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Effect of Coexisting Minerals on the Graphitization of Carbon under Pressure. IV. Accelerating Effect of Calcium Oxide

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Heat treatments of polyvinylchloride coke in the presence of three kinds of calcium oxide calcined at different temperatures were carried out in order to study the effect of the reactivity of calcium oxide on the acceleration of graphitization of carbon under the quasihydrostatic pressure of 3.2 kbar. A remarkable difference in the accelerating effect on graphitization was confirmed. In the presence of the most reactive calcium oxide calcined at 920°C, the graphitization of the carbon began at about 1100°C and the content of the graphitic component became 100% by heat treatment at 1500°C for 60 min. While in the presence of the least reactive calcium oxide calcined at 1470°C, the graphitic component, an even hump on the corresponding diffraction angle, could not be detected in specimens heat-treated below 1500°C. The content of graphitic component and the distribution of calcium in heat-treated specimens were measured by an electron microprobe analyzer. It was found that the part having a larger content of calcium had a larger content of the graphitic component. A possible mechanism of the accelerating effect of calcium compound on graphitization is considered to be chemical concerning the intermediate formation of carbide or metal. The formation of the graphitic component seems to proceed by the reaction:

$$\mathrm{CaO+C\ (amorphous) \rightarrow Ca+CO \rightarrow CaO + C\ (graphite)} \qquad (\mathbf{1})$$

below 1300°C, and above 1300°C, mainly by the reaction:

$$\mathrm{CaO+3C(amorphous) \rightarrow CaC_2+CO \rightarrow CaO+3C\ (graphite)} \qquad (\mathbf{2})$$

and also by reaction (1). The driving force of the formation of the graphitic component through these reactions is the difference in the free energy between amorphous carbon and graphite, *viz.*, disordered and ordered graphite.

It was reported previously[1-3] that the graphitization of carbon was accelerated by the coexistence of calcium carbonate and hydroxide during heat treatment under the pressure of 3.2 kbar. A graphitic component began to appear in the carbon specimen at about 1100°C[1,2] in contact with calcium carbonate or limestone and at about 600°C[3] in contact with calcium hydroxide. The (002) diffraction line of these carbon specimens had a composite profile, *viz.*, graphitic component existed side by side with turbostratic component. The turbostratic component had transformed directly to the graphitic component without going through intermediate state. Though this heterogeneous process of graphitization seems to be similar to that observed on the same carbon heat-treated under pressure without any coexisting mineral,[2,4] the mechanisms of accelerating effects of these two processes were considered to be different from each other. The intermediate formation of unstable carbide seems to be formed by a chemical reaction of carbon and coexisting calcium compounds as one of the possible mechanism of the accelerating effect.

In the present work, calcium oxide specimens calcined at different temperatures were used as the coexisting mineral in the heat treatment of carbon under the pressure of 3.2 kbar. The object of the experiments was to study the effect of reactivity of calcium oxide on the acceleration of graphitization.

Experimental

The carbon sample used was the same polyvinyl chloride coke (PV-7) as that used in the previous works.[1-3] Three kinds of calcium oxide were prepared by the calcination of calcium carbonate at 920, 1050 and 1470°C for 60 min and were pressed into disks of 8.0 mm in diameter and 3.5 mm in thickness. It was confirmed by X-ray diffraction method whether calcium carbonate had decomposed completely or not. The disks were covered with calcium oxide powder and kept in an evacuated desiccator. The crystallite size

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1) T. Nod, M. Inagaki, S. Hirano and K. Amanuma, This Bulletin, **41**, 1245 (1968).

2) T. Noda, M. Inagaki, S. Hirano and H. Saito, *Kogyo Kagaku Zasshi*, **72**, 643 (1969).

3) T. Noda, M. Inagaki, S. Hirano and H. Saito, This Bulletin, **42**, 1738 (1969).

4) T. Noda, K. Kamiya and M. Inagaki, *ibid.*, **41**, 485 (1968).

