activated carbon is not affected significantly by the heat treatment condition because the physical properties of the activated carbon did not change.

Table 5. Axial Dispersion Coefficient, n-Hexane [cm$^2$/sec]  

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature</th>
<th>0.20 mm</th>
<th>0.34 mm</th>
<th>0.93 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>240 °C</td>
<td>0.25</td>
<td>0.668</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>265 °C</td>
<td>0.35</td>
<td>0.498</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>290 °C</td>
<td>0.46</td>
<td>0.808</td>
<td>0.88</td>
</tr>
<tr>
<td>500 °C-10 h</td>
<td>240 °C</td>
<td>-</td>
<td>0.648</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>265 °C</td>
<td>0.13</td>
<td>0.72</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>290 °C</td>
<td>-</td>
<td>0.99</td>
<td>-</td>
</tr>
<tr>
<td>900 °C-10 h</td>
<td>240 °C</td>
<td>-</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>265 °C</td>
<td>0.18</td>
<td>0.28</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>290 °C</td>
<td>-</td>
<td>0.79</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6. Effect of heat treatment on second central moment.

Second Central Moment Analysis

As indicated in equation (8), the intercepts of the plot of $\mu_2/(2z/u)$ vs. $1/u^2$ give information regarding the values of $\delta_f$, $\delta_d$, and $\delta_i$, the film mass transfer resistance and macro and micro pore diffusivities, respectively. The slope of the curve contains information regarding the axial dispersion coefficient. Experimental second central moment data for n-hexane is shown in Figure 6 and the axial dispersion coefficients are summarized in Table 5. Axial dispersion coefficients of an adsorbate are caused by the molecular diffusion and turbulent mixing that arises from the splitting and recombination of flows around the adsorbent particles. Increased axial dispersion results in a decrease of the gas separation efficiency. As can be seen in the Table, the axial dispersion coefficient was ca. 0.1 0.99 cm$^2$/sec and it increased upon increasing the adsorption temperature. These findings agree with previous results [15,17]. However, heat treatment did not affect the axial dispersion coefficient of n-hexane over activated carbon. This result implies that heat treatment did not provide any structural change and, therefore, the adsorbate-adsorbent interaction did not change significantly.

According to equations (10) 3, the y-intercept is given by $\delta_f + \delta_d + \delta_i$ if the contribution of $k_f R$ is...
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Figure 7. Second central moment plot with respect to the particle size.

independent of the particle size. These equations can be rearranged to equation (14) as a function of particle radius.

\[
\frac{15\varepsilon}{(1-\varepsilon)} = -\frac{a^2K\rho}{D_a^\frac{5}{2}} + \left(\frac{1}{D_a} + \frac{5}{k_fR}\right)(1+\frac{K\rho}{\varepsilon})^2R^2
\]

(14)

In this equation, the slope of the line is equal to \(-\frac{a^2K\rho}{D_a^\frac{5}{2}} + \left(\frac{1}{D_a} + \frac{5}{k_fR}\right)(1+\frac{K\rho}{\varepsilon})^2\) and, therefore, the diffusivities of n-hexane in the macropores and micropores can be calculated. The effect of particle size on the second central moment, with variation of adsorption temperature, is shown in Figure 7. We can determine the values of \(D_{ai}\) and \(D_{ab}\) from the slope and intercept if \(k_fR\) is known. Gas film resistance can be determined using equation (15) which is known as the Wakao relation. If the value of \(N_{Re}\) is not high, the relation converges to 2.0 and then the equation can be simplified to \(k_fR=D_{ab}\).

\[
\frac{2(k_fR)^2}{D_{ab}} = 2.0 + 0.6\left(\frac{\mu}{\rho D_{ab}}\right)^\frac{1}{2}\left(\frac{\mu}{\rho D_{ab}}\right)^\frac{1}{3}
\]

(15)

The molecular diffusivities of n-hexane in helium gas can be calculated using the Hirshfelder equation. Table 6 shows the calculated diffusivities. The calculated molecular diffusivities of n-hexane were ca. 0.79 ~ 93 cm²/sec and they increased upon increasing the temperature. The macropore diffusivities (\(D_a\)) of n-hexane were ca. 10⁻² cm²/sec; i.e., the same order of magnitude of the Knudsen diffusivities. Normal hexane is a non-polar solvent and, therefore, the variation of surface oxide complexes does affect the diffusion of n-hexane in micropores.

From the intercepts, the micropore diffusivities can be determined; the values were ca. 10⁻¹⁰ ~ 10⁻¹¹ cm²/sec. This result means that the micropore diffusion of n-hexane was governed by a surface diffusion mechanism. Surface diffusion is strongly related to the interaction energy between the adsorbate and the adsorbent surface, because surface diffusion occurs through random hopping. Therefore, an increased surface adsorption energy also requires a higher activation energy of the adsorbate; therefore, the surface diffusivities in the micropores becomes higher at higher temperatures.

