On the Carbon Dioxide and Benzene Adsorption on Activated Carbons To Study Their Micropore Structure

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Introduction

In a previous paper it has been shown that the micropore volumes obtained from the Dubinin–Astakhov equation applied to CO₂ adsorption isotherms at 273 K on activated carbons with a medium to high degree of activation are affected by the adsorption on the mesopore surface. However, the real micropore volume and its distribution and dispersion, as well as the mesopore surface area of the activated carbons, can be obtained from the benzene adsorption isotherms by applying the Dubinin–Stoeckli equation corrected with the Dubinin–Zaverina equation.

The activated carbons studied in the above paper were prepared by steam activation of a Spanish bituminous coal with an ash content of 11.5%. This mineral matter present in the coal can play an important role in the activation process by increasing the rate of the carbon steam reaction.

The aim of the present work is to study the porous texture from the benzene isotherms of a series of activated carbons obtained by steam activation of the same parent coal as that used in a previous study. In this work, however, the parent coal was demineralized by froth flotation prior to being activated. The textural characteristics of these activated carbons will be compared with those corresponding to the activated carbons from the untreated parent coal in order to discover the effect of the mineral matter in coals on the porosity of the resulting activated carbons.

Experimental Section

A bituminous coal (A) from Puertollano (Spain) was demineralized by froth flotation (sample AF) in a glass column with an ash content of 4.0%. As in the parent coal, the main minerals detected by FTIR and XRD experiments in the demineralized coal were illite, kaolinite, and quartz. The proximate analysis of the parent coal (wt%, dry basis) is VM = 21.5, ash = 11.5, and C_{fixed} = 67.0. After its demineralization, the ash content of this coal was 4.0%. As in the parent coal, the main minerals detected by FTIR and XRD experiments in the demineralized coal were illite, kaolinite, and quartz.

Three activated carbons were obtained from the demineralized coal. The coal was pyrolized at 1123 K (10 K min⁻¹) in N₂ for 1 h (sample AFP) and then activated in steam at 1113 K for different periods of time (2.5, 5, and 10 h). Experimental details of this process were reported elsewhere. These activated carbons will be referred to in the text as AFP followed by a number that corresponds to the percentage burn-off.

All activated carbons were characterized by N₂ and CO₂ adsorption at 77 and 273 K, respectively, and by mercury porosimetry, as explained in detail elsewhere. Some of the most important parameters are summarized in Table 1, where W₀ and W₄ are the micropore volume and the characteristic adsorption energy, respectively, obtained by the application of the Dubinin–Astakhov (DA) equation to the CO₂ adsorption data, and V₄ is the exponent of this equation. Values of n between 1 and 4 are observed for most carbon adsorbents, with a value of n > 2 for molecular sieve carbon or carbon adsorbents with highly homogeneous, small micropores and values of n = 2 for strongly activated carbons and heterogeneous carbons. The values of n and V₄ in Table 1 decrease when the degree of activation increases because this enhances the heterogeneity of the micropores and their width.

Results and Discussion

Benzene adsorption isotherms for the AFP samples obtained at 303 K in gravimetric equipment following the method described elsewhere. Prior to carrying out the adsorption runs, samples were outgassed overnight at 383 K with a dynamic vacuum of 10⁻⁸ Torr.

(2) Dubinin, M. M.; Stoeckli, H. F. J. Colloid Interface Sci. 1980, 75, 34.
parameters can be used to describe the adsorption isotherms of the activated carbon micropore structure can be related to the distribution curve's maximum, \( L_0 \), which indicates that there is a progressive development of micro- and mesoporosity with the degree of activation. \(^{19}\)

The adsorption–desorption isotherms of benzene on the activated carbons show a H4 type hysteresis loop, \(^{22}\) characterized by the presence of multilayer adsorption on the nonmicroporous surface (mesopores, macropores, and the external surface).

In this series of isotherms there is an opening of the knee and an increase in the slope of the linear branch, which indicates that there is a progressive development of micropores and mesoporosity with the degree of activation. \(^{19}\)

The theory of volume filling of micropores (TVFM) \(^{18,22,23}\) describes the porous structure of microporous activated carbons. \(^{2,8,19,22,23}\) According to this theory, three parameters of the activated carbon micropore structure can be obtained: the micropore volume, \( W_0 \); the micropore width at the distribution curve maximum, \( L_0 \); and the dispersion, \( d \), that characterizes the micropore distribution range. These three parameters can be determined from the benzene adsorption isotherms by applying the Dubinin–Stoeckli (DS) equation. \(^{2,8,19,22,23}\)

