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Etching process of silicon oxycarbide from polysiloxane by chlorine

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ABSTRACT

The etching process of silicon oxycarbide (SiOC) by dry chlorine was investigated as a function of etching temperature. Data show the etching reaction for SiOC can occur at low temperature of 450 °C and follows the interface reaction-controlled mechanism at 525 °C. At 600 °C and above, a visible arising of mesopores was observed owing to the Si—O bond-breaking while microporosity is attributed to Si—C bond-breaking. Increasing etching temperature will lead to better carbon crystallinity and larger porosity. Some carbon–oxygen surface groups and residue silica were determined, whose relative content also depended on the etching temperature.

1. Introduction

Carbide derived carbons (CDCs) have received increasing attentions in recent decades for their applications as electrode for supercapacitors or batteries, effective adsorbent for separation processes or gas storage, tribological coatings for ceramics, and biomedical devices [1–4]. CDCs are attractive materials because tunable pore structures and narrow pore sizes can be achieved by selectively etching metal carbides [5–7]. Thus, carbide species have been considered as one of the most important factors which can affect the pore structure of CDCs. Other major factors include etching temperature, time, post-synthetic treatment, etc. To date, numerous carbides have been adopted as precursors, and are generally classified into two categories: binary metal carbides (SiC, TiC, BC_4, etc) and ternary carbides (Ti_3SiC_2, Ti_2AlC, etc). These previous studies demonstrated that CDCs synthesized from different carbide precursors yielded different pore structures and material properties [8–13].

Polymer derived carbides (PDCs) have also been used as precursors for CDCs in recent five years [14–16]. PDCs (e.g., SiCN, SiOC and SiC) can provide additional degree of freedom for optimizing CDC porosity and performance by controlling the pyrolysis conditions (e.g., temperature, dwelling time and atmosphere). Ordered mesoporous CDCs (OM-CDCs) can also be fabricated during PDC-CDC synthesis by adopting some templates [17–19]. However, few studies focus on the etching process of PDCs, which could be very important for understanding the formation of CDCs and improving the control of CDC pore structure [20–22]. Previous studies in our lab have proved the etching mechanism of SiC powders in micrometers and the properties of SiC-DCs from polysiloxane are strongly associated with the etching temperature [23]. Unlike thermodynamically-stable SiC ceramics, silicon oxycarbide (SiOC) is thermodynamically-unstable. Its unique and predominantly amorphous structure may have a significant impact on its chlorination. By Gogotsi et al. [15], two kinds of silicon oxycarbide derived carbons (SiOC-DCs) were obtained and showed different compositions, structures and properties, which were finally attributed to the different carbon contents in raw materials. Nevertheless, the etching process for SiOC was rarely discussed. Thus, this article aims to studying the etching process of SiOC ceramics by dry chlorine. The compositional and structural evolution was systematically investigated as a function of etching temperature. Based on the etching process of SiC from polysiloxane, the etching mechanism for SiOC was also discussed.

2. Experimental

2.1. Materials

SiOC ceramics were produced using a commercially available polymethyl(phenyl)siloxane resin (Dow Corning 249 flake resin). The polysiloxane precursor was first cross-linked at 250 °C in air for 4 h, and crushed into powders using a disintegrator. The cross-linked powders with particle sizes ranging from 150 to 250 μm were obtained by filtration between 60 and 100 sieve meshes. The powders were placed in a graphite crucible and heated to 1200 °C for 2 h under nitrogen (99.999% pure) with a heating

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rate of 5 °C/min and then allowed to cool naturally. The final samples (SiOC-DCs) were produced by chlorination of ball-milled SiOC powders (<50 μm particle size). First, the powders were placed in a horizontal tube furnace (diameter 6 cm), purged in nitrogen flow. Then they were heated to a temperature in the range of 450–1050 °C with the rate of 5 °C/min and finally exposed to dry chlorine gas (15–20 cm^3/min) for 3 h. The mass of the precursor carbide was measured before the experiment and after the reaction (after the reactor had been cooled down). Partially reacted carbides were not further used for the kinetic study, i.e. the reaction time was varied based on experiments with fresh SiOC.

2.2. Characterization methods

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. Magic angle spinning-nuclear magnetic resonance (MAS-NMR) experiments were conducted on a MSL 400 Bruker spectrometer. For the ^{29}Si NMR experiments, pulse width and relaxation delays were 2.5 μs and 60 s, respectively. Peaks were labeled with the conventional M^n, D^n, T^n and Q^n notation. M, D, T and Q refer to $SiC_{4-x}O_x$ units with $x = 1, 2, 3$ or 4, respectively. 'n' is the number of bridging O atoms surrounding Si. The ^{13}C CP MAS-NMR were recorded using contact times of 1 ms and relaxation delays of 6 s. XPS experiments were carried out on a K-Alpha 1063 system (Thermo Fisher Scientific) with Al Kα 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). The software of Thermo Avantage (v4.84, Thermo Fisher Scientific) was employed to analyze the C1s spectra of all samples.

