

Massive Preparation of Coumarone-indene Resin-based Hyper-crosslinked Polymers for Gas Adsorption

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Electronic Supplementary Information

Abstract Hyper-crosslinked polymers (HCPs) are promising materials for gas capture and storage because of their low cost and easy preparation. In this work, we report the massive preparation of coumarone-indene resin-based hyper-crosslinked polymers *via* one-step Friedel-Crafts alkylation. Low-cost coumarone-indene resin serves as the new building block and chloroform is employed as both solvent and external crosslinker. A maximum surface area of $966 \text{ m}^2 \cdot \text{g}^{-1}$ is achieved, which is comparable with that of previously-reported coal tar-based porous organic polymers. Most importantly, a large number of heteroatoms including inherent oxygen atoms and introduced chlorine atoms in obtained HCPs further enhance the interaction between specific sorbate molecule and adsorbent. Therefore, optimal structural and chemical property endow the new coumarone-indene resin-based HCPs with decent gas storage capacity (14.60 wt% at 273 K and 0.1 MPa for CO_2 ; 1.18 wt% at 77.3 K and 0.1 MPa for H_2). These results demonstrate that new HCPs are potential candidates for applications in CO_2 and H_2 capture.

Keywords Coumarone-indene resin; Friedel-Crafts alkylation; Gas adsorption; Microporous organic polymers

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INTRODUCTION

Microporous organic polymers (MOPs) have received an increased level of research interest because of their vital importance in many applications such as heterogeneous catalysis^[1], sensors^[2], organic electronics^[3], gas storage^[4] and separation^[5]. A wide variety of MOPs have been prepared by incorporating optional organic building blocks and multitudinous synthetic routes, including polymers of intrinsic microporosity (PIMs)^[6], conjugated microporous polymers (CMPs)^[7], covalent organic frameworks (COFs)^[8,9], crystalline triazine-based frameworks (CTFs)^[10], porous polymer networks (PPNs)^[11] and porous aromatic frameworks (PAFs)^[12]. However, most MOPs were produced *via* noble-metal-catalyzed polymerization processes^[13] and the high-cost and multistep synthesis of monomers^[14], such as halogenations, which limited their scale-up preparation and practical applications.

Different from the above mentioned MOPs, hyper-crosslinked polymers (HCPs) are kinds of low-cost and easily prepared microporous organic materials. The synthesis of HCPs is mainly based on Friedel-Crafts alkylation

reaction which provides a fast kinetics to form strong linkages resulting in a highly crosslinked network with predominant porosity. Usually, the Friedel-Crafts alkylation reaction is catalyzed by inexpensive Lewis acids (such as FeCl_3 or AlCl_3) under room temperature reaction conditions^[15, 16]. Up to now, a great diversity of aromatic monomers have been exploited for the preparation of MOPs with high specific surface area^[17–20]. However, to further reduce the cost of HCPs to achieve large-scale production, more sustainable and cheaper monomers are desirable.

In our previous work, we successfully prepared a new kind of HCPs using low cost petroleum pitch and coal tar as building blocks *via* one-step Friedel-Crafts reaction^[21, 22]. Since petroleum pitch and coal tar are mainly composed of aromatic heterocyclic compounds, large amounts of Friedel-Crafts reaction sites are available, resulting in high crosslinking degrees and high Brunauer-Emmett-Teller (BET) surface area after hyper-crosslinked reaction. The obtained maximum BET surface area is $929 \text{ m}^2 \cdot \text{g}^{-1}$ by optimizing reaction conditions. Inspired by this work, we are encouraged to seek the other low-cost and sustainable building blocks for new MOPs.

Coumarone-indene resin (CR) is a copolymer of coumarone and indene, containing lots of aromatic heterocyclic compounds. Due to its low cost, CR has been widely used as softeners and softener-extenders in rubber

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processing. Therefore, it is supposed to be another ideal sustainable original material to prepare HCPs through Friedel-Crafts reaction. In this paper, we report the large-scale preparation of coumarone-indene resin-based hyper-crosslinked polymers (CHCPs) *via* Friedel-Crafts alkylation. A maximum surface area of $966 \text{ m}^2 \cdot \text{g}^{-1}$ is achieved, which is comparable with that of coal tar-based porous organic polymers. In addition, the introduction of a large amount of heteroatoms (chlorine and oxygen) further enhances the interaction between HCPs and gas molecules. Therefore, these new HCPs are endowed with decent gas storage capacity (14.6 wt% at 273 K and 0.1 MPa for CO_2 ; 1.18 wt% at 77.3 K and 0.1 MPa for H_2).

