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Hypercrosslinked microporous organic polymer networks derived from silole-containing building blocks

Yinghua Zhang [a], Yuda Li [b], Feng Wang [b,*], Yang Zhao [a], Chong Zhang [a], Xiaoyan Wang [a], Jia-Xing Jiang [a,*]

[a] School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, PR China
[b] Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, Wuhan 430073, PR China

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ABSTRACT

Three silole-containing hypercrosslinked microporous organic polymer networks were designed and synthesized via Friedel–Crafts alkylation promoted by anhydrous $FeCl_3$. The results demonstrated that the substitution of methyl group connected with silicon atom by benzene has negligible effect on the surface area and gas uptake ability of the polymer networks. The network-1 produced from 1,1-dimethyl-2,3,4,5-tetraphenylsilole shows a surface area up to 1236 $m^2\ g^{-1}$ with the hydrogen uptake ability of 1.33 wt% (77.3 K/1.13 bar) and a carbon dioxide capture capacity of 2.94 mmol g^{-1} at 273 K/1.13 bar. The isosteric heats of carbon dioxide sorption for all of the polymer networks exceed 25 kJ/mol at the zero coverage because the introduction of silicon atom into the polymer skeleton enhanced the binding affinity between the adsorbent and CO_2 molecules. In addition, the selectivity of the polymer networks for CO_2/N_2 and CO_2/CH_4 were found to be around 35 and 6 at 273 K, respectively. These results show that these materials are potential candidates for applications in post-combustion CO_2 capture and separation.

1. Introduction

Microporous organic polymers (MOPs) have attracted much attention because they have a broad potential in a variety of applications such as molecular separation, heterogeneous catalysis and gas storage [1–3]. Various polymerization methods, monomer building blocks and synthetic methods have been exploited to develop a range of MOPs. These include mainly polymers of intrinsic microporosity (PIMs) [4,5], hypercrosslinked polymers (HCPs) [6–8], conjugated microporous polymers (CMPs) [9–11], and covalent organic frameworks (COFs) [12–14]. Unlike most other MOPs that are often synthesized using noble metal catalyzed polymerization (*e.g.* Pd-catalyzed Sonogashira-Hagihara cross coupling, Ni(0)-catalyzed Yamamoto homocoupling, Pd-catalyzed Suzuki coupling, and Co(0)-catalyzed trimerization of aromatic alkynes), HCPs could be synthesized by using simple and inexpensive chemicals such as benzene via Friedel–Crafts alkylation promoted by anhydrous $FeCl_3$, which avoids the use of noble metal coupling catalysts, and also avoids the need for monomers with specific polymerisable groups when an external linker such as formaldehyde dimethyl acetal is employed [7]. This could make HCPs strong candidates for carbon capture and clean energy storage, and have been the subject of intense recent interest [8]. To date, a range of HCPs have been prepared using various monomer building blocks and formaldehyde dimethyl acetal as an external linker for carbon dioxide capture. For example, benzene-based HCPs showed a surface area up to 1391 $m^2\ g^{-1}$ with a CO_2 uptake capacity of 3.61 mmol g^{-1} (1.0 bar/273 K) [7]. Tetraphenylmethane-based HCP with a surface area of 1679 $m^2\ g^{-1}$ exhibited the CO_2 uptake capacity of 1.66 mmol g^{-1} (1.0 bar/273 K) [15], and tetraphenylethylene-based HCP with a higher surface area of 1980 $m^2\ g^{-1}$ exhibited the CO_2 uptake capacity of 3.63 mmol g^{-1} (1.0 bar/273 K) [16]. It has been also suggested that the incorporation of heteroatom and polar functional groups into the skeleton of MOPs could enhance the binding affinity between the adsorbent and CO_2 molecules which results in the increase of CO_2 capture capacity. For example, heterocyclic-based HCPs with moderate surface areas up to 726 $m^2\ g^{-1}$ showed a CO_2 uptake capacity of 2.88 mmol g^{-1} (1.0 bar/273 K) [17]. Binaphthol-based HCPs showed an improved CO_2 uptake capacity as high as 3.96 mmol g^{-1} (1.0 bar/273 K) [18]. The HCP of TSP-2 bifunctionalized with carbazole and triazine groups showed an efficient CO_2 capture ability of 4.1 mmol g^{-1} (1.0 bar/273 K) [19]. These results demonstrated that such functionalized HCPs have great potential to increase the CO_2 capture capacity.

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* Corresponding authors.
E-mail addresses: psfwang@gmail.com (F. Wang), jiaxing@snnu.edu.cn (J.-X. Jiang).

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Silole and its derivatives have been studied widely in the areas of aggregation-induced emission and organic solar cells [20–22]. Many polymers based on silole derivatives are grafted with flexible groups to render them soluble in common solvents, these solubilizing functionalities combined with a strong tendency for interchain π-stacking could render the materials non-porous. Here, we describe the synthesis of a novel class of hypercrosslinked microporous polymer networks from the rigid silole building blocks with formaldehyde dimethyl acetal as a crosslinker promoted by anhydrous $FeCl_3$. The resulting silole-containing polymer networks show high levels of porosity and high CO_2 uptake ability.

2. Experimental section

2.1. Materials

Formaldehyde dimethyl acetal (FDA), anhydrous $FeCl_3$, 1,2-dichloroethane (DCE) and other chemicals were obtained from *J&K* Scientific Ltd. The monomers of 1,1-dimethyl-2,3,4,5-tetraphenylsilole (monomer-1), 1-methyl-1,2,3,4,5-pentaphenylsilole (monomer-2), and hexaphenylsilole (monomer-3) were prepared according the literatures [23].

