Structural evolution and CO₂ capture performance of silicon oxycarbide-derived carbon by thermal-treatment under an Ar atmosphere

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Abstract. In this paper, we investigated the effect of thermal-treatment under an Ar atmosphere on the structural evolution of silicon oxycarbide-derived carbons (SiOC-DCs) by adjusting the temperature from 1200 to 2100°C, which will be characterized by means of N₂ adsorption, X-ray diffraction, Raman and transmission electron microscopy techniques, and studied their CO₂ capture performances. The results show that the structure of SiOC-DCs varied regularly with treatment temperature. The porosity and crystallinity of the as-received sample are almost stable when the thermal-treatment temperature is < 1500°C. Subsequently, increasing the temperature (especially up to 1800°C) will lead to an obvious improvement in the carbon crystallinity at the cost of pore structure breakage, which can be characterized by a quick decrease in the surface area and total pore volume of SiOC-DCs. Interestingly, the as-received SiOC-DC sample exhibits good CO₂ capture performance at 0°C under ambient pressure, up to 3.16 mmol g⁻¹. The thermal-treatment process under an Ar atmosphere in the range of 1200–1500°C could further help in increasing the CO₂ adsorption ability by increasing the ultra-micropore ($d < 0.6$ nm) volume.

Keywords. Silicon oxycarbide; carbon; thermal-treatment; porosity; crystallinity; CO₂ capture performance.

1. Introduction

Carbide-derived carbons (CDCs) have been attracting much attention in recent years due to their high efficiency in a large number of applications such as gas (CO₂, H₂ and CH₄) storage [1–4], electrode materials in supercapacitors [5–7] or Li-ion batteries [8], for protein sorbents [9,10] and tribological films [11,12]. For CO₂ capture application, CDCs belong to the family of carbonaceous adsorbents which can be classified as adsorption technology, offering a clean, environmental friendly and economical alternative. In comparison with other carbon materials fabricated by conventional methods (e.g., activation techniques and template techniques), one of the biggest CDC advantages is their pore structure and crystallinity can be tuned by choosing the carbide precursor, chlorination temperature and post-treatment. A recent review on CDC materials is shown in ref. [13].

Our previous study [14] has also demonstrated the obvious regular structural evolution with etching temperature, and their considerable electrochemical performance variation when the pyrolysis temperature changed [15]. Meanwhile, it is interesting to find that the predominant structure among all our samples tends to be a kind of amorphous

state, and the discernible carbon ribbon by high resolution transmission electron microscopy (HRTEM) technique was already there before the silicon oxycarbide was turned to carbon, which could be ascribed as high pyrolysis temperature.

Besides, it is well demonstrated that the CDC porosity and properties depend mainly on the carbide species, which simultaneously leads to a limitation of the pore structures and performances of CDCs. To meet the requirements of applications, some structural or surface modifications are necessary, such as post-treatments of CDCs by KOH [16], CO₂ [17], air [18], urea [19] and Ar atmosphere [20,21]. In fact, the CDC porosity and ordering may be influenced together during the treatment, especially, when treated at high temperature, which has hitherto not explored very well. Moreover, the CO₂ capture performance of SiOC-DCs and the variation from the thermal-treatment under an Ar atmosphere have never been discussed. Herein, in this paper, we explore the influence of thermal-treatment under an Ar atmosphere on the structural evolution of silicon oxycarbide-derived carbons (SiOC-DCs), and then show their CO₂ capture performance, which may also be affected by the thermal-treatment.

2. Experimental

2.1 Sample preparation

The as-received sample (SiOC-DCs) was produced by chlorination of ball-milled SiOC powders (particle size of $<50\mu\text{m}$). SiOC ceramics were produced using a commercially available polymethyl(phenyl)siloxane resin (Dow Corning 249 flake resin). The as-received polysiloxane precursor was first cross-linked at 250°C in air for 4 h, and crushed into powder by using a disintegrator. The powder with the particle size ranging from 150 to $250\mu\text{m}$, 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^{-1} and then allowed to cool naturally. The powders were placed in a horizontal tube furnace (diameter 6 cm), purged in a nitrogen flow, heated to 900°C with a rate of 5°C min^{-1} and exposed to dry chlorine gas ($15\text{--}20\text{cm}^3\text{ min}^{-1}$) for 3 h. After chlorination, the samples were treated with NH_3 at 600°C for 2 h to remove residual chlorine and volatile chlorides trapped in pores. Last, the SiOC-DC was thermally treated under an Ar atmosphere at predetermined temperatures (1200 , 1500 , 1800 and 2100°C) for 2 h, which led to the obtainment of final samples.