EXPERIMENTAL

Materials

Coumarone-indene resin (CR) was purchased from Puyang Hengtai Petrochemical Industry Co., Ltd. Elemental analysis (wt%): C 91.58, H 5.29, O 3.13. Anhydrous aluminium trichloride (AlCl_3) was purchased from Alfa Aesar. Ethanol, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), acetone, dichloromethane (CH_2Cl_2), CaH_2 , tetrahydrofuran (THF), and chloroform (CHCl_3) were obtained from Sinopharm chemical reagent Co., Ltd (Shanghai, China). CHCl_3 was dried with CaH_2 overnight and subsequently distilled. Unless specifically noted, all chemical reagents were analytical grade and used as received without further purification.

Preparation of CHCPs

In a typical experiment, CR (0.468 g, 4 mmol, calculated according to the phenyl group) was dissolved in 8 mL of CHCl_3 in a two-necked flask. AlCl_3 (1.6 g, 12.0 mmol) was then added to the flask at room temperature. Five minutes later, the mixture was heated to 58°C and reacted at this temperature for 24 h. The resulting product was collected by filtration, washed with ethanol and THF at least three times, and Soxhlet extracted in ethanol and THF for 12 h each. Finally, the black solid was obtained after being dried in a vacuum oven for 24 h. A series of CHCP-*x* were prepared, and *x* represents different molar ratios of AlCl_3 to CR. The amounts of the raw materials used in each experiment are

listed in Table S1 (in the electronic supplementary information, ESI).

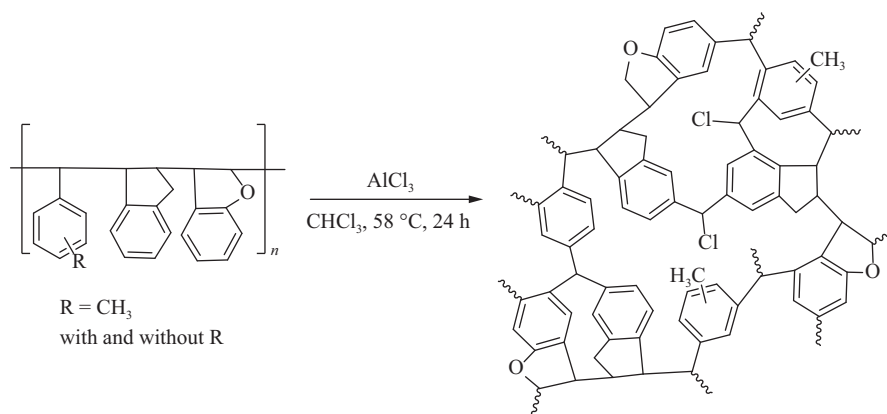
Characterization

The morphologies of CHCPs were observed by using field-emission scanning electron microscopy (FE-SEM, SU-70, Hitachi) with an accelerating voltage of 10 kV and a working distance of 15 mm. All the samples for SEM observation were coated with a thin layer of gold for better conductivity. Solid state ^{13}C cross-polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) was recorded with a Bruker AVIII-400 M NMR spectrometer operating at a spinning rate of 12 kHz resonance (CP/MAS NMR) spectrometer (WB 400 MHz BRUKER AV III spectrometer). Fourier transform infrared (FTIR) spectra in the region from 400 cm^{-1} to 4000 cm^{-1} were collected on a NICOLET iS10 spectrometer by using the conventional KBr pellet method. Powder X-ray diffraction (XRD) was recorded on a Bruker D8 Advance X-ray diffractometer. Elemental analysis was performed by using an Elementar Vario EL III elemental analyzer. Nitrogen adsorption/desorption isotherms at 77.3 K were obtained using a Micromeritics TriStar II 3020 static volumetric analyzer. The N_2 adsorption isotherms were measured at 77.3 K up to 0.1 MPa. Prior to adsorption measurements, the samples were degassed for 12 h at 100°C ensuring that the residual pressure fell below 1 kPa. The Brunauer-Emmett-Teller surface area was calculated within the relative pressure (P/P_0) range of 0.05 to 0.2. The total volume was calculated at $P/P_0 = 0.99$. The CO_2 adsorption isotherms were measured at 273 and 298 K using a Micromeritics TriStar II 3020 static volumetric analyzer. The H_2 adsorption isotherms were obtained using a Micromeritics ASAP 2020 static volumetric analyzer at 77.3 K up to 0.1 MPa.