When the activated carbon has a sufficiently developed mesopore surface, the contribution of the adsorption on mesopores to the total adsorption is considerable. In this case, the application of the DS equation to the experimental benzene adsorption isotherm yields the effective values of the parameters \( W_0, L_0, \) and \( d \). These effective parameters can be used to describe the adsorption isotherms quantitatively but cannot be used to calculate the micropore volume distribution with size. The experimental isotherm must, in this case, be corrected for the adsorption on mesopores according to Dubinin, \(^{4}\) the experimental values of the adsorption isotherms, \( a_{\text{exp}} \), are composed of the adsorption in micropores, \( a_{\text{mi}} \), and in mesopores, \( a_{\text{me}} \):

\[
a_{\text{exp}} = a_{\text{mi}} + a_{\text{me}}
\]  

Equation 1 can be converted to

\[
a_{\text{exp}} = a_{\text{mi}} + \gamma S_{\text{me}}
\]

where \( \gamma \) is the adsorption of the vapor (benzene) at a given temperature per unit mesoporous surface area of the adsorbent and \( S_{\text{me}} \) is the surface area of the mesopores.

The value of \( \gamma \) was experimentally obtained by Dubinin and Zaverina, \(^{4,8,24}\) for carbonaceous adsorbents from the adsorption isotherm of benzene on a nonporous carbon black, whereas the results obtained were further extended for other organic adsorbents, and this more general equation is known as the modified Dubinin–Zaverina equation:

\[
\gamma = \frac{8.14 \times 10^{-4}}{\nu} \exp\left[\frac{A}{6.35\beta}\right] \text{mmol/m}^2
\]

where \( \nu \) is the millimolar volume of the adsorbate and was taken as 0.0898 for benzene and 6.35 is the characteristic adsorption energy, in kJ mol\(^{-1}\), on a mesoporous surface. By using eqs 1 and 2, the plot of \( a_{\text{exp}} \) against \( \gamma \) should be a straight line whose slope is the value of the mesopore surface area, \( S_{\text{me}} \).

The experimental benzene adsorption isotherms were corrected at each adsorption point for adsorption on mesopores according to eqs 1 and 2 using the values of \( S_{\text{me}} \). The DS equation was applied to the corrected adsorption isotherms obtained. From this calculation, the real parameters \( W_0, L_0, \) and \( d \) of the micropore structure of the activated carbons were determined.

The effective and real parameter values obtained from the benzene adsorption isotherms are reported in Table 2 along with \( S_{\text{me}} \) values. The parameters were determined from the DS equation by minimizing the residual sum of squares by iteration. \(^{3,25}\)

The micropore size distribution was obtained from the real parameters \( W_0, L_0, \) and \( d \) by applying the normal distribution equation:

\[
dW = \frac{W_0}{2d\sqrt{2\pi}} \exp\left[\frac{-(L_0 - L)^2}{8d^2}\right] 
\]

Table 1. Textural Parameters of the Activated Carbon Series

<table>
<thead>
<tr>
<th>sample</th>
<th>% ash</th>
<th>( S_{\text{H2}} ), m(^2) g(^{-1})</th>
<th>( S_{\text{CO2}} ), m(^2) g(^{-1})</th>
<th>( W_0(\text{CO2}) ), cm(^3) g(^{-1})</th>
<th>( E_0(\text{CO2}) ), nm</th>
<th>( n(\text{CO2}) )</th>
<th>( V_2 ), cm(^3) g(^{-1})</th>
<th>( V_B ), cm(^3) g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFP-14</td>
<td>7.2</td>
<td>447</td>
<td>453</td>
<td>0.172</td>
<td>24.7</td>
<td>1.26</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>AFP-24</td>
<td>8.2</td>
<td>634</td>
<td>688</td>
<td>0.261</td>
<td>19.9</td>
<td>1.70</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>AFP-53</td>
<td>13.2</td>
<td>1002</td>
<td>1085</td>
<td>0.412</td>
<td>15.2</td>
<td>1.49</td>
<td>0.14</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 2. Parameters Obtained from the Dubinin–Stoeckli Equation Applied to the Benzene Adsorption Isotherms