2.2 Characterization methods

N_2 adsorption–desorption isotherms were obtained using Quantachrome instruments at 77 K. Brunauer–Emmett–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 analyse the pore size distributions (PSDs) and pore volume. 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 performed using a Rigaku diffractometer

with $\text{CuK}\alpha$ radiation ($k = 0.154\text{ nm}$) operating 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 and 70° (2θ). Raman spectra were recorded with a LABRAM-HR (JOBIN YVON) microspectrometer using an argon-ion laser (514.5 nm , lateral spot size of $\sim 1\mu\text{m}$).

The CO_2 adsorption isotherms of all SiOC-DC samples were 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 model was used to analyse the PSDs in the range of $0.3\text{--}1.5\text{ nm}$.

3. Results and discussion

Figure 1 shows the N_2 adsorption–desorption isotherms and the corresponding PSDs of samples thermal-treated at different temperatures. All the samples exhibit type I isotherms (figure 1a) according to IUPAC classification [22] characterized by the pronounced vertical parts in the beginning. Nevertheless, the vertical parts get shorter as the thermal-treatment temperature increases, which indicates a decreasing content for micropores in the samples. At the relatively middle pressure ($P/P_0 = 0.05\text{--}0.4$), the curves are slanting and a small hysteresis loop was observed, suggesting the presence of mesopores in these materials. Besides these, the curves show some tiny tails at relatively high pressure ($P/P_0 > 0.9$), implying that a few macropores also exist in these samples. The curves experience relatively big changes when the temperature reaches up to 1800°C and above, indicating that the pore structures suffered a lot by thermal-treatment. In other words, the pore structure is relatively stable at the

Figure 1. (a) N_2 sorption isotherms and (b) the corresponding PSDs of all samples.

Table 1. Summary of pore parameters of all samples.

Sample	SSA (m ² g ⁻¹)	V _t (cm ³ g ⁻¹)	Average <i>D</i> (nm)	V _a (<i>d</i> < 0.6 nm) (cm ³ g ⁻¹)	V _b (cm ³ g ⁻¹)	V _c (cm ³ g ⁻¹)	V _b /V _t
As-received	2121.6	1.668	3.1	0.033	1.045	0.490	0.626
1200°C	2164.3	1.610	3.0	0.048	1.069	0.373	0.664
1500°C	1972.3	1.550	3.1	0.038	0.927	0.488	0.598
1800°C	1418.3	1.338	3.8	0.021	0.596	0.617	0.450
2100°C	501.2	0.474	3.8	0.009	0.145	0.262	0.310

V_t: total pore volume, calculated at $P/P_0 = 0.99$. V_a: ultra-micropore volume, estimated $d \leq 0.6$ nm by the HK method. V_b: micropore volume, estimated $d \leq 2$ nm by the QSDFT method using the equilibrium model for slit pores; V_c: mesopore volume, estimated $2 < d \leq 50$ nm by the QSDFT method using the equilibrium model for slit pores.

thermal-treatment temperature below 1800°C for SiOC-DCs. Figure 1b shows the corresponding PSDs of the samples activated at different temperatures, which are calculated by the QSDFT method. Before 1800°C, the samples exhibit two peaks at about 1 and 2 nm, respectively. When the temperature reaches up to 1800°C and above, the PSDs get wider and flatter, inferring a massive disappearance of porosity (especially for microporosity).