RESULTS AND DISCUSSION

Synthesis and Characterization of CHCPs

The large-scale preparation of coumarone-indene resin-based hyper-crosslinked polymers was performed in CHCl_3 , which served as an economical solvent, electrophilic reagent and external cross-linker at low temperature. The reaction process is schematically shown in Scheme 1, as described in



Scheme 1 Schematic of the preparation strategy of CHCPs

the experimental section.

Fourier transform infrared (FTIR) spectroscopic measurement was first employed to study the polymerization products (Fig. 1a). In the spectra of the CHCPs, the characteristic C—H stretching vibrations of aromatic rings at approximately 3042 cm^{-1} also become weakened while the signals of the fingerprint region ranging from 900 cm^{-1} to 650 cm^{-1} , assigned to the out-of-plane bending vibrations of C—H on the aromatic rings in CHCPs, reduce significantly. These results confirm that the aromatic hydrogen atoms are substituted successfully. Meanwhile, these products were also characterized by solid state ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP/MAS NMR). All the spectra of CHCPs exhibit similar signal distribution. As shown in Fig. 1(b), the peak intensity at approximately 137 ppm, which belongs to the substituted aromatic carbons, increases significantly and the peak intensity of unsubstituted aromatic carbons at 127 ppm decreases obviously after the Friedel-Crafts reaction^[23]. The new peak at 65 ppm, appearing in the spectra of CHCPs, is ascribed to the signal peak of heteroatom-substituted aliphatic carbons from methylene bridge between aromatic rings^[24]. Inherent aliphatic carbon signal is located at 36 ppm, appearing in the spectra of both CHCPs and CR. Moreover, energy-dispersive spectrometry (EDS) reveals that coumarone-indene resin (CR) does not contain detectable chlorine, whereas chlorine content of CHCP-3 is 12.08 wt% (Fig. 1c). The result indicates that CHCl_3 has participated in the reaction and partial chloride atoms in CHCl_3 can be unsubstituted, probably due to steric

hindrance. Therefore, FTIR, ^{13}C CP/MAS NMR and EDS results all confirm that CR were successfully crosslinked through a one-step Friedel-Crafts reaction with CHCl_3 as the external crosslinker and a large number of heteroatoms (oxygen and chlorine) were introduced into CHCPs.

Moreover, all obtained CHCPs are insoluble in common organic solvents, such as DMSO, DMF, acetone, THF, and CH_2Cl_2 due to the highly crosslinked structure. As shown in Figs. S1(c) and S1(d) (in ESI), the TEM images of CHCP-3 do not show long-range ordered domains corresponding to their amorphous nature. The amorphous nature of CHCP-3 is further demonstrated by powder X-ray diffraction measurements that display no diffraction peaks (Fig. S2, in ESI). According to the SEM images, CHCP-3 has a bulky morphology with no pores on its smooth surface (Figs. S1a and S1b, in ESI).

The porosity parameters and surface area of CHCPs were investigated by nitrogen adsorption/desorption isotherms at 77.3 K. As shown in Fig. 2(a), all the isotherms of CHCPs show a similar combination of type I and II nitrogen sorption isotherms according to the IUPAC classification. The steep increase of N_2 uptake at very low relative pressure ($P/P_0 < 0.01$) and evident hysteresis loop at medium pressure ($P/P_0 = 0.4\text{--}0.7$) suggest the abundant micropores and mesopores in the CHCPs, respectively^[25]. A slight rise in the nitrogen isotherms for all the CHCPs, is also observed at high relative pressures ($P/P_0 > 0.9$), indicating the presence of small amounts of macropores from inter-particle porosity or voids. Pore size distribution was estimated using nonlocal density functional theory (NLDFT) calculations (Fig. 2b). The most