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. And the residue element is considered to be O. 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. [24]. It is calculated that nearly 29.56 wt.% of the as-received SiOC 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.

Sample morphology and composition was characterized 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. 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.

X-ray diffraction (XRD) analysis was managed using a Rigaku diffractometer with CuKα 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 between 10 (2θ) and 90 (2θ) degrees. Raman spectra were recorded with a LABRAM-HR (JOBIN YVON) microspectrometer using an argon-ion laser (514.5 nm, ~1 μm lateral spot size). Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449C instrument, and carried out with a minimal ambient air flow rate of 40 ml/min in the temperature range between 25 and 800 °C, with a heating rate of 5 °C/min.

N_2 adsorption–desorption isotherms were obtained using a Quantachrome instrument at 77 K. Brunauer–Emmertt–Teller (BET) analyses were used to determine the total specific surface area (S_{BET}). The quenched solid density functional theory (QSDFT) method was used to analyze CDC pore size distributions (PSDs) and pore volume.

3. Results and discussion

3.1. Compositional evolution of SiOC in chlorine

Fig. 1 shows a typical infrared (IR) spectrum of SiOC, as well as spectra of the products following the chlorine etching process. As expected, the SiOC sample shows two broad peaks at 1041 cm^{-1} and 824 cm^{-1}, which are assigned to the νSi—O—Si and νSi—C absorptions, respectively. A weak and sharp absorption centered at 465 cm^{-1}, is also observed and is characteristic of νSi—O. Interestingly, all samples exhibit an absorption near 1580 cm^{-1} after the 3 h etching treatment, which could be assigned to the stretching modes of aromatic rings and/or highly conjugated C═O groups [25]. A small peak present between 1710 and 1750 cm^{-1} indicates the formation of surface oxygen complexes and could be attributed to C═O stretching vibrational modes in carboxylic, anhydride, and/or lactone groups [26]. The broad band ranging from 1000 to 1300 cm^{-1} is associated with the stretching modes of C—O and C—Cl groups [27]. However, the broad band near 1100 cm^{-1} may also be overlapped by Si—O stretching modes from residual SiO_2, which is challenging to completely etch away by chlorine, particularly at low temperatures. The peak at 824 cm^{-1} almost completely disappeared after etching, an effect which was nearly independent of etching temperature. The broad peaks in the range of 600–800 cm^{-1} may also be associated with C—Cl vibrations. In comparison with the samples etched at 750 °C and 900 °C, the samples etched at lower temperatures (450–600 °C) exhibited stronger absorption signals for the peak centered at 465 cm^{-1}. This suggests that at lower temperatures the etching process is incomplete, and the etching process can near completion only when the etching temperature exceeds 750 °C. To summarize, the etched samples are likely to contain functional groups including C—C, C—O, C═O, C—Cl, as well as a few possible residual Si—O groups. Unfortunately, IR analysis cannot confirm the exact structure and composition of the silicon–oxygen and carbon–oxygen complexes. More information from NMR and XPS analysis is necessary to provide this level of insight.

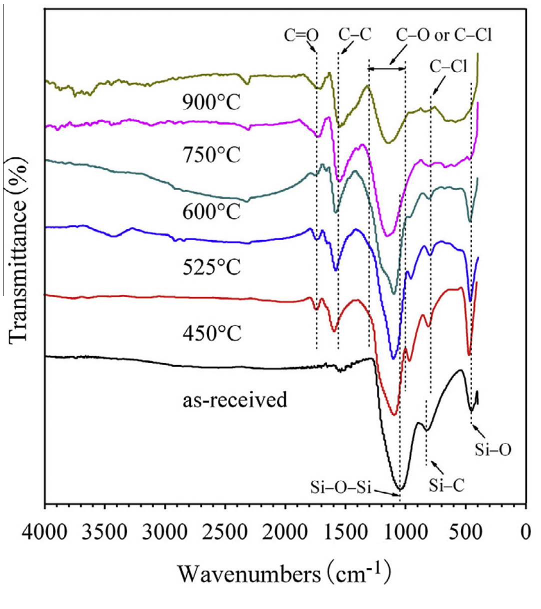

Fig. 1. FTIR spectra of etched sample at different temperature.