Supporting information

Massive Preparation of Pitch-based Organic Microporous Polymers for Gas Storage

Wenqing Li, b Aijuan Zhang, b Hui Gao, b Mingjie Chen, b Anhua Liu, b Hua Bai b and Lei Li a,b

a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, People’s Republic of China
b College of Materials, Xiamen University, Xiamen 361005, People’s Republic of China

E-mail: lilei@xmu.edu.cn
Tel: +86-592-2186296 Fax: +86-592-2183937.
Experimental Section

Instrumentation. The infrared spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (NICOLET iS10). The $^{13}$C cross-polarization magic angle spinning (CP/MAS) NMR spectra were obtained on a WB 400 MHz BRUKER AV III spectrometer. Measurements were made with a 4 mm MAS probe spinning at 12 kHz. Elemental analysis were performed on an Elementar Vario EL III elemental analyzer. The morphology of samples was observed by scanning electron microscopy (SEM) (SU-70, Hitachi) under an electron beam with an accelerating voltage of 10 kV and a working distance of 15 mm. The high-resolution transmission electron microscopy (HRTEM) images were observed by JEM-2100 (JEOL) with an acceleration voltage of 200 kV. Nitrogen adsorption isotherms were measured at 77.3 K using a Micromeritics TriStar II 3020 static volumetric analyzer. Prior to adsorption measurements the polymers were degassed for 12 h at 100 °C ensuring that the residual pressure fell below 10 mbar. The Brunauer-Emmett-Teller surface area was calculated within the relative pressure range 0.05 to 0.2. Total volume was calculated at $P/P_0=0.99$. The CO$_2$ adsorption isotherms were measured at 273 K and 298 K using Micromeritics TriStar II 3020 static volumetric analyzer. The N$_2$ storage adsorption isotherms were measured at 273 K up to 1.0 bar. The H$_2$ adsorption isotherms were measured using a Micromeritics ASAP 2020 static volumetric analyzer at
77.3 K up to 1.13 bar. Thermal Gravity Analysis (TGA) was performed on a thermal analyzer (Q500 V6.7 Build 203) under N₂ atmosphere with a heating rate of 10 °C min⁻¹.

**Materials.** Pitch was purchased from Dalian Mingqiang Chemical Industry Co., Ltd, and it is a mixture which consists of 20.7 % asphaltenes (Aₚ), 23.9 % saturates (S), 46.8 % aromatics (Aᵣ) and 8.4 % resins (R), determined by the method described in Chinese national standard (GB/T0618-1993). The softening point is 250 °C measured according to GB/T4507-2014. Elemental combustion analysis (%) of pitch afford: C: 94.42 %, H: 5.10 %, N: 0.13 %, O: 0.35 %, C/H = 1.54. Anhydrous ferric chloride (FeCl₃) was purchased from Alfa Aesar Company. Formaldehyde dimethylacetal (FDA, 98 %) was purchased from Tokyo Chemical Industry Co., Ltd. Methanol, dichloromethane, N-heptane, toluene, concentrated sulfuric acid (H₂SO₄, 98 %), sodium hydroxide (NaOH), Sodium carbonate (Na₂CO₃), calcium hydride (CaH₂), 1,2-dichloroethane (DCE) were obtained from Sinopharm chemical reagent Co., Ltd (Shanghai, China). DCE was washed with concentrated H₂SO₄, deionized water, aqueous solution of Na₂CO₃ and water sequentially. Then, after drying for night with CaH₂, it is refluxed with CaH₂ and fractionally distilled. Unless specifically noted, all the chemical reagents were analytical grade and used as received without further purification.
**Component Analysis of pitch.** The component analysis of pitch was performed following the Chinese national standard GB/T0618-1993.

A.) Pitch (m, 1.0490 g) was dissolved in 60 mL n-heptane, and heated to reflux for 1 h. Then, the solution was transferred to a new conical flask (1), sealed and kept still for 2 h in the dark.

B.) The n-heptane solution in conical flask (1) is filtered into conical flask (2). The residues on the filter paper were extracted by n-heptane solution in conical flask (2) for 1 h. Then, the residues were extracted again by toluene (60 mL) in conical flask (1) for 1 h.

C.) When conical flask (1) is cooled to room temperature, the toluene was removed, then the conical flask (1) was dried under reduced pressure at 105 °C for 1 h. The residue in conical flask (1) was weighted ($m_1 = 0.2171$ g).

