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The effect of etching temperature on the compositional and structural evolution of ceramer from polysiloxane in chlorine

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ABSTRACT

In this paper, we used a novel carbide (or ceramer) as the carbon precursor and studied the effect of etching temperature on its compositional and structural evolution in chlorine condition. The ceramer produced from a commercially available polymethyl(phenyl) siloxane resin at 600 °C under nitrogen still includes some organic groups (e.g., Si—H, Si—CH_3, Si—Ar), which cannot survive in chlorine for 3 h in range of 450–900 °C. The ceramer can be completely converted to carbon while the etching temperature exceeds 600 °C. Higher ordering at elevated etching temperatures and apparent increasing of mesopores at 600 °C were observed.

1. Introduction

As an unique and important role in the area of carbon materials, carbide derived carbon (CDC) has received increasing interests for its tunable porosity and widespread application as electrode for supercapacitors or batteries, tribological coatings, support for Pt catalyst, effective adsorbent for gas storage and sensors [1–5]. Precursor is one of the most important factors, which can even decide its etching behavior and final features of CDC. Polymer derived carbides (PDCs, e.g., SiCN, SiOC, SiC, etc.) have been used as precursors for CDC in recent years [6–11]. It is well demonstrated that this method can provide additional degree of freedom for optimizing CDC porosity and performance by controlling the pyrolysis conditions.

Among all kinds of polymers, polysiloxane (PSO) has received much attention over several decades owing to its good properties and wide applications [12–14]. It is not only commercially available but also very cost-effective. Studies in our lab have shown inorganic SiOC and SiC ceramics can be easily obtained by pyrolysis of polysiloxane at certain temperature under ambient or low pressure [15–19]. The compositions and structures (morphology, porosity, crystal degree) for these ceramics depend strongly on the pyrolysis condition (e.g., temperature, dwelling time, atmosphere). Interestingly, Wilhelm et al. [20] reported a pyrolysate (or ceramer) at 600 °C from polysiloxane. It was still in an intermediate state between organic polymer and inorganic ceramics owing to the existence of H atoms. Besides, the ceramer owned transient high porosity and exhibited good behavior in removing volatile organic compounds.

In our previous work [21–24], SiOC or SiC ceramics from polysiloxane can be converted to carbon materials. And they exhibited good electrochemical performance as electrode for supercapacitors or CO_2 capture performance due to their high porosity and tunable pore size distributed in micro and mesopore range. However, there have hitherto been no reports on CDC made from ceramer which contains four elements (Si, C, O and H) and some organic groups (C—H, Si—H). This kind of carbide with unique composition and structure may vary a lot with SiC or SiOC, which could have a significant effect on its etching process. More importantly, this carbide owns some advantages compared with binary metal carbides (SiC, TiC, etc.) and ternary carbides (SiOC, SiCN, etc.) in the synthesis of CDC. Because a lower pyrolysis temperature is adopted for ceramer, more energy can be saved. And further tuning of carbon porosity may be also afforded by controlling the H

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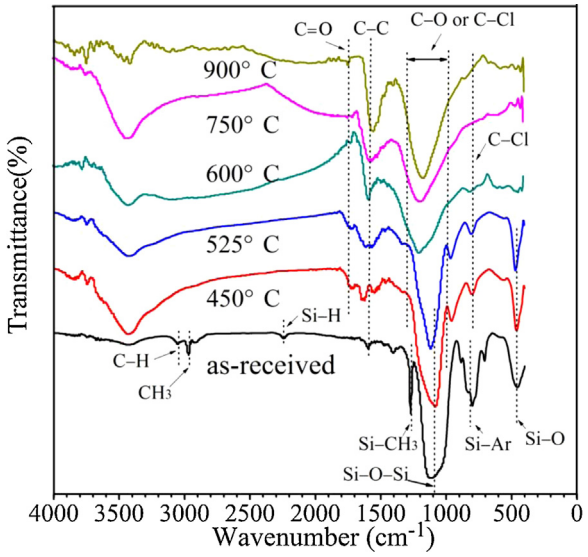

Fig. 1. FTIR spectra of etched sample at different temperatures.