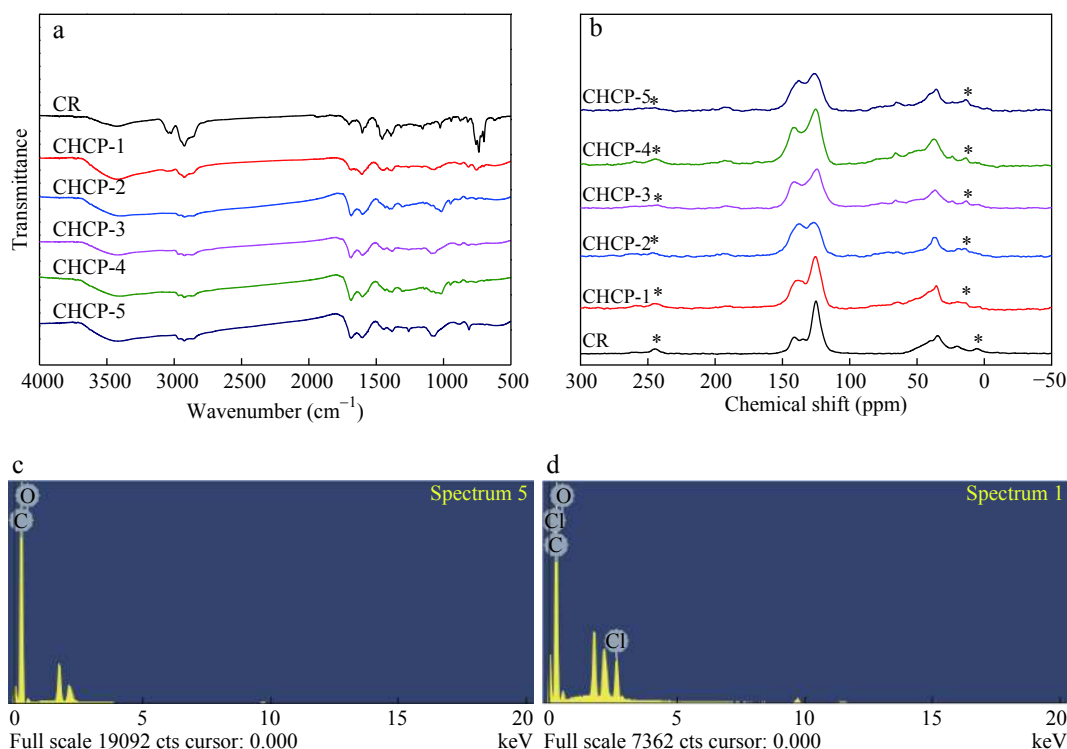


Fig. 1 (a) FTIR and (b) ^{13}C CP-MAS NMR spectra of CR and CHCPs (* side bands); EDS of (c) CR and (d) CHCP-3 (The online version is colorful.)

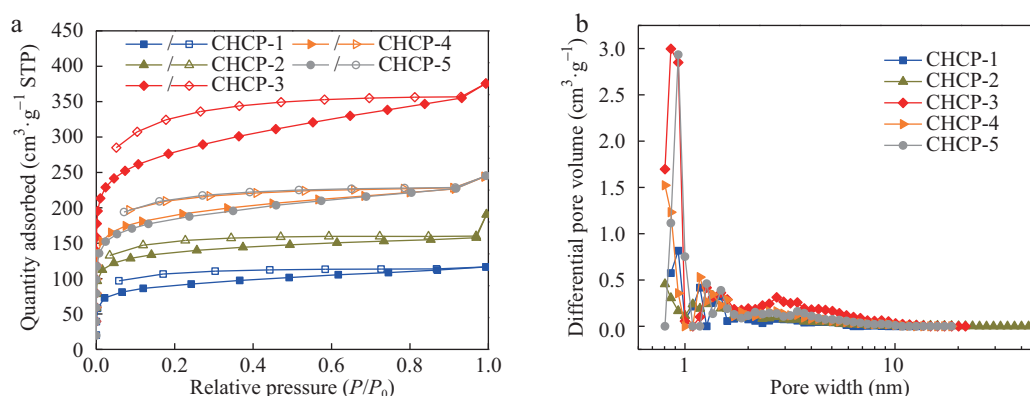


Fig. 2 (a) Nitrogen sorption isotherms and (b) pore size distribution curves (calculated using NLDFT methods) of CHCPs

prevalent pores are centered below 2 nm, indicating that the polymer is predominantly microporous. Listed in Table 1 are the key porosity parameters derived from the isotherms, such as total specific surface area, micropore surface area, micropore volume and pore volume.

