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Fabrication and CO_2 capture performance of silicon carbide derived carbons from polysiloxane

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ABSTRACT

Microporous silicon carbide derived carbons (SiC-DCs) were obtained by chlorination with post treatment in ammonia (NH_3) using a commercially available polymethyl(phenyl)siloxane resin. In this paper, attentions were focused on the compositional and structural evolutions as well as the CO_2 capture performances of SiC-DCs as a function of chlorination temperature or affected by post-treatment. Microscopy analysis showed that the geometry and macrostructure, as well as the observed graphite ribbons were finely inherited from the as-received silicon carbide. Post-treatment under NH_3 could introduce a few nitrogen-contained groups to SiC-DCs, and has an advantage on increasing the ultra-microporosity with little effect on the carbon crystallinity, both of which finally help increasing the CO_2 adsorption capacity. Increasing etching temperature (900–1100 °C) would lead to a tiny increase of carbon crystallinity and porosity (specific surface area and total pore volume). However, the ultra-micropore volume decreased instead, thus leading to a decrease of CO_2 adsorption capacity. The final SiC-DCs samples exhibit excellent CO_2 capture performances at 0 °C under the ambient pressure, with a maximum value of 5.75 mmol/g. Under the same condition, the N_2 adsorption is as low as 0.46 mmol/g, suggesting a potential selective adsorbent for CO_2 and N_2 separation.

1. Introduction

CO_2 capture technique from flue gas for sequestration or other use has attracted much attention and has been recognized as a viable near-term option for green house gas mitigation [1–4]. Current or proposed methods of CO_2 capture from flue gas include absorption, adsorption, cryogenic distillation, and membrane separation. Chemical absorption in amines is a most mature technology [5]. However, the toxicity of such solvents is an issue that makes this technique an environmentally unattractive option. Thereby, increasingly more interests are shifted to adsorption technology, which can offer a cleaner, more environmentally friendly, and perhaps more economical alternative. Up to now, many kinds of adsorbents have been used in CO_2 capture, such as porous carbon materials, silica gels [6], metal oxide [7], zeolites [8], and metal organic framework [9]. Thereinto, porous carbon materials have been extensively studied in gas storage (H_2, CO_2, CH_4) due to their highly developed porosity, huge surface area, surface chemistry, and excellent thermal stability. Compared with other adsorbents, porous carbon materials own some advantages in structural stability and inherently hydrophobic characteristic in CO_2 capture [10,11]. And many species, including activated carbons, activated carbon fibers, carbon molecular sieves, carbon nanotubes, and graphite nanofibers are studied as adsorbents for CO_2 capture. However, their widespread utilizing is always limited by some issues, such as limited adsorption ability owing to unsuitable pore size, over-high expense on fabrication.

Carbide derived carbons (CDCs) received increasing attentions owing to their high specific surface area and large pore volume, tunable porosity (pore size and relative distribution) and structures by selectively etching carbides or choosing suitable etching temperature. Bhatia and his coworkers [11–13] have shown SiC derived carbons (SiC-DCs) may be a good potential candidate in CO_2 capture through prediction or experiment, and also found its CO_2 capture performance had some connections with graphitization degree and pore structures, which finally attributed to the particle size of carbide, chlorination temperature, and heat treatment time.

Herein, we prepared a series of SiC-DCs from polysiloxane and studied their CO_2 capture performance. The etching process of polysiloxane derived SiC has been shown in previous work [14]. The main difference in this paper from Bhatia's work is that the SiC-DCs samples are post-treated under ammonia (NH_3) other than Ar or H_2 flow after chlorination process. According to Portet et al.

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[15], CDCs post-treated with NH_3 possess a lowest content of chlorine (Cl) and equal porosity compared with other two methods under H_2 or Ar flow. Besides, the NH_3 post treatment may change the surface chemistry and pore structure of SiC-DCs or other carbons [16], and finally may influence their property, such as CO_2 capture performance. As we all know CO_2 capture contains physical adsorption and chemical adsorption. The former is strongly associated with porosity (specific surface, pore size distributions, etc) of adsorbents while surface functional groups for the latter as an interface between adsorbents and CO_2 molecules [17]. Nevertheless, these have hitherto not been discussed for CDCs. Thereby, the composites and structures of SiC-DCs before and after post-treatment under NH_3 were studied in this paper. The effect of etching temperature and post-treatment under NH_3 on the CO_2 capture performance of SiC-DCs was also investigated and discussed.

2. Experimental

2.1. Sample preparation

SiC ceramics were produced by pyrolysis of a commercially available polymethyl(phenyl)siloxane resin (Dow Corning 249 flake resin). The polysiloxane precursor was firstly cross-linked at 250 °C in air for 4 h, and crushed into powders by using disintegrator. The powders (with particle size ranging from 150 to 250 μm) were placed in a graphite crucible and heated to 1200 °C for 2 h under nitrogen (99.999% pure) with a heating rate of 5 °C/min and then allowed to cool naturally. To obtain SiC ceramics, the ball-milled powders (or SiOC ceramics with particle size of below 20 μm) were placed in graphite furnace and thermal-treated at 1600 °C with the rate of 5 °C/min under vacuum for 6 h. The SiC powders were placed in horizontal tube furnace (diameter 80 mm), purged in nitrogen flow, heated to appointed temperature (900–1100 °C) with the rate of 5 °C/min and exposed to dry chlorine gas (15–20 cm^3/min) for 3 h. After chlorination, the samples were post-treated at 600 °C for 2 h under ammonia (NH_3) flow in order to remove residual chlorine and volatile chlorides trapped in pores.

