Decomposition of silicon carbide in the presence of organic compounds under hydrothermal conditions

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The synthesis of different carbon polymorphs such as graphite, diamond, amorphous carbon or diamond-like carbon, fullerenes, carbon nanotubes, etc., has attracted considerable interest for a long time because of their importance in science and technology. There are great uncertainties about the phase stabilities of these polymorphs as some of them do not find a place in the carbon pressure–temperature (P–T) diagram and are also known for their contrasting physical properties. The exact physico–chemical phenomena responsible for their formation are yet to be understood. Attempts to synthesize these forms with varied conditions and techniques, sometimes even violating the thermodynamic principles, have met with a fair amount of success. The stabilities of graphite and diamond in nature were mainly controlled by P–T–fO\textsubscript{2} in the C–O–H system [1–6]. The role of C–O–H fluids [7,8], as well as the hydrothermal and organic origin [9,10] of these polymorphs, especially with reference to diamond genesis, prompted the material scientists to explore the possibility of synthesizing them at fairly low pressure and temperature conditions. The hydrothermal technique is highly promising for reactions involving volatiles as they attain the supercritical fluid state and supercritical fluids are known for their greater ability to dissolve non-volatile solids [11]. Silicon carbide powder has been used for the synthesis of carbon polymorphs [12–14], and Gogotsi et al. [15] have reported decomposition of silicon carbide in supercritical water and discussed the formation of various carbon polymorphs. Here we explore the possibility of producing carbon polymorphs under hydrothermal conditions through decomposition of silicon carbide in the presence of organic compounds instead of pure water. The organic compounds decompose into various C–O–H fluids; the main components are CO, OH, CO\textsubscript{2}, and C\textsubscript{2}H\textsubscript{2} radicals. It is very well known that these fluids play a significant role in creating a highly reducing environment in the system and also assist in the dissociation of silicon carbide and precipitation of the carbon phase.

Hydrothermal experimental runs were carried out in the pressure–temperature range of 100–200 MPa and 600–850\textdegree C employing conventional Roy–Tuttle reactor vessels and gold tubes. The starting materials such as silicon carbide and organic compounds in 1:1 mol were encapsulated in gold tubes and placed in the reactor vessels after ensuring for any leakage. The silicon carbide used in the present study is fine grained \textbeta \text{-SiC} powder with a specific area of less than 8 m\textsuperscript{2} g\textsuperscript{–1}, and the organic compounds used in the present investigation are malonic acid, glycolic acid, citric acid, sucrose, formic acid, acetic acid, ascorbic acid, succinic acid and malic acid. All these compounds are of pure reagent grade chemicals from Wako and Kanto, Japan. The experiments were quenched after 40–80 h. The capsules were cut open and the run products were dried and examined under an optical microscope. It is interesting to note that sufficient gas evolved with a pungent smell while opening the capsule, which indicates the capsule was intact during the run and possibly the presence of CH\textsubscript{4} (methane) as one of the gas phases inside the capsule. The run products were further characterized by Cu K\textalpha X-ray diffraction (XRD), scanning electron microscopy (SEM) and micro Raman spectroscopy (Ar\textsuperscript{+} laser).

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The carbon formation was noticed in almost all runs at temperatures above 600°C and pressures above 100 MPa, when the charge materials were devoid of excess water in the system. Experiments with excess water yielded mainly silica with a small amount of carbon or no carbon precipitation, hence the amount of water inside the capsule was restricted to the water released through the decomposition of organic compounds. The run products were examined under the optical microscope and were found to contain black material admixed with silica. XRD studies of the run products showed only the silica peaks and no carbon, except in a few runs where the carbon phase was identified to correspond to the carbon JCPDS file Nos. 18-0311 and 22-64. The silica (SiO\textsubscript{2}) is usually occurring as well faceted crystals, crystallizing either as the quartz or cristobalite phase. Micro Raman spectroscopy is a powerful technique for the characterization of carbon materials. Typical representative Raman spectra of carbon obtained through decomposition of silicon carbide in the presence of malonic acid (hds-56), glycolic acid (hds-57) and succinic acid (hds-58) are shown in Fig. 1. All the results discussed here were replicated and showed good reproducibility. The two strong and sharp bands at \(\approx 1336\) cm\(^{-1}\) and \(\approx 1560\) cm\(^{-1}\), which are referred to D and G band C--C stretching vibrations, respectively, noticed in runs hds-56 and hds-57 could be attributed to a particular type of carbon structure. We would like to point out that spectra of similar kind were described as from a diamond like carbon (DLC) by Visscher et al. [16], and also Gogotsi et al. [15] have discussed at length the positioning of the D-band and G-band, with a similar opinion. The Raman spectrum of hds-58 is the same as that of the spectra for the carbon material obtained in all other runs with other organic compounds. This spectrum has broad peaks around the D-band and G-band region and the positions of these correspond to that of 1356 cm\(^{-1}\) and 1590 cm\(^{-1}\), which is more characteristic of glassy carbon or disordered graphite [17].

Thus, in the present study we found that the silicon carbide dissociates in the presence of organic compounds in to silicon dioxide and carbon phases above 600°C and 100 MPa. The carbon phase formed is mainly of two types, one is glassy or disordered graphite carbon and the other is nano- or micro-sized spherical-shaped carbon particles. The reproducible spherical shaped carbon particles, which are of particular interest because of possible application in catalysis. These preliminary observations reveal the possibility of nucleating and synthesizing carbon particles using the above mechanism without the assistance of any metal catalysis and also without using a diamond seed. Thus, the authors are of the opinion that experiments with increased concentration of C\(_{2}\)H\(_{4}\) radicals and low f\(_{O_2}\) inside the capsules, may help in synthesizing the sp\(^2\) and sp\(^3\) bonded carbon phases under hydrothermal conditions without using any metal catalysts or seed crystals.

![Fig. 1. Micro Raman spectra of carbon from hydrothermal runs – hds-56 with malonic acid, hds-57 with glycolic acid and hds-58 with succinic acid (hds-58 spectra are same for the carbon phases encountered with all other organic compounds used in the present study).](image-url)
Fig. 2. Scanning electron images of the spherical shaped carbon particles (a) and (c) individual spherules as well as linked chains, (b) carbon spherules having characteristic surface pattern, (d) enlarged image of a particle surface.

Fig. 3. Plot of C–O–H species of the organic compounds used in the present study. Note that they all fall on three tie lines and are promising to precipitate the carbon at low P–T conditions.

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References

Attack of graphite by liquid sodium: some kinetic data

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The synthesis of ternary graphite–sodium–halogen GICs by heating pyrographite samples in a large excess of sodium and one or two of its halides has been described in a previous work [1]. After cooling, the reaction products are separated from the sodium and halide gangue by washing with water. Acetylene has been characterized in the evolved gas by its brilliant flame and by precipitation of the acetylide $\text{Cu}_2\text{C}_2$ from a solution of cuprous chloride in ammonia.

In parallel, a loss of carbon from pristine pyrographite samples has been observed. Indeed, it is clear that pyrographite partly dissolves in liquid sodium in the form of the acetylide $\text{Na}_2\text{C}_2$.

We attempted to measure the velocity of this reaction as a function of temperature $T$:

$$v = \frac{1}{S} \frac{\Delta m}{\Delta t}$$

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