The BET surface area and pore volume vary with the molar ratios of AlCl_3 to coumarone-indene resin. It is also found that the change of pore volume (total pore volume and micropore volume) consistently matches with that of specific surface area (total surface area and micropore surface area). With the increase of $R_{A/C}$ from 1.0 to 3.0, both the surface area and pore volume increase sharply. This demonstrates that a higher crosslinking degree can be achieved at higher $R_{A/C}$ values^[24]. It is worth emphasizing that CHCP-3 reaches the highest specific surface area ($966 \text{ m}^2\cdot\text{g}^{-1}$), micropore surface area ($710 \text{ m}^2\cdot\text{g}^{-1}$), total pore volume ($0.58 \text{ cm}^3\cdot\text{g}^{-1}$) and micropore volume ($0.42 \text{ cm}^3\cdot\text{g}^{-1}$) among all CHCPs samples. Further increase of $R_{A/C}$ results in a slight loss of porosity, which suggests that the crosslinking degree of CHCPs decreases slightly. When the excess AlCl_3 is added, the initial crosslinked products wrapped in catalyst have difficulty in further crosslinking reaction^[22].

Gas Adsorption Properties

Coumarone-indene resin-based hyper-crosslinked polymers with a high specific surface area and a narrow pore distribution may interact attractively with small gas molecules, which inspires us to investigate their gas (CO_2 and H_2) uptake. The CO_2 uptake capacities of CHCPs measured at 273 and 298 K are shown in Fig. 3. Among all the samples, CHCP-3 features the highest CO_2 capture capacity of 14.60 wt% at 273 K and 8.89 wt% at 298 K, which is comparable with that of coal tar-based porous

organic polymers. The greatly enhanced CO_2 capture capacity may be ascribed to the highest surface area, pore volume and the incorporation of heteroatoms. Interestingly, as shown in Table S2 (in ESI), these CO_2 uptake values are not only obviously higher than those of a large number of microporous materials with a similarly specific surface area but also comparable to the reported values of porous aromatic frameworks with large surface area, such as PAF-1 (9.1 wt%, $\text{SSA} = 5600 \text{ m}^2\cdot\text{g}^{-1}$)^[26], PTPA-4 (11.7 wt%, $\text{SSA} = 1543 \text{ m}^2\cdot\text{g}^{-1}$)^[27], and HCP-BDM (12.6 wt%, $\text{SSA} = 847 \text{ m}^2\cdot\text{g}^{-1}$)^[28]. In the low-pressure region, the CO_2 uptakes of all CHCPs increase sharply because of a strong interaction between CO_2 and pore walls. The CO_2 uptake continuously increases with the experimental pressure and does not reach saturation in 0.1 MPa, suggesting that a larger adsorption capacity could be achieved at higher CO_2 pressure^[29].

For practical applications, recyclability of a porous adsorbent is of great importance in addition to the adsorption capacity. Regeneration of the present CHCP was therefore examined. As shown in Fig. 3(c) and Fig. S3 (in ESI), consecutive CO_2 adsorption/desorption were carried out for four cycles, and there was no visible loss of adsorption capacity. This suggests that, by means of changing pressure, CO_2 molecules on the pore walls are readily regenerated, which may give the chance for these materials to be applied in the pressure swing adsorption (PSA) technology^[30]. The chemical stability of porous materials is another important aspect for practical applications. As shown in Fig. S4 (in ESI), the surface area of CHCP-3 did not show obvious loss upon exposure to acidic condition. However, huge changes in properties were observed after it was treated with NaOH solution ($1 \text{ mol}\cdot\text{L}^{-1}$) for 24 h. The CHCP also exhibited high thermal stability as evidenced by thermogravimetric analysis

Table 1 Surface area and porosity of CHCPs

Sample	$R_{A/C}$ ^a	S_{BET} ^b ($\text{m}^2\cdot\text{g}^{-1}$)	S_{micro} ^c ($\text{m}^2\cdot\text{g}^{-1}$)	V_{total} ^d ($\text{cm}^3\cdot\text{g}^{-1}$)	V_{micro} ^e ($\text{cm}^3\cdot\text{g}^{-1}$)
CHCP-1	1.0	313	233	0.18	0.14
CHCP-2	2.0	472	400	0.29	0.21
CHCP-3	3.0	966	710	0.58	0.42
CHCP-4	4.0	654	509	0.38	0.29
CHCP-5	5.0	639	477	0.38	0.28

