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

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A general challenge for organic microporous polymers (MOPs) is to use cheap and sustainable building blocks while retain the advanced functions. We demonstrate a strategy to massively prepare pitch-based MOPs, which are thermal and chemical stable. A maximum BET surface area of 758 m^2/g and high gas storage capacity were achieved.

The design and preparation of organic microporous polymers (MOPs) have attracted significant attention in both academic and industrial interests, due to their potential applications ranging from gas storage,[1] separation,[2] and chemical catalysis[3] to capture of toxic heavy metal ions.[4] Compared with their inorganic cousins (zeolites[5] and metal-organic frameworks (MOFs)[6]), MOPs can be constructed by using a plethora of organic reactions and building blocks, which provides flexibility for the material design to achieve inherent lightweight, desirable structures, properties and functions.[7] In the past decades, various preparation strategies have been developed to create new MOPs. For example, covalent organic frameworks (COFs)[8] are crystalline organic networks which are analogous to MOFs; polymers of intrinsic microporosity (PIMs)[9] are insoluble networks or linear, soluble polymers prepared with highly contorted monomers; conjugated microporous polymers (CMPs)[10] have conjugated network structure and are achieved by the cross-coupling reactions between conjugated building blocks. However, the monomers used in these reactions must bear halogen,[11] ethynyl[12] or stereo-controlled structures,[13] which require tedious synthesis. In addition, the successful preparation of the above MOPs need expensive catalysts and high lab cost. Therefore, the unsustainable mass production and high cost limit the practical applications of MOPs prepared by the above-mentioned strategies. Hyper-cross-linked polymers (HCPs) have aroused more and more attention, because of the simple chemical preparation. A representative example of HCPs is the

Davankov resins, which was for the first time described in scientific literature in the early 1970s,[14] and substantially came into routine practice by the end of 1980s. Therefore, considering the simplicity of the hyper-cross-linking reaction, the remained challenge will be to find and use cheaper and more sustainable building blocks while retain the advanced function in developing new HCPs.[15]

Pitch is the by-product of crude oil distillation, and the total amount of pitch in the world is 275 million tons in the year of 2014, and the price is as low as \$470/ton.[16] The effective utilization of pitch for the sustainable development is critical for the clean world. Pitch has long been known as an excellent raw material in the carbon manufacturing industry, because it contains large amounts of aromatic heterocyclic compounds, and can produce carbon with different characteristic structures and properties.[17] On the other hand, one of the most widely used strategies to prepare HCPs is Friedel-Crafts (F-C) reaction, in which aromatic rings on the polymers are cross-linked, producing highly porous hyper-cross-linked materials.[1c, 18] A variety of polymerization reactions catalysed by $FeCl_3$, including self-condensation of benzyl alcohol (BA),[19] vinyl benzyl chloride (VBC)[20] and benzene cross-linked with formaldehyde dimethylacetal (FDA)[21] have been reported. The resultant HCPs showed high surface areas and good gas storage capability. Here, we demonstrate a versatile strategy to massively prepare pitch-based HCPs based on F-C reaction, which utilize cheap and sustainable building block. Pitch is polymerized under mild conditions, and the resultant HCPs have high surface area, abundant microporous structures and diverse pore features by adjusting cross-linker ratio, which show good CO_2 and H_2 gas absorption capacity.

In this one-step cross-linking approach, FDA was used as an external cross-linker to react with pitch. Typically, pitch (0.304 g) was dissolved in 5 ml DCE under argon atmosphere, then a certain amount of dimethoxymethane (FDA) and $FeCl_3$ were added into the solution (Table S1). The resulting mixture was stirred under reflux for 24 h. The solid product was collected by filtration and washed three times with methanol, extracted in a Soxhlet extractor by methanol and dichloromethane sequentially, and finally dried under reduced pressure at 80 °C for 24 h. The obtained HCPs with different FDA/pitch weight ratio of 0.3, 0.6, 1.0, 1.5, 2.0, 2.5 and 3.0 are referred to as HCP-1, -2, -3, -4, -5, -6, and -7, respectively. All samples were

