



# Triazine-based hyper-cross-linked polymers with inorganic-organic hybrid framework derived porous carbons for CO<sub>2</sub> capture

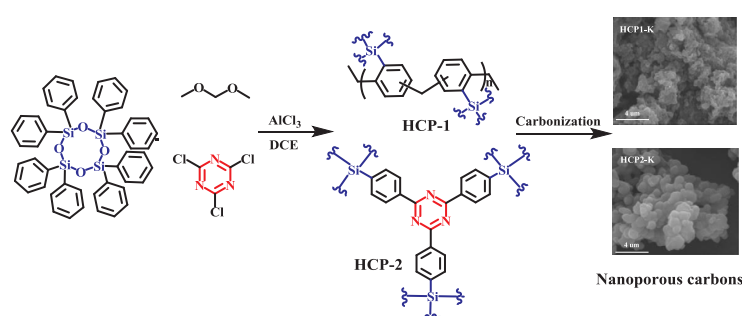
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## HIGHLIGHTS

- A facile preparation of the hyper-cross-linked polymers and derived carbons was proposed.
- The porous structure and nitrogen content of the carbons were effectively tuned.
- The microporosity was distinctly improved as the carbonization temperature increased.
- The high pressure adsorption of CO<sub>2</sub> and the real separation of CO<sub>2</sub> from N<sub>2</sub> were performed.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Hyper-cross-linked polymers  
Friedel-Crafts reaction  
Porous carbons  
CO<sub>2</sub>  
Adsorption

## ABSTRACT

Herein, octaphenylcyclotetrasiloxane was used as the substrate, cyanuric chloride was applied as the cross-linker, and a series of novel hyper-cross-linked polymers with organic-inorganic hybrid framework and spherical morphology was fabricated by a typical Friedel-Crafts reaction. These polymers were used as the excellent precursors for the synthesis of N-doped porous carbons. After KOH-activation carbonization, the spherical morphology of the polymers was retained while the porosity was significantly enhanced. Interestingly, the Brunauer-Emmett-Teller surface area ( $S_{BET}$ ), total pore volume ( $V_{total}$ ), micropore volume ( $V_{micro}$ ), and  $V_{micro}/V_{total}$  of the carbons could be finely tuned in the range of 237–2058 m<sup>2</sup>/g, 0.12–1.08 cm<sup>3</sup>/g, 0.10–0.93 cm<sup>3</sup>/g, and 79.4–88.5%, respectively, and the microporosity was distinctly improved as the carbonization temperature increased. These carbons owned decent CO<sub>2</sub> uptake (80–263 mg/g), HCP2b-K700 had the highest CO<sub>2</sub> uptake of 263 mg/g at 273 K and 1.0 bar and it arrived at 590 mg/g at 298 K and 10 bar. These carbons had moderate isosteric heat of adsorption (20.3–41.8 kJ/mol) and acceptable CO<sub>2</sub>/N<sub>2</sub> selectivity (IAST: 10.8–43.7). The porous carbons developed therein had high surface area and outstanding microporosity, endowed them with promising application prospect in CO<sub>2</sub> capture and sequestration.

## 1. Introduction

The burning of coals, oils, and gases brings about massive emission of the greenhouse gases such as CO<sub>2</sub>, CH<sub>4</sub>, and NO<sub>x</sub>, as a consequence results in the increasingly serious greenhouse effect [1]. Specially, the

drastically increased concentration of CO<sub>2</sub> in the atmosphere is considered to be the primary reason for the global climate warming, and which has become a serious concern for human beings [2]. To reduce the CO<sub>2</sub> emission, developing carbon-free energy sources, improving the production efficiency, and the carbon capture and sequestration

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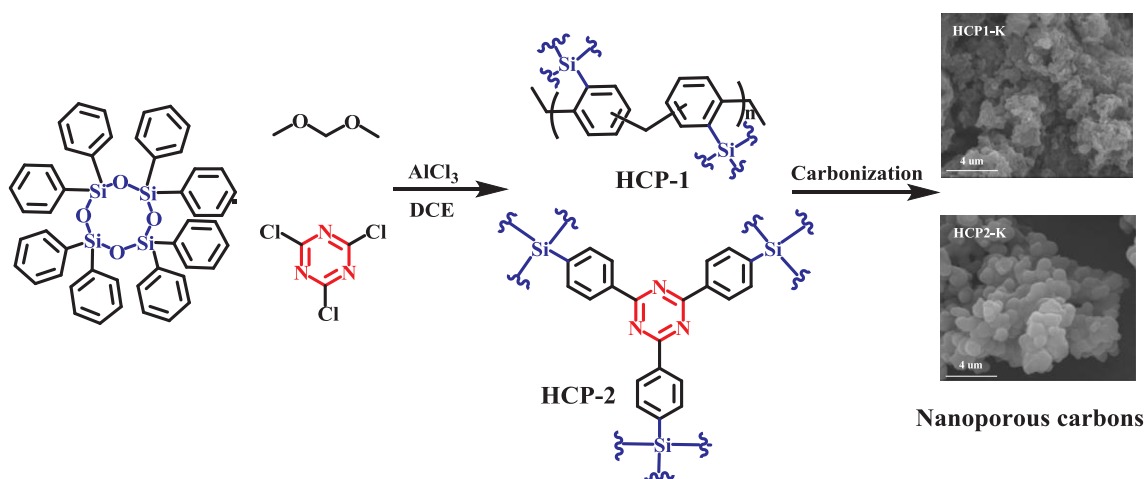
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<https://doi.org/10.1016/j.cej.2018.07.108>

Received 30 May 2018; Received in revised form 13 July 2018; Accepted 14 July 2018

Available online 17 July 2018

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**Scheme 1.** The synthetic procedure of the hyper-cross-linked polymers (HCP1 and HCP2) and porous carbons.