D.) The n-heptane solution in conical flask (2) was concentrated to 10 mL, then the solution was separated by column chromatography silica gel (45 g) at 50 °C, with n-heptane (80 mL), toluene (80 mL), toluene/ethanol (1:1(v/v),40 mL), toluene (40 mL) and ethanol (40 mL) as the eluant, successively. The last three fractions were merged, thus finally three fractions were obtained. The three solutions were then dried under reduced pressure at 105 °C for 1 h, and finally weighted. The mass of the three fractions was: $m_2 = 0.2508$ g, $m_3 = 0.4909$ g, $m_4 = 0.0881$ g, respectively. Accordingly, the content of Asphaltenes ($A_s$), Saturates (S), Aromatics
(A_r), and Resins (R) were calculated to be:

\[
A_s = \frac{m_1}{m} \times 100\% = 20.7\%
\]

\[
S = \frac{m_2}{m} \times 100\% = 23.9\%
\]

\[
A_r = \frac{m_3}{m} \times 100\% = 46.8\%
\]

\[
R = \frac{m_4}{m} \times 100\% = 8.4\%
\]

**Synthesis of HCPs.** At room temperature, pitch (0.304 g) was dissolved in 5 mL DCE under argon atmosphere, then FDA (0.304 g), FeCl\(_3\) (1.296 g) was added to the homogeneous solution. The mixture was mixed uniformly by agitation at room temperature, then refluxed under stir at 80 °C for 24 h. Then, the solid product was washed three times with methanol, and extracted in a Soxhlet extractor by methanol and dichloromethane for 12 h, respectively. Finally the obtained powder was dried under reduced pressure at 80 °C for 24 h.

**Table S1** The amount of FDA and FeCl\(_3\) in each experiment.\(^a\)

<table>
<thead>
<tr>
<th>NO.</th>
<th>HCP-1</th>
<th>HCP-2</th>
<th>HCP-3</th>
<th>HCP-4</th>
<th>HCP-5</th>
<th>HCP-6</th>
<th>HCP-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{F/P})</td>
<td>0.3</td>
<td>0.6</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>FDA(g)</td>
<td>0.091</td>
<td>0.182</td>
<td>0.304</td>
<td>0.456</td>
<td>0.608</td>
<td>0.760</td>
<td>0.912</td>
</tr>
<tr>
<td>FeCl(_3)(g)</td>
<td>0.390</td>
<td>0.780</td>
<td>1.296</td>
<td>1.944</td>
<td>2.592</td>
<td>3.240</td>
<td>3.888</td>
</tr>
</tbody>
</table>

\(^a\) The fixed amount of pitch is 0.304 g in all experiments.
Fig. S1 Digital photo of the Pitch-based HCP.

Fig. S2 SEM images of HCP-2(a) and HCP-3(b).

Fig. S3 HRTEM images of HCP-2(a, b), and HCP-3(c, d).
Fig. S4 Isosteric heat of adsorption for HCP-3 determined from CO$_2$ adsorption isotherms at 273 K and 298 K.

Fig. S5 Adsorption isotherms of CO$_2$ and N$_2$ gases at 273 K for HCP-3.
Fig. S6 Adsorption selectivity of CO$_2$ over N$_2$ for HCP-3 derived from the initial slope method at 273 K.

Table S2 Surface Areas and Pore Properties of HCP-3 before and after immerging in strong alkali, strong acid solution.

<table>
<thead>
<tr>
<th>NO.</th>
<th>$S_{\text{BET}}$(m$^2$/g)</th>
<th>$S_{\text{Micro}}$(m$^2$/g)</th>
<th>PV(cm$^3$/g)</th>
<th>MPV(cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP-3</td>
<td>758</td>
<td>571</td>
<td>0.52</td>
<td>0.33</td>
</tr>
<tr>
<td>HCP-3-alkali$^a$</td>
<td>510</td>
<td>410</td>
<td>0.33</td>
<td>0.22</td>
</tr>
<tr>
<td>HCP-3-acid$^b$</td>
<td>607</td>
<td>495</td>
<td>0.41</td>
<td>0.26</td>
</tr>
</tbody>
</table>

$^a$ the sample after being immersed in 1M NaOH solution for 12 h; $^b$ the sample after immersing in 1M H$_2$SO$_4$ solution for 12 h.

Fig. S7 Nitrogen adsorption/desorption isotherms for HCP-3 before (black) and after being immersed and stirred in 1M NaOH (red) and 1M H$_2$SO$_4$ (blue) for 12 h, respectively.
Fig. S8 TGA curve of the HCP-3.
In this, we given the data of the FTIR spectra (Fig. S9) and N$_2$ sorption isotherms (Fig. S10) for the HCPs with three kinds of pitches coming from differ. Sample 1 is the pitch used in our experiments, Sample 2 is a kind of coal tar pitch and Sample 3 is a kind of petroleum pitch.

![FTIR spectra](image1.png)

**Fig. S9** The FTIR spectra of Sample 1, Sample 2 and Sample 3.

![Nitrogen adsorption isotherms](image2.png)

**Fig. S10** Nitrogen adsorption and desorption isotherms at 77.3 K.