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obtained as dark brown powder. The massive preparation can be completed in the standard reaction kettle (Fig. S1).
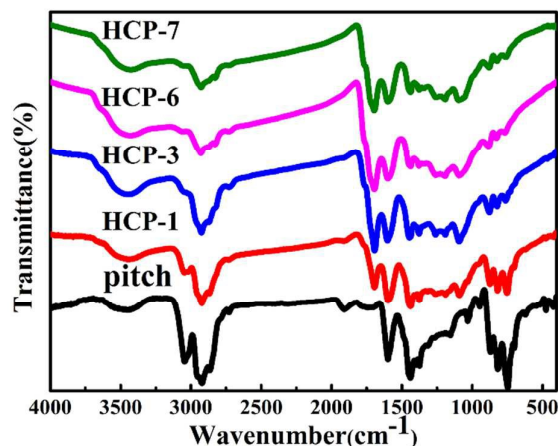

Fig. 1 The FTIR spectra of pitch and HCP-1, 3, 6, 7.

The hyper-cross-linking reaction using FDA as the external cross-linker has been investigated by other groups.[21, 22] Here, we demonstrate that more complex aromatic compounds can also be cross-linked by the same polymerization reaction. The cross-linking products were first investigated by Fourier transform infrared (FTIR) spectroscopy. As shown in Fig. 1, the band at 3046 cm^{-1} in the spectrum of pitch is assigned to C-H stretching vibrations of aromatic rings, and bands ranging 1600 cm^{-1} -1500 cm^{-1} are attributed to the vibrations of aromatic ring C=C skeleton. These bands indicate the existence of large amount of aromatic compounds in the pitch. The characteristic band at 3046 cm^{-1} is weakened significantly in the spectra of HCPs, and its intensity decreases with the increase of FDA feeding ratio. Meanwhile, the in-plane bending vibrations of C-H on the aromatic rings ranging 900-600 cm^{-1} in HCPs also disappear or weaken. These results demonstrate that the aromatic hydrogen atoms are substituted, thus pitch has reacted with FDA. As expected, C=O stretching vibration at 1690 cm^{-1} is found in the spectra of HCLPs, due to the small amount of carbonyl groups forming during the F-C reaction.[23]
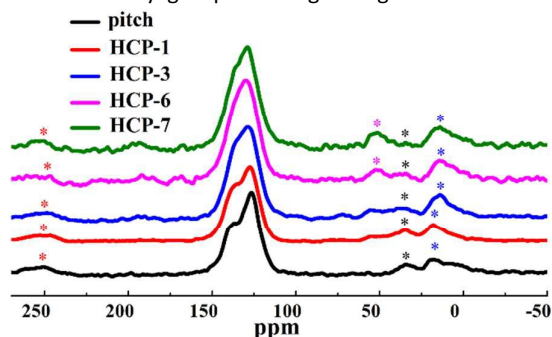

Fig. 2 Solid state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectra of pitch and HCP-1, 3, 6 and 7. Red asterisks (*) denote the spinning side bands.

Solid state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectrum was also used to characterize the HCPs. As depicted in Fig. 2, the NMR spectra of the pitch and HCP-1 are almost identical. The peaks near 22 ppm marked with blue asterisks are assigned to methyl carbon in pitch. The resonance peaks near 34 ppm marked with black asterisks are

assigned to aliphatic carbon in the pitch or in the methylene linker formed during the F-C reaction. The peaks marked with pink asterisks denote methoxy carbon in unreacted FDA. The resonance peaks near 131 ppm and 126 ppm are attributed to the substituted aromatic carbon and the non-substituted aromatic carbon, respectively. The peak at 131 ppm rises with the feeding amount of FDA, indicating that the fraction of substituted aromatic carbon increases. The above spectral data confirm that the pitch has reacted with FDA and a cross-linked structure has formed.