(CCS) are identified as the appropriate choices [3], and CCS is proven essential. The conventional approach for CO<sub>2</sub> capture is chemical absorption by aqueous amine solution, while it is limited in industry due to its several drawbacks such as volatility, corrosiveness, and high energy consumption [4]. On the other hand, the adsorption by porous materials is a promising alternative strategy [5], and many adsorbents including porous organic polymers (POPs) [6–12], metal-organic frameworks (MOFs) [13,14], zeolites [15,16], and porous carbons [17] are extensively investigated. In particular, porous carbons have gained many attentions for the CO<sub>2</sub> adsorption due to their physiochemical stability, tunable textural property, and various chemical functionalities.

More recently, many researches are devoting to preparing the porous carbons from hyper-cross-linked polymers (HCPs), because the HCPs have fascinating features such as diversified monomers, simple one-pot synthesis, and unique structure [11]. However, most of the as-prepared porous carbons have irregular micro-nano morphology, low heteroatom doping content, and inferior CO<sub>2</sub>/N<sub>2</sub> selectivity. Hence, the development of novel building blocks for the HCPs is essential to the fabrication of distinctive porous carbons with high CO<sub>2</sub> uptake and decent CO<sub>2</sub>/N<sub>2</sub> selectivity. Polyhedral oligomeric silsesquioxane (POSS) as a kind of organic-inorganic hybrid monomer has excellent structural character including cage framework, inorganic kernel, and nanoscale, and it is a popular building unit to construct hybrid materials. Particularly, the POSS-based HCPs have many potential applications in the catalysis [18], organic optoelectronic materials [19], fluorescent probes [20], energy storage [21], and adsorption [22]. For instance, Okubo et al. [23] reported a hierarchical microporous and mesoporous hyper-cross-linked siloxane-organic hybrid material by self-condensation of octa-((benzylchloride) ethenyl)silsesquioxane, and the resulting material has ultrahigh surface area (2500 m<sup>2</sup>/g) and high H<sub>2</sub> uptake (1.25% at 77 K and 1.0 bar). Wu et al. [24] fabricated a kind of well-defined microporous carbon by carbonization of xPh-POSS, which is synthesized from octaphenyl-POSS, and the obtained carbon exhibits high surface area (2264 m<sup>2</sup>/g) and excellent supercapacitance property. Tan et al. [22] found that the POSS-based material has CO<sub>2</sub> uptake of 9.73 wt% at 273 K and 1.0 bar. Liu et al. [20] prepared a series of hybrid luminescent polymers that exhibit high surface area (up to 841 m<sup>2</sup>/g), and they can be served as outstanding fluorescent probes for multianalyte detection. More recently, Yuan et al. [25] prepared a series of HCPs based on octaphenylcyclotetrasiloxane (OPCTS) and they found that the derived porous carbons are superior adsorbents for CO<sub>2</sub> capture. However, the above POSS/OPCTS-based HCPs and the derived porous carbons are absent of the basic nitrogen (N) atom, which can interact with CO<sub>2</sub> by formation of acid-base complex and hence enhance the CO<sub>2</sub> adsorption.

For this purpose, in this report, OPCTS was used as the organic-inorganic hybrid monomer, N-containing monomer like cyanuric chloride (CC) was employed as the cross-linker, and a series of hyper-cross-linked polymers were prepared by AlCl<sub>3</sub>-catalytic Friedel-Crafts reaction. The porosity and N content of the polymers were carefully tuned by adjusting the feeding amount of CC. More importantly, the porous carbons were derived from the as-prepared polymers by KOH-activation carbonization, and these carbons have uniform spherical morphology, high surface area, and high microporosity. These porous carbons were applied for CO<sub>2</sub> adsorption. The CO<sub>2</sub> uptake, CO<sub>2</sub>/N<sub>2</sub> selectivity, isosteric heat of adsorption, and regeneration were determined, and the effect of the porosity on the CO<sub>2</sub> uptake was discussed in detail.

## 2. Materials and methods

### 2.1. Materials

OPCTS (98%) and formaldehyde dimethyl acetal (FDA) (≥99%) were obtained from Xiya Chemical Co. Ltd, China. CC was purchased from Tokyo Chemical Industry. Anhydrous AlCl<sub>3</sub> was gained from Sigma Chemical Reagent Co. Ltd. 1,2-dichloroethane (DCE) and potassium hydroxide (KOH) were received from Tianjin Kemiou Chemical Reagent Co. Ltd. All agents were analytical agents and used without further treatment.

### 2.2. Synthesis of the hyper-cross-linked polymers

Scheme 1 shows the synthetic procedure of the hyper-cross-linked polymers and Table S1 displays the feeding amounts of the monomers and the corresponding yields of the polymers. Typically, under N<sub>2</sub> atmosphere, OPCTS (1.951 g, 2.46 mmol) and FDA (2.170 g, 28.55 mmol) were dissolved in DCE (80 mL). Anhydrous AlCl<sub>3</sub> was then added and the mixture was heated to 80 °C and kept this temperature for 24 h. After cooling to room temperature, the crude product was filtrated and successively rinsed with 1 mol/L HCl and methanol. The yellow powdered product denoted HCP1 (2.332 g) was further extracted by Soxhlet extraction with methanol for 24 h and dried under vacuum. Similarly, CC was adopted as the cross-linker in place of FDA, and the HCP2 series (HCP2a, HCP2b, and HCP2c) were synthesized using the similar process as above. The mole ratio of CC in relation to OPCTS was adjusted to 4:1, 8:1 and 12:1, respectively, and correspondingly the products were named as HCP2a, HCP2b, and HCP2c.

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