^a $R_{A/C}$ represents the molar ratio of AlCl_3 and phenyl group; ^b Total surface area calculated from the nitrogen adsorption isotherms at 77.3 K using the BET equation; ^c Micropore surface areas calculated from the nitrogen adsorption isotherms at 77.3 K using the t-plot equation; ^d Pore volume calculated from the 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 the t-plot equation

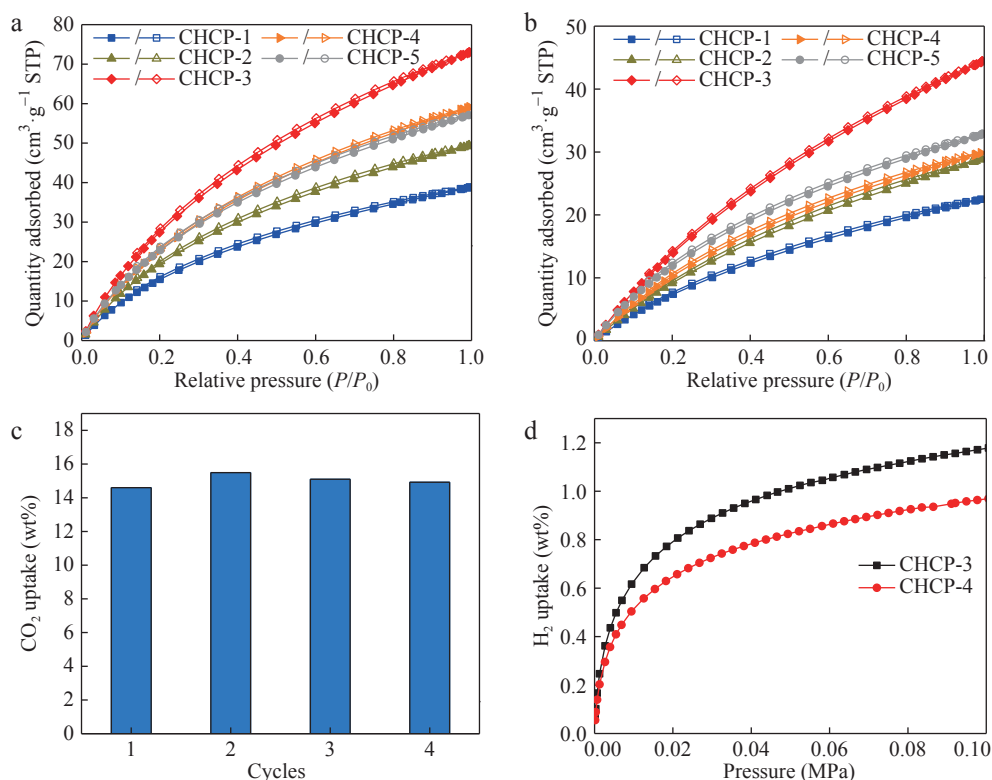


Fig. 3 CO₂ adsorption isotherms at (a) 273 K and (b) 298 K of CHCPs; (c) CO₂ uptake of CHCP-3 in four adsorption/desorption cycles, measured at 273 K and 0.1 MPa; (d) H₂ adsorption/desorption isotherms on CHCP-3 and CHCP-4 at 77.3 K

($T_{\text{dec}} > 400$ °C, Fig. S5 in ESI).

To understand the CO₂ adsorption process, the isosteric enthalpies (Q_{st}) of CHCPs toward CO₂ were calculated from the adsorption isotherms at 273 and 298 K using the Clausius-Clapeyron equation. As shown in Fig. 4(a), the maximum value of Q_{st} for CO₂ is 29.1 kJ·mol⁻¹ for CHCP-1 at low uptake of CO₂. Q_{st} for CHCP-1 is competitive with those of many other porous polymers, such as porous polybenzimidazole BILP-1 (26.5 kJ·mol⁻¹)^[31] or HCP materials (24.0 kJ·mol⁻¹)^[32]. The high Q_{st} can be attributed to the strong interaction between heteroatoms (oxygen and chlorine) and CO₂ molecules, and also the inherent microporosity of the polymer networks which is more

favorable for CO₂ desorption. Moreover, all Q_{st} slightly decreases with the increase of CO₂ uptake. This suggests the heterogeneity of adsorption sites in polymer network. CO₂ molecules prefer to occupy the stronger binding sites at first, and thus only weak binding sites are available at high CO₂ loading^[33–35]. However, it is worth noting that the heats of absorption for the networks still remain below the energy of chemisorptive processes (> 40 kJ·mol⁻¹), confirming the strong physisorption nature of the process.