The arrehenius plot of n-hexane is shown in Figure 8 with the data obtained by Chihara and coworkers [4]. The microdiffusivities of n-hexane were of a similar order of magnitude with those of benzene, which suggests that the hydrocarbon structure does not affect the diffusivities in micropores. Diffusion in a micropore is so-called activated diffusion, which is described as the molecules or atoms hopping from one adsorption site to another across the energy barrier which separates the adjacent sites. Therefore, the degree of micropore diffusion is proportional to the adsorption energy [17] and the isosteric heats of adsorption of benzene and n-hexane are similar over the temperature range tested in this study.

**Table 6. Summary of Diffusivities**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Diffusivity 240 °C</th>
<th>Diffusivity 265 °C</th>
<th>Diffusivity 290 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>(\frac{D_{ai}}{a^{\frac{5}{2}}}[\text{sec}^{-1}])</td>
<td>(\frac{D_{ai}}{a^{\frac{5}{2}}}[\text{sec}^{-1}])</td>
<td>(\frac{D_{ai}}{a^{\frac{5}{2}}}[\text{sec}^{-1}])</td>
</tr>
<tr>
<td>D_{ai} [cm²/sec]</td>
<td>7.46×10⁻²</td>
<td>5.81×10⁻²</td>
<td>4.23×10⁻²</td>
</tr>
<tr>
<td>D_{ab} [cm²/sec]</td>
<td>0.79</td>
<td>0.86</td>
<td>0.93</td>
</tr>
<tr>
<td>D_{ab} [cm²/sec]</td>
<td>7.95×10⁻²</td>
<td>8.15×10⁻²</td>
<td>8.35×10⁻²</td>
</tr>
</tbody>
</table>

**Figure 8. Arrehenius plots of diffusivity in the micropores.**

**Conclusions**

To investigate the effect of the surface functionalities of activated carbon on the adsorption of n-hexane, moment...
analysis was performed using a chromatograph equipped with a TCD. Neither the equilibrium adsorption constants nor the isosteric heat of adsorption of \( n \)-hexane were affected by the amount of surface oxygen on activated carbon. Axial dispersion constants of \( n \)-hexane were ca. 0.1 to 0.99 cm\(^2\)/sec, and they increased upon increasing the adsorption temperature. The diffusion coefficients of \( n \)-hexane were 10\(^{-2}\) cm\(^2\)/sec and 10\(^{-11}\) cm\(^2\)/sec, respectively, which suggest that Knudsen diffusion prevails in the macropores and surface diffusion prevails in the micropores. From these data obtained quantitatively, we found that the interactions between \( n \)-hexane and the surface oxide complexes were not significant.

**Acknowledgment**

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**Nomenclature**

\( a \) : micro particle radius [m]
\( C \) : adsorbate concentration in mobile phase at column outlet [mol/m\(^3\)]
\( c' \) : intraparticle concentration [mol/m\(^3\)]
\( C_e \) : elution concentration [mol/m\(^3\)]
\( D_a \) : molecular diffusivity in macropore [m\(^2\)/sec]
\( D_{AB} \) : molecular diffusion coefficient of A in dilute solution of solute B [m\(^2\)/sec]
\( D_i \) : molecular diffusivity in micropore [m\(^2\)/sec]
\( E_z \) : axial dispersion coefficient [m\(^2\)/sec]
\( K_a \) : equilibrium adsorption constant [m\(^3\)/g]
\( k_f \) : external (fluid-to-particle surface) mass transfer coefficient [m/sec]
\( N_0 \) : flux at the surface of particles [mol/m\(^2\) · sec]
\( N_i \) : flux at the surface of microparticles [mol/m\(^2\) · sec]
\( q \) : amount absorbed per unit mass of adsorbent [mol/kg]
\( R \) : radius of the macroparticle [m]
\( r \) : radial position in a particle [m]
\( r_i \) : radial position in a microparticle [m]
\( t \) : time [sec]

\( u \) : interstitial flow velocity [m/sec]
\( z \) : length of packing in column [m]

**Greek letters**

\( \delta_0, \delta_1, \delta_{ax}, \delta_0, \delta_i \) : moment contributions defined by Eqs. (9) to (13)
\( \varepsilon \) : void fraction in bed
\( \varepsilon_a \) : intraparticle void fraction
\( \mu_1 \) : first absolute moment at column outlet
\( \mu_2 \) : second central moment at column outlet
\( \rho_p \) : apparent density of particle [kg/m\(^3\)]

**References**