2.2. Characterization methods

2.2.1. Compositional and structural analysis

Quantitative elemental analysis (EA) of the samples was performed on LECOCS600 for carbon in SiC ceramics. The perchloric acid dehydration gravimetric method was adopted for the determination of Si content. Given that the C atom should connect with itself or Si atom while O atom connects with Si atom only, atomic formula and calculated composition could be obtained according to Belot et al. [18]. It is calculated that nearly 4.13 wt.% of the as-received SiC ceramics from PSO is assigned to free carbon. For CDCs, their compositions were determined by X-ray photoelectron spectroscopy (XPS) technique and X-ray spectrometer (EDS) technique. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a K-Alpha 1063 system (Thermo Fisher Scientific) with Al K ⟨alpha⟩ radiation. Unless otherwise specified, the X-ray anode was run at 72 W and the high voltage was kept at 12.0 kV. The base pressure of the analyzer chamber was about 1×10^{-9} mbar. A whole spectrum scan (0–1400 eV) and regional scans of all the elements at a very high resolution were recorded for each sample. Binding energies were calibrated using the carbon 1s peak (C1s = 284.6 eV). Infrared spectroscopy (IR) between 4000 and 400 cm^{-1} was carried out with a resolution of 4 cm^{-1} on a Thermo Niocolet Fourier Transform Spectrum, using the KBr disk method.

Raman spectra were recorded with a LABRAM-HR (JOBIN YVON) microspectrometer using an argon-ion laser (514.5 nm, ~1 μm lateral spot size). X-ray Diffraction (XRD) analysis was managed using a Rigaku diffractometer with CuK ⟨alpha⟩ radiation (k = 0.154 nm) operated at 30 mA and 40 kV. XRD patterns were collected using step scans, with a step size of 0.01° (2θ) and a count time of 2 s per step.

2.2.2. Microscopic investigations

Scanning electron microscopy (SEM) was performed on samples with no sputter coating using a HITACHI FEG S4800 scanning electron microscope operating at 10 kV, and the energy dispersive X-ray spectrometer (EDS) was operated at 15 kV. All SEM samples were analyzed without the application of any sputter coating. Transmission Electron Microscopy (TEM) samples were prepared by dispersing powders in ethanol and placing the solution over a copper grid. TEM measurements were performed using a JEOL JEM2100F microscope operating at 200 kV.

2.2.3. Gas sorption measurement

N_2 adsorption–desorption isotherms were obtained using Quantachrome instruments at 77 K. Brunauer–Emmertt–Teller (BET) analyses were used to determine the total specific surface area (SSA). The quenched solid density functional theory (QSDFT) method was used to analyze the pore size distributions (PSDs) and micropore volume ($d \leqslant 2$ nm). Horvath-Kawazoe (HK) method was used to analyze the ultra-micropore volume ($d \leqslant 0.6$ nm).

2.3. CO_2 capture measurement

The CO_2 adsorption isotherms of all SiC-DCs samples were measured using Quantachrome instruments at 0 °C. For comparison, the N_2 adsorption isotherm of the SiC-DCs sample post-treated with NH_3 (Cl_2-900, NH_3) was measured using Quantachrome instruments at 0 °C. Prior to each adsorption experiment, the samples were degassed for 4 h at 150 °C to ensure that the residual pressure was below 1×10^{-3} mbar. After the samples were cooled down to 0 °C, CO_2 was introduced into the system. The CO_2 adsorption capacity in terms of the adsorbed volume under standard temperature and pressure was then recorded. The non-local density functional theory (NLDFT) model was used to analyze the pore size distributions in range of 0.3–1.5 nm.

3. Results and discussion

3.1. Composite and structure of SiC-DCs

For the as-received SiC sample, four elements (Si, O, C and N) were determined by X-ray photoelectron spectroscopy (XPS) (Table 1). Whereas, only two signals (Si and C) were detected by X-ray spectrometer (EDS) technique. This distinction may attribute to the very low content of oxygen or nitrogen in SiC. Owing to chlorination, the extraction of Si atoms from SiC sample led to highly porous carbon (which will be discussed later) by the following reaction [19]:

$$SiC(s) + 2Cl_2(g) = SiCl_4(g) + C(s) \tag{1}$$

The gaseous $SiCl_4$ as the by-product mostly escaped from the SiC-DCs during the preparation, and a small part might retain in the nanopores. It is demonstrated that the reaction (Eq. (2)) for the removal of C as CCl_4 is much less thermodynamically favorable compared with reaction Eq. (1), which could account for the broad application of CDC technique in fabricating nanoporous carbon.

$$SiC(s) + 2Cl_2(g) = CCl_4(g) + Si(s) \tag{2}$$

Besides, all etched samples were post-treated under NH_3 after chlorination. The Cl element in the etched samples, especially on