Adsorption Properties of Porous Carbons: Influence of Preadsorbed Water on Gas Adsorption Behavior


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1. Introduction
   - Characteristics and applications of porous carbons
   - Enhanced interaction potential in micropore
   - Adsorption characteristics of various molecules in micropore
2. Experimental
3. Results
   - Remarkable weight increase for water–preadsorbed ACF
   - Gas composition analyses
4. Hysteresis-assisted pressure-shift-induced water adsorption mechanism
5. Verification of the mechanism
6. Influence of adsorption hysteresis of water or temperature
7. Conclusion
Porous Carbons

Characteristics
- Large surface area
- Confined space
- Surface functionality

Applications
- Storage
- Gas storage
- Separation
  - Decolorization
  - Deodorization
  - Desalination
  - Solvent recovery
  - Desiccation
  - Gas separation
- Catalysis
  - Catalyst
- Support
  - Catalyst support

Schematic illustration of slit-shaped graphitic micropore
Steele’s 10–4–3 potential

\[ \Phi(z) = 2\pi \varepsilon_{sf} \rho_s \sigma_{sf}^2 \left\{ \left( \frac{2}{5} \right) \left( \frac{\sigma_{sf}}{z} \right)^{10} - \left( \frac{\sigma_{sf}}{z} \right)^4 - \frac{\sigma_{sf}^4}{3\Delta(z + 0.61\Delta)^3} \right\} \]

Overlapping of potentials from face-to-face surfaces

\[ \Phi(z)_{\text{pore}} = \Phi(z) + \Phi(H-z) \]
Adsorption Isotherms of Various Gases

$W = f(T, P, \text{solid, fluid})$

Adsorption and desorption isotherms of various gases on ACF P20

- **N$_2$ @77 K**
- **CH$_4$ @114 K**
- **H$_2$O @303 K**
- **CH$_4$ @303 K (supercritical)**

Adsorption amount $W$ in mg g$^{-1}$

Relative pressure, $P/P_0$
Pre-Mixed Gas Adsorption

Slit-shaped micropore

Time dependence after introduction of pre-mixed gas of CH\(_4\) and H\(_2\)O (\(P_W = 2.5\) kPa) to ACF P20 at 303 K
Measured by Mr. T. Kanda
Experimental

Sample

Pitch-based Activated Carbon Fiber (ACF): P20

<table>
<thead>
<tr>
<th>Specific surface area ( a_s ) /m² g⁻¹</th>
<th>Micropore volume ( W_0 ) /cm³ g⁻¹</th>
<th>Average pore width ( w ) /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P20</td>
<td>1800</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Pretreatment conditions

383 K, ≤ 1 mPa, 2 h

Apparatuses

- Mixed gas adsorption apparatus (gravimetric technique)
- Gas Chromatography, GC–8AIT (TCD)
Schematic Illustration of Gas Introduction Steps

**Step 1**
Preadsorption of water

**Step 2**
Mixing gases

**Step 3**
Introduction of mixed gas

Slit-shaped micropore
Effect of Preadsorbed Water

Time dependence of weight change after introduction of mixed gas to H₂O-preadsorbed ACF P20 at 303 K

$\phi_{W}^{ads} = 0.4$, $P_M = 4.5$ kPa

Max within 1–2 h

Possible reason of weight change

- Enhanced adsorption of CH₄
- Additional adsorption of H₂O

Long relaxation time

Quantitative analysis of gas composition

CH₄ ⋯ Gas Chromatography
H₂O ⋯ Karl Fischer method
### Quantitative Analyses of Gas Composition by GC

<table>
<thead>
<tr>
<th>Time /Hour</th>
<th>Weight change /mg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Before</td>
</tr>
<tr>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>40</td>
<td>200</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
</tr>
<tr>
<td>80</td>
<td>100</td>
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</table>

Mostly due to additional adsorption of H₂O

#### Graph 1: Weight change over time

- **Graph 2: GC peak area**
  - Before introduction
  - After introduction

- **Introductions**
  - Before
  - After

- **Gases**
  - CH₄
  - Ar

Amounts of Ar or CH₄ in gas phase before and after introduction of mixed gas
Hysteresis-Assisted Pressure-Shift-Induced Water Adsorption Mechanism

A ⇒ B
1. Compression of water vapor
2. Increase of effective water pressure around sample (ΔP)
3. Additional adsorption of water (ΔW)

B ⇒ C
4. Relaxation of pressure
5. Partial desorption of water (ΔW - ΔW')

**Transient Compression Effect**

**Point A**
- **CH₄**
- **H₂O**
- Close

**Point B**
- Open
- Valve open

**Point C**
- Open
- Long equilibrium period
Adsorption and desorption scanning curves of H$_2$O on ACF P20 at 303 K
Verification of the Mechanism

Adsorption and desorption scanning curves of H$_2$O on ACF P20 at 303 K

- ○, □: Adsorption
- ●, ■: Desorption

Time dependence after introduction of mixed gas from H$_2$O desorption isotherm to H$_2$O–preadsorbed ACF P20 at 303 K

\[ \phi_{W_{\text{des}}} = 0.34, \ P_M = 3.6 \text{ kPa} \]
Water Adsorption Isotherms of Microporous Carbons

Pitch–based Activated Carbon Fiber
P5, P10, P15, and P20 (Adol Co.)

KOH–activated Coal–based Activated Carbon
SAC31 (Kansai Coke Co.)

Micropore structural parameters obtained from $\alpha_S$ analysis

<table>
<thead>
<tr>
<th></th>
<th>$a_S$ /m$^2$ g$^{-1}$</th>
<th>$W_0$ /cm$^3$ g$^{-1}$</th>
<th>$w$ /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5</td>
<td>880</td>
<td>0.29</td>
<td>0.67</td>
</tr>
<tr>
<td>P10</td>
<td>960</td>
<td>0.41</td>
<td>0.86</td>
</tr>
<tr>
<td>P15</td>
<td>1310</td>
<td>0.60</td>
<td>0.94</td>
</tr>
<tr>
<td>P20</td>
<td>1800</td>
<td>0.95</td>
<td>1.1</td>
</tr>
<tr>
<td>SAC31</td>
<td>2290</td>
<td>1.33</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Adsorption and desorption isotherms of H$_2$O on ACFs at 303 K
Relationship between Adsorption Hysteresis Area and Adsorption Uptake

Time dependence after introduction of mixed gas on H$_2$O-preadsorbed carbons at 303 K

Time dependence for P5 was measured by Mr. T. Kanda.

Relationship between area of adsorption hysteresis of H$_2$O and final adsorption uptake
Temperature Dependence

Time dependence after introduction of mixed gas to H₂O-preadsorbed ACF P20 at various temperatures

Relationship between temperature and final adsorption uptake or \( P₀ \) of bulk water
Interpretation of Temperature Dependence

Compliance effect

HOT

H2O

CH4

Valve open

Valve open

WEAK

STRONG
Hysteresis-Assisted Pressure-Shift-Induced Water Adsorption Mechanism

We must avoid usage of porous carbons near 50% relative pressure, especially at high temperature.
Thank you for your attention.

İlginiz için teşekkür ederiz.

ご静聴ありがとうございました。