In addition to the high CO₂ uptake and reversibility, a high selectivity for CO₂ over N₂ is one of the necessary properties for a material to be used as a CO₂ adsorbent. The CO₂/N₂ selectivity of CHCP-3 was estimated by measuring the CO₂

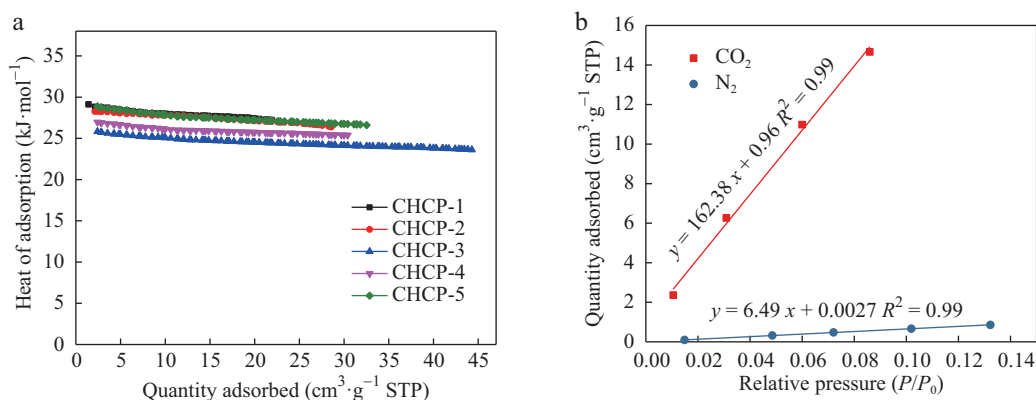


Fig. 4 (a) Isosteric heat of adsorption for CHCPs determined from CO₂ adsorption isotherms at 273 and 298 K; (b) Adsorption selectivity of CO₂ over N₂ for CHCP-3 derived from the initial slope method at 273 K

and N₂ adsorption isotherms at 273 K. On the basis of initial slope calculations in the low-pressure range, CHCP-3 showed the selectivity of 25.0:1 (Fig. 4b). Although these values are low in comparison with some other networks, they are comparable to many other types of polymer networks, such as porous polymer frameworks (PPFs) (14.5:1), microporous organic polymers (MOPs) (17.3:1), polymers of intrinsic microporosity (PIMs) (9.9:1)^[36–38].

Another important application of CHCPs is the storage of H₂. The H₂ adsorption performance on CHCPs is investigated at 77.3 K/0.1 MPa. The results are displayed in Fig. 3(d) and summarized in Table 2. In contrast to the CO₂ adsorption, the enhancement of H₂ uptake can be mainly related to modified textural properties rather than the effects of heteroatoms due to the very low polarizability of H₂^[39]. The isotherms are fully reversible and exhibit a steep rise at low pressures and then reach 1.18 wt% and 0.97 wt% for CHCP-3 and CHCP-4 at 0.1 MPa, respectively. These values are comparable with other porous materials^[21, 22].

Table 2 CO₂ and H₂ adsorption capacity of CHCPs

Sample	CO ₂ uptake ^a (wt%)		H ₂ uptake ^b (wt%)
	273 K	298 K	77.3 K
CHCP-1	7.77	4.57	–
CHCP-2	9.88	5.78	–
CHCP-3	14.60	8.89	1.18
CHCP-4	11.82	6.06	0.97
CHCP-5	11.54	6.58	–

^a CO₂ uptake at 0.1 MPa; ^b H₂ uptake at 0.1 MPa.

CONCLUSIONS

In summary, we successfully prepared coumarone-indene resin-based HCPs with high specific surface area *via* one-step Friedel-Crafts reaction. A maximum surface area of 966 m²·g^{−1} was achieved. Particularly, the introduction of a large amount of heteroatoms (chlorine and oxygen) enhances the interaction between specific sorbate molecules and CHCPs. Therefore, these materials are endowed with decent gas storage capacity (14.60 wt% at 273 K and 0.1 MPa for CO₂; 1.18 wt% at 77.3 K and 0.1 MPa for H₂), which are comparable with that of coal tar-based porous organic polymers. Considering the low cost monomer, the outstanding gas sorption performances, and the facile preparation strategy, these polymer networks are promising candidates for clean energy and environmental applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2127-6>.

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