| sample | \( W_0 \), cm\(^3\) g\(^{-1}\) | \( L_0 \), nm | \( d \), nm | \( E_0 \), kJ mol\(^{-1}\) | \( S_{\text{me}} \), m\(^2\) g\(^{-1}\) | \( W_0 \), cm\(^3\) g\(^{-1}\) | \( L_0 \), nm | \( d \), nm | \( E_0 \), kJ mol\(^{-1}\) |
|--------|----------------|--------------|----------|----------------|----------------|----------------|--------------|----------|----------------|----------------|
| AFP    | 0.004          | 1.53         | 0.199    | 18.7           | 1              | 0.003          | 1.42         | 0.096    | 19.9           |
| AFP-14 | 0.130          | 1.16         | 0.207    | 19.6           | 44             | 0.110          | 1.09         | 0.139    | 22.8           |
| AFP-24 | 0.250          | 1.18         | 0.216    | 19.5           | 67             | 0.220          | 1.12         | 0.139    | 22.0           |
| AFP-53 | 0.440          | 1.49         | 0.243    | 15.1           | 226            | 0.360          | 1.20         | 0.149    | 16.2           |

Figure 1. Benzene adsorption–desorption isotherms on activated carbons at 303 K: (○) AFP; (△) AFP-14; (◇) AFP-24; (△) AFP-53.

Notes


MicroporesizedistributionsoftheAFPactivatedcarbons
series are shown in Figure 2.

Data in Table 2 indicate that the values of the real
parameters are lower than their corresponding values
obtained for the effective parameters, which is due to the
development of the mesopore area ($S_{me}$) that, in the
activated carbon series, increases with the percentage of
burn-off, varying from 44 m$^2$ g$^{-1}$ for the activated carbon
whose burn-off is 14% to 226 m$^2$ g$^{-1}$ for that with a burn-
off equal to 53%.

As shown in Table 2 and Figure 2, the micropore volume,
$W_0$, and the mean micropore width increase with activation.
In all cases, the value of $S_{CO_2}$ is slightly higher than
$S_N_2$ (Table 1), which indicates that the value of $W_0(CO_2)$
obtained by applying the DA equation to the CO$_2$ isotherm is
increased due to the fact that this also accounts for the
CO$_2$ adsorbed on the mesopore surface. Thus, the real parameter $W_0$
obtained from benzene (Table 2) is, in all cases, lower than the $W_0(CO_2)$ values (Table 1).

Table 3 shows the real parameters obtained with
benzene for the other two series of activated carbons
prepared from the untreated parent coal (series AP)
and from the parent coal demineralized by acid treatments
with HCl and HF at 333 K (series CP). The results
listed in this table have been discussed in a previous
paper, and they are given in this work to compare them
with those obtained with the series AFP.

Table 3. Real Parameters Obtained from the
Dubinin–Stoeckli Equation Applied to the Benzene
Adsorption Isotherms

<table>
<thead>
<tr>
<th>sample</th>
<th>% ash</th>
<th>$S_{me}$ m$^2$ g$^{-1}$</th>
<th>$W_0$ cm$^3$ g$^{-1}$</th>
<th>$L_0$ nm</th>
<th>$d$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-16</td>
<td>13.6</td>
<td>58</td>
<td>0.13</td>
<td>0.71</td>
<td>0.107</td>
</tr>
<tr>
<td>AP-30</td>
<td>16.7</td>
<td>94</td>
<td>0.20</td>
<td>1.14</td>
<td>0.115</td>
</tr>
<tr>
<td>AP-48</td>
<td>24.7</td>
<td>183</td>
<td>0.23</td>
<td>1.37</td>
<td>0.136</td>
</tr>
<tr>
<td>CP-40</td>
<td>1.7</td>
<td>124</td>
<td>0.26</td>
<td>1.11</td>
<td>0.116</td>
</tr>
<tr>
<td>CP-55</td>
<td>2.2</td>
<td>208</td>
<td>0.31</td>
<td>1.34</td>
<td>0.139</td>
</tr>
</tbody>
</table>

Figure 3. Relationship between the mesoporous surface area of the activated carbons and their percentage burn-off: ○ AFP series; □ AP series; Δ CP series.

Figure 4. Micropore volume from benzene isotherm (real parameter) as a function of percentage burn-off: ○ AFP series; □ AP series; Δ CP series.

Conclusions
The micropore volume of the activated carbons obtained
from the Dubinin–Astakhov equation applied to CO$_2$
adsorption at 273 K is affected by adsorption on external
surface. Thus, to determine the real parameters of the
micropore structure, it was necessary to apply the
Dubinin–Stoeckli equation to the benzene adsorption
isotherms at 303 K corrected by the Dubinin–Zaverina
approach.

The demineralization treatments given to the parent coal prior to its activation affected microporosity development, whereas the mesopore surface area was independent of these treatments and linearly increased with the percentage BO.

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