Pore parameters are summarized in table 1. We can observe that both the specific surface area (SSA) and total pore volume decrease at elevated thermal-treatment temperatures. Actually, the SSA decreases by 76% for the sample treated at 2100°C for 2 h in comparison with that of the as-received sample. It is noted that the micropore volume (V_b) basically decreases, while the mesopore volume increases at the treatment temperature below 2100°C, which leads to the increase in the average pore size from 3.1 to 3.8 nm, suggesting a transition from the micropore structure to the mesopore structure. When the temperature reaches up to 2100°C, nearly all values for pore parameters show some decrease, demonstrating a serious breakage of the pore structures.

Figure 2 depicts the TEM images obtained from the as-received sample and the samples thermal-treated at different temperatures for 2 h. We can observe that the samples show relatively small changes at the thermal-treatment temperature of below 1500°C. Their structures are predominantly amorphous. When the temperature increases to 1500°C and above, we can observe that the morphology of the samples gets more meso- or macro-porous (figure 2a, c, e, g and i), which is in line with the results from N₂ adsorption. Besides, the ribbons can be observed more easily (figure 2b, d, f, h and j) at elevated temperatures after the treatment process. Initially, these ribbons were randomly and homogeneously distributed in these kinds of samples. Furthermore, these ribbons are entangled to each other and have no ends, but rather merge and separate at confluences [23]. Hence, a much higher thermal-treatment temperature (above 2100°C) should be adopted for further graphitization of SiOC-DCs. It still deserves to note that according to our previous study [15], there are already a few ribbons in the as-received SiOC-DC sample, which were

preserved from the polysiloxane-derived SiOC ceramics due to their insensitivity to chlorine [1,24]. The ordering of these ribbons may increase during thermal-treatment. Besides this, the treatment can induce the graphitization of predominate amorphous SiOC-DCs, and form some new ribbons possibly. Therefore, we can infer that the obvious ribbons might be composed of two parts. One part was derived from the pyrolysate (SiOC) and the other part originated from the chlorination of SiOC ceramics and further graphitization by high temperature thermal-treatment under an Ar atmosphere.

To investigate the carbon crystallinity as a function of thermal-treatment temperature further, an XRD technique was adopted in this study as shown in figure 3. For the samples treated below 1800°C, two broad haloes centred at ~26 and ~44°, respectively, were observed, which were designated with a typical characteristic of amorphous carbon. Besides this, the discrepancy between these images could nearly be neglected for all samples, suggesting little impact on carbon crystallinity by thermal-treatment. However, when the temperature is increased to 1800°C and above, the patterns get stronger and sharper. These changes demonstrate an increasing ordering at elevated temperatures by thermal-treatment. This is in agreement with the results obtained using the TEM technique.

Raman spectroscopy was used to acquire additional information on carbon materials as shown in figure 4. For all samples, we observed two in-plane modes: the characteristic disorder-induced D-mode near 1333–1343 cm⁻¹ and the graphite G-mode at 1584–1588 cm⁻¹. In the second-order region, two combination modes ~2678 cm⁻¹ (2D) and ~2826 cm⁻¹ (D + G) are also observed. Nevertheless, obvious changes can be observed from the pattern shapes owing to the thermal-treatment at different temperatures. From Lorentzian fits, the intensity ratio of D and G bands (I_D/I_G) and the G band width (full-width at half maximum (FWHM)) are listed in table 2. A continual decline of the FWHM and G-mode position at elevated thermal-treatment temperatures is observed, while the I_D/I_G increases at first and decreases above 1800°C subsequently. This means a higher ordering can be obtained at elevated thermal-treatment temperatures, and 1800°C can be considered as a key turning point for the

Figure 2. TEM images of all samples investigated (**a** and **b**: as-received sample; **c** and **d**: 1200°C; **e** and **f**: 1500°C; **g** and **h**: 1800°C and **i** and **j**: 2100°C).

structure from the amorphous phase to crystal graphite [25–27]. The pattern of the sample thermal-treated at 1800°C starts to show a tiny shoulder-peak at around 1620 cm^{-1} , which is further evidence for this transition.