2.2. Synthesis of silole-based hypercrosslinked microporous polymer networks

All of the silole-containing hypercrosslinked microporous organic polymer networks were synthesized by Friedel–Crafts alkylation from monomers (1–3) using a formaldehyde dimethyl acetal external crosslinker promoted by anhydrous $FeCl_3$ [7]. All polymerization reactions were carried out at a fixed molar monomer concentration (50 mmol/L) and a fixed reaction temperature and reaction time (80 °C/24 h).

Network-1: To the mixture of monomer-1 (1.0 mmol, 0.415 g) and FDA (4.0 mmol, 0.304 g) in 20 mL 1,2-dichloroethane, $FeCl_3$ (4.0 mmol, 0.649 g) was added at room temperature. The mixture was heated to 80 °C and stirred for 24 h under a nitrogen atmosphere. After cooling down to room temperature, the precipitated polymer network was filtered and washed with methanol, distilled water, dichloromethane and acetone successively, until the filtrate was nearly colorless. The further purification of the network was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C to give dark brown powder (Yield: 98.7%). Elemental combustion analysis (%): C 81.46, H 4.58.

Network-2: Monomer-2 (1.0 mmol, 0.477 g), FDA (5.0 mmol, 0.380 g) and $FeCl_3$ (5.0 mmol, 0.812 g) were used in this polymerization (Yield: 99.5%). Elemental combustion analysis (%): C 78.93, H 4.44.

Network-3: Monomer-3 (1.0 mmol, 0.538 g), FDA (6.0 mmol, 0.456 g) and $FeCl_3$ (6.0 mmol, 0.975 g) were used in this polymerization (Yield: 98.3%). Elemental combustion analysis (%): C 69.29, H 4.77.

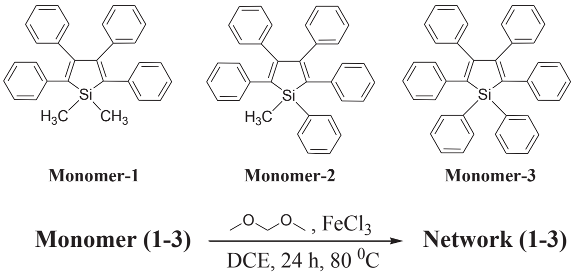
2.3. Characterization

The thermal properties of the polymer networks were evaluated using thermogravimetric analysis (TGA) with a differential thermal analysis instrument (Q1000DSC + LNCS + FACS Q600SDT) over the temperature range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C/min. Elemental analysis was carried out on a EURO EA3000 Elemental Analyzer. The FT-IR spectra were collected in transmission on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. Solid state magic angle spinning ^{13}C CP/MAS NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. The morphology of the polymer networks were carried out on an environmental scanning electron microscope (FEI, Quanta 200). Powder X-ray diffraction measurement (PXRD) was carried out on X-ray Deffractometer (D/Max-3c). Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. The surface areas were calculated in the relative pressure (P/P_0) range from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory. Samples were degassed at 120 °C for 15 h under vacuum (10^{-5} bar) before analysis. Gas sorption isotherms were measured on an ASAP 2420-4.

3. Results and discussion

The three silole-containing hypercrosslinked microporous polymer networks were synthesized by Friedel–Crafts alkylation from monomers (1–3) using a formaldehyde dimethyl acetal external crosslinker promoted by anhydrous $FeCl_3$ (Scheme 1). All of the polymerizations gave dark brown powders. Yields of the resulting polymer networks were quantitative, as observed for most other reported HCPs [7,16,24]. The silole-based polymer networks are insoluble in conventional organic solvents because of their highly crosslinked structures and the rigid skeleton. The polymer networks show less thermal stability, as revealed by TGA (up to 250 °C, Fig. S1) in nitrogen atmosphere, compared with other types of MOPs (*e.g.* CMPs showed high thermal stability up to 400 °C [9], and covalent organic polymer, COP-3 showed superior thermal stability up to 370 °C in nitrogen atmosphere owing to its robust aromatic nature of the framework) [25], which could be attributed to the presence of cross-linker of methylene groups in the HCPs which reduced their thermal stability. The FT-IR spectra for the networks were consistent with the expected networks showing unsaturated C=C vibration band from the benzene at around 1600 cm^{-1}, and C–H stretching vibrations originating from $-CH_2-$ at 2900 cm^{-1} (Fig. S2). The structures of the polymer networks are also characterized and confirmed by the solid state ^{13}C CP/MAS NMR spectra (Fig. S3). Powder X-ray diffraction measurements indicated that the polymer networks are amorphous in nature (Fig. S4).

The porous properties of the polymer networks were analyzed by nitrogen adsorption analysis at 77.3 K. As shown in Fig. 1a, all of the polymer networks show Type–I nitrogen sorption isotherms with steep increases at low relative pressure ($P/P_0 < 0.001$), suggesting that micropores are dominant in these polymer networks. A steep rise in the nitrogen adsorption isotherms for network-3 was also observed at high relative pressures ($P/P_0 > 0.9$), indicating the presence of some mesopores and/or macropores in the polymer network as well, which are probably due to inter-particle porosity or void [26]. Significant hysteresis was observed for all of the



Scheme 1. Synthesis route to the polymer networks.