The surface morphologies of HCPs were observed by field emission scanning electron microscopy. All the samples are composed of loose agglomerates of tiny particles with an irregular shape (Fig. S2). The high-resolution transmittance electron microscopy images illustrate that there are uniform nano-channels throughout the whole networks (Fig. S3). Since porous structure is created by the hyper-cross-linking reaction with single carbon atom spacer, the pore size is small and no ordered structure exists in the film. Therefore, the surface areas and porosity parameters of the polymers were further studied by physical sorption of N_2 at 77.3 K. The N_2 adsorption isotherms (Fig. 3a) of all samples show a steep N_2 uptake at low relative pressure (P/P$_0$ < 0.001), reflecting the existence of abundant micropores. The adsorption isotherms of HCP-1, HCP-2 and HCP-3 show an evident hysteresis loop at medium pressure region (P/P$_0$ = 0.4-0.7), indicating that a large number of mesopores exist in these HCPs. Besides, a sharp rise at high pressure region (P/P$_0$ = 0.8-1.0) is also observed in the adsorption and desorption isotherms of these HCPs, revealing the presence of macropores in these materials.[24] For HCP-4, HCP-5 and HCP-6, the isotherms show a relatively small hysteresis loop, and a modest rise at high pressure region, thus the volume fractions of mesopores and macropores are small in these materials. The pore size distributions shown in Fig. 3b also confirm such heterogeneous porous structure in HCPs.
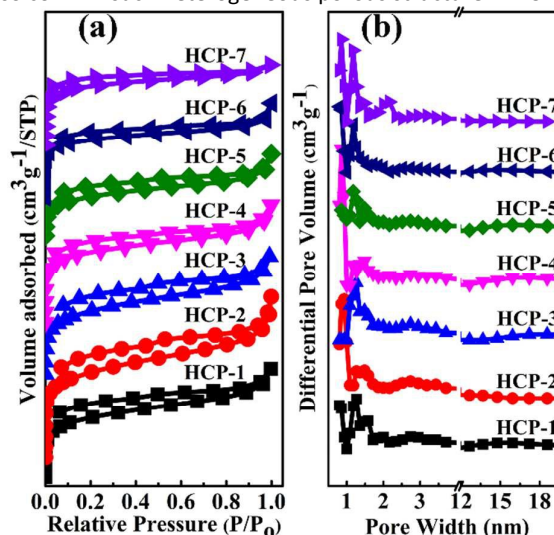

Fig. 3 (a) Nitrogen adsorption and desorption isotherms at 77.3 K; (b) Pore size distribution curves, as calculated using DFT methods (slit pore models, differential pore volume vs. pore width).

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Table 1. Surface Areas, Pore Properties and Gas Adsorption of Pitch-based HCPs.

No.	$R_{F/P}$ [a]	S_{BET} [b] (m^2/g)	S_{Micro} [c] (m^2/g)	PV [d] (cm^3/g)	MPV [e] (cm^3/g)	CO_2 uptake [f] (wt %)	H_2 uptake [g] (wt %)
HCP-1	0.3	500	344	0.38	0.21	7.53	-
HCP-2	0.6	695	476	0.53	0.30	11.81	0.93
HCP-3	1.0	758	571	0.52	0.33	9.95	0.95
HCP-4	1.5	584	434	0.41	0.25	10.17	-
HCP-5	2.0	553	435	0.38	0.24	10.22	-
HCP-6	2.5	481	386	0.32	0.21	9.94	-
HCP-7	3.0	439	351	0.27	0.19	9.03	-

[a] Weight ratio of FDA to monomer. [b] Surface area calculated from nitrogen adsorption isotherms at 77.3 K using BET equation. [c] Micropore surface area calculated from nitrogen adsorption isotherms at 77.3 K using t-plot equation. [d] Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.99$, 77.3 K. [e] Micropore volume calculated from the nitrogen isotherm at $P/P_0 = 0.15$, 77.3 K using t-plot equation. [f] CO_2 uptake determined volumetrically at 1.0 bar and 273 K. [g] H_2 uptake determined volumetrically at 1.13 bar and 77.3 k

The data of specific surface areas, the pore properties and gas adsorption for pitch-based HCPs are summarized in Table 1. It is found that the specific surface areas, pore volume vary with the weight ratios of FDA to pitch ($R_{F/P}$). The highest BET surface area and micropore surface area (758 m^2/g, 571 m^2/g) are obtained in HCP-3. With the increase of $R_{F/P}$ from 0.3 to 1.0, the BET surface area increases from 500 m^2/g to 758 m^2/g, and micropore surface area from 344 m^2/g to 571 m^2/g. The larger BET surface area and micropore surface area at large $R_{F/P}$ can be explained as the results of higher crosslinking degree. However, further increase of the $R_{F/P}$ leads to a decrease in the specific surface area. The reason is that when excess FDA is used, only one of the two methoxy groups in FDA reacts with the aromatic rings. As a result, the crosslinking degree of HCP decreases. The other methoxy group on FDA is converted into carbonyl group, as demonstrated by the FTIR spectra of the HCPs.
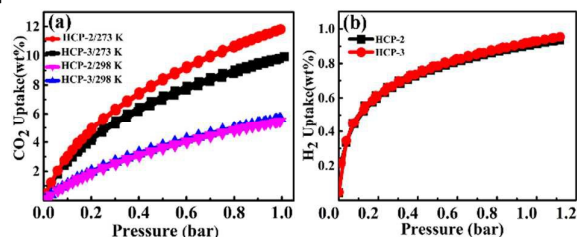

Fig. 4 (a) Adsorption and desorption isotherms of CO_2 at 273 K and 298 K for HCP-2 and HPC-3; (b) Adsorption and desorption isotherms of H_2 at 77 K for HCP-2 and HCP-3.