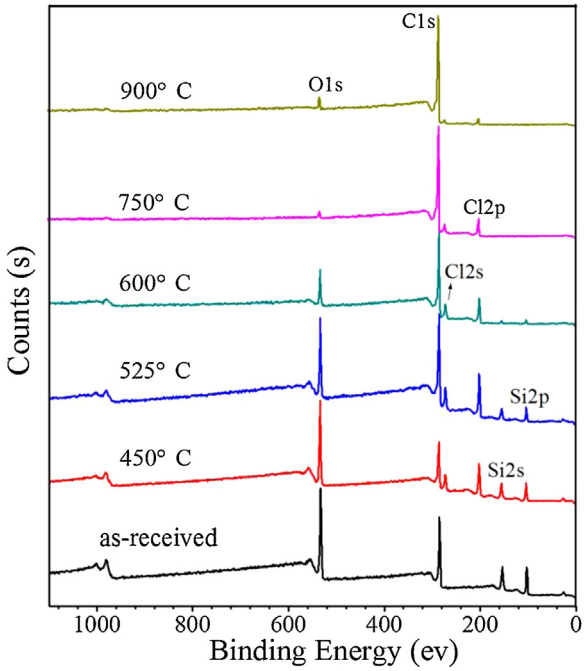

Fig. 3. XPS survey spectra of etched samples at different temperatures.

content of ceramer. However, such work has been rarely investigated. Herein, this article aims to study the etching process of ceramer by dry chlorine. The compositional and structural evolution in chlorine was systematically investigated as a function of etching temperature.

2. Experimental

2.1. Materials

The as-received sample (or ceramer) was prepared by using a commercially available polymethyl(phenyl) siloxane resin (Dow Corning 249 flake resin) as the raw material. The precursor was thermally cross-linked in air at 250 °C for 4 h and subsequently pyrolyzed under N_2 atmosphere (99.99%) at 600 °C for 2 h with a heating rate of 5 °C/min and then allowed to cool naturally. The ceramer contains four elements (Si, O, C and H), and their weight percentages are 36.93, 15.89, 36.80 and 6.74 wt.%, respectively.

The final samples were obtained by chlorination of ceramer powders (ball-milled to below 50 μm particle size). The powders were placed in a horizontal tube furnace (diameter 6 cm), purged in nitrogen flow, heated to a temperature in the range of 450–900 °C with the rate of 5 °C/min and exposed to dry chlorine gas (15–20 cm^3/min) for 3 h.

2.2. Characterization methods

Quantitative elemental analysis (EA) of the ceramer was performed on LECOCS600 for the C content. The perchloric acid dehydration gravimetric method was adopted for the determination of Si content. The O and H content were determined by TCH600 analyzer. For ceramer derived carbons, 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 Ka radiation. Unless oth-

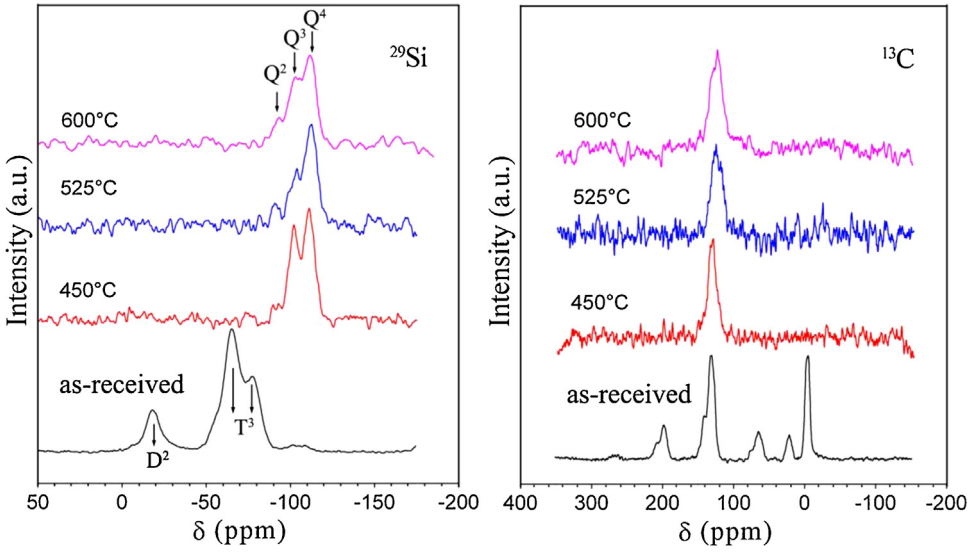

Fig. 2. ^{29}Si and ^{13}C MAS NMR spectra of etched samples at different temperatures.