A similar work has also been discussed by Bae *et al* [20,21]. They found that the heat treatment at 1100°C for 1 and 3 days under a pure Ar atmosphere had a significant influence on the structure and gas storage performance of SiC

or Ti_3SiC_2 -derived carbons. They believed that short ranged C–C restructuring arose from chemical interactions between neighbouring atoms, which tend to reduce the active sites or defects, and led to only a subtle change in the size of pore bodies, but significant modification of the pore network connectivity. This structural change can basically suit the samples heat treated for only 2 h at relatively low temperature (1200–1500°C) under an Ar atmosphere in our

Figure 3. XRD patterns of all samples investigated.

study, whose ultra-micropore volume (V_a) increased after the thermal-treatment. For other samples treated at higher temperature under an Ar atmosphere, the ordering of samples was increased significantly owing to the high level of structural rearrangement, which led to an obvious shrinkage of the sample pore structure simultaneously.

It is interesting to find that the as-received SiOC-DC sample exhibits a relatively high CO_2 adsorption capacity of 3.16 mmol g^{-1} at 0°C under ambient pressure (figure 5). Undoubtedly, the main reason for this high performance in CO_2 adsorption should be explained by the high porosity,

Figure 4. Raman spectra of all samples investigated.

characterized by their large SSA ($2121.6 \text{ m}^2 \text{ g}^{-1}$) and big pore volume ($1.668 \text{ cm}^3 \text{ g}^{-1}$), which can contribute to strong physical adsorption. However, this adsorption value is relatively smaller than that from a previous study [28]. The reason is that the present SiOC-DC sample has fewer small pores ($d < 0.6 \text{ nm}$) and wider PSD than the SiC-DC samples, though a higher specific surface area and pore volume were obtained in the present study.

It is also observed that the CO_2 adsorption capacity of SiOC-DC was significantly influenced by the thermal-treatment under an Ar atmosphere. The CO_2 adsorption performance increases after the treatment ranging from 1200 to 1500°C , which is due to the increase in the ultra-micropore volume (V_a in table 1). The possible reason for these phenomena is that the thermal-treatment under an Ar atmosphere in a suitable temperature range could induce short-range C–C restructuring, which attributes to the increase in the pore network connectivity, in accordance with the result from the N_2 adsorption and Raman technique [4,20,21]. Figure 6 depicts the PSDs of all SiOC-DC samples treated at different temperatures from CO_2 full isotherms. We can observe two peaks

Table 2. Summary of Raman data of all samples investigated.

Sample	G peak		D peak	
	Position (cm^{-1})	FWHM (cm^{-1})	Position (cm^{-1})	I_D/I_G
As-received	1597	60.4	1339	1.81
1200°C	1594	59.2	1333	1.82
1500°C	1589	58.4	1339	1.86
1800°C	1588	46.6	1338	2.08
2100°C	1580	36.6	1343	1.65

Figure 5. CO₂ adsorption capacity of all samples investigated.

Figure 6. PSDs of all samples investigated from CO₂ full isotherms.

centred at 0.6 and 0.8 nm, respectively. Moreover, the curves change with the temperature, consistently with the rules from N₂ adsorption. Of course, the ordering was also increased during the treatment process, especially under very high temperature (above 1800°C). However, over high temperature treatment will induce a significant collapse of micropores at the same time, leading to an obvious deterioration of CO₂ capture performance.

4. Conclusion

In conclusion, the effect of thermal-treatment under an Ar atmosphere on the structural evolution of SiOC-DCs and their CO₂ adsorption performance, was studied in this paper. By varying the treatment temperature from 1200 to 2100°C,

the pore structure and crystallinity can be further modified effectively. We observed that the structure of SiOC-DCs had a little change in the thermal-treatment temperature range of 1200–1500°C. Afterwards, carbon crystallinity was greatly improved at a very high temperature of 1800°C and above, with the cost of micropore structure breakage, characterized by a quick decrease in the surface area and total pore volume. The CO₂ adsorption capacity of SiOC-DC was also significantly influenced by the thermal-treatment under an Ar atmosphere. After the treatment ranging from 1200 to 1500°C, the CO₂ adsorption performance increases owing to the increase in the ultra-micropore ($d < 0.6$ nm) volume. A further increase in the temperature during the thermal-treatment will lead to a significant collapse of micropores, and an obvious deterioration of CO₂ capture performance, though their ordering was obviously improved.

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