With the worsening global environmental crisis and the increasing energy demand, CO_2 capture has become one of the attractive topics in chemical and material researches. Microporous materials are believed as promising candidates for this purpose. Therefore, we investigated the performance of HCPs in CO_2 capture (Fig. 4a and Table 1). At 273 K and 1.0 bar, the largest CO_2 uptake of HCP-2 was measured to be 11.81 wt %, higher than those of the most materials reported so far.[9a, 18a, 21] The excellent CO_2 uptake performance is attributed to the large micropore surface area, as well as the heteroatoms in the HCPs.

To further understand the pore surface properties and the adsorption process, the isosteric heat (Q_{st}) of CO_2 adsorption on HCP-3 was calculated from the adsorption isotherms at 273 K and 298 K in term of Clausiuse-Clapeyron equation, and shown in Fig. S4. At a very low CO_2 uptake, the HCP-3 has the

highest Q_{st} value of 30.4 kJ/mol that is higher than those of some HCPs, some CMPs and other porous polymers.[24] The higher Q_{st} may be attributed to the proper pore structures for CO_2 adsorption and the heteroatoms in the HCPs that can enhance the interaction between CO_2 molecules and the pore surfaces of HCPs. The Q_{st} slightly decreases to 29.1 kJ/mol as the CO_2 uptake increase to 27.7 cm^3/g. This phenomenon of Q_{st} decrease was also found when other MOPs were used to adsorb CO_2,[25] and can be the result of the inhomogenous pore structures in the HCPs. On the other hand, as shown in the Fig. S5, the uptake of CO_2 is remarkably higher than that of N_2 at 273 K. The CO_2/N_2 selectivity of HCP-3 derived from the initial slope method is 30.5 (Fig. S6), higher than those of CTFs (16.1-24.1),[26] and APOPs (23.8-27.5).[27]

Another important application of microporous materials is the storage of hydrogen. As depicted in Fig. 4b and Table 1, the hydrogen uptake capacities reach up to 0.93 wt % and 0.95 wt % for HCP-2 and HCP-3 at 1.13 bar and 77.3 K, respectively. These values are comparable to those of hyper-cross-linked polymers[21, 28] and other microporous polymers.[8b, 29]

Most applications for porous solids will require stability in air as a minimum. We respectively soaked HCP-3 in 1M alkali, acid solution, and polar organic solvents overnight, small change in the properties was observed, suggesting the high chemical stability of the HCPs (Fig. S7, Table S2). Besides, the HCPs also exhibited high thermal stability as demonstrated by the thermogravimetric analysis under N_2 atmosphere. The thermal decomposition temperature ($T_{5\%}$) of HCP-3 is over 400 °C (Fig. S8). Compared with some MOFs[30] and MOPs,[31] the HCP-3 shows higher thermal stability. This excellent chemical and thermal stability of pitch-based HCPs is attributed to their inert chemical structure and high crosslinking degree. In addition, we also obtained high surface areas HCPs with pitches from different origins, indicative of the generalization of the polymerization strategy, as shown in Fig. S9 and Fig. S10.

In summary, we developed a new kind of HCPs, using low-cost pitch as the starting material. The cross-linkage is based on F-C reaction between the polycyclic aromatic hydrocarbons in pitch and the cross-linker. FTIR and CP/MAS NMR characterization confirmed the formation of the hyper-cross-linked structures. The obtained HCPs shows high specific surface area and large pore volume, which can be tuned by changing the weight ratio of FDA to pitch. Moreover, the HCPs present high CO_2 capture capacities of 11.8 % (1.0 bar, 273 K),

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and H_2 uptake of 0.95 % (1.13 bar, 77.3 K), with excellent thermal stability and high resistance to strong acid and alkali solution. Our work also demonstrates that the polymerization strategy is general for the pitches from different origins, and this inspires us to seek for other cheaper and sustainable building blocks for the scale-up preparation of OMPs.

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