Table 1

Sample	Calcination °C	Calcination min	Crystallite size, Å	Bulk density g/cm	Prosity %
CaO-9	920	60	720	2.78	18
CaO-10	1050	60	950	2.88	15
CaO-11	1470	60	1000	2.95	13

and bulk density of the three kinds of calcium oxide (designated as CaO-9, CaO-10 and CaO-15) are given in Table 1. Calcium oxide calcined at lower temperature is known to be more reactive than that calcined at higher temperature.[5–7]

The heat treatment of the carbon sample in the presence of calcium oxide was carried out at various temperatures between 900 and 1500°C for 60 min under the quasi-hydrostatic pressure of 3.2 kbar in a simple piston-cylinder type pressure vessel. The cell arrangement and the procedure for the experiments were exactly the same as reported previously.[1–3] Temperature of heat treatment was estimated from the relation between temperature and input power. Pressure was calibrated by the transition points of KNO_3 and AgI.[8]

The diffraction profile of (002) line was measured for the central part of the heat-treated carbon specimen by using Ni-filtered Cu$K\alpha$ radiation and a recording goniometer. The composite profile observed was separated graphically into two component profiles corresponding to the graphitic component G_M and turbostratic component A_M.[*1] The c_0-spacing and crystallite size L_c were measured from the (002) profile by the same method as reported previously.[1] The content of the graphitic component G_M was obtained from the ratio of the area under the profile for the component G_M to the total area under the composite profile. The area ratio was corrected for the preferred orientation of crystallite in the X-ray specimen by a conventional method.[2] The heat-treated specimens were also observed under an electron microscope. The specimen for electron microscopy was dispersed in trichloroethylene by ultrasonic vibration and then supported on an evaporated carbon film.

Results and Discussion

Each carbon specimen heat-treated above 1000°C was obtained as a caked tablet. In these caked specimens, calcium oxide was always detected by X-ray diffraction method. Its amount increased with the increase in heat treatment temperature (HTT). In the specimens heat-treated above 1300°C in the presence of CaO-9 and those heat-treated above 1400°C in the presence of CaO-10, calcium carbide was detected in the part where carbon and calcium oxide contacted each other. Recrystallization of calcium oxide was not observed

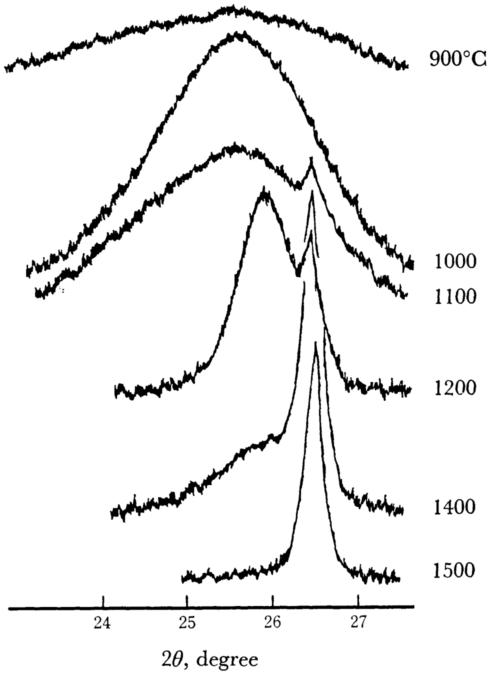
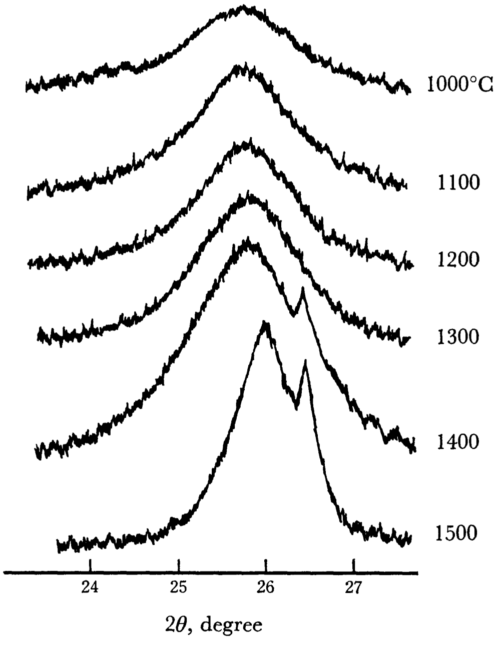


Fig. 1. Profiles of (002) diffraction line of carbon (PV-7) heat-treated under 3.2 kbar.
a) in the presence of calcium oxide calcined at 920°C for 60 min (CaO-9)



b) in the presence of calcium oxide calcined at 1050°C for 60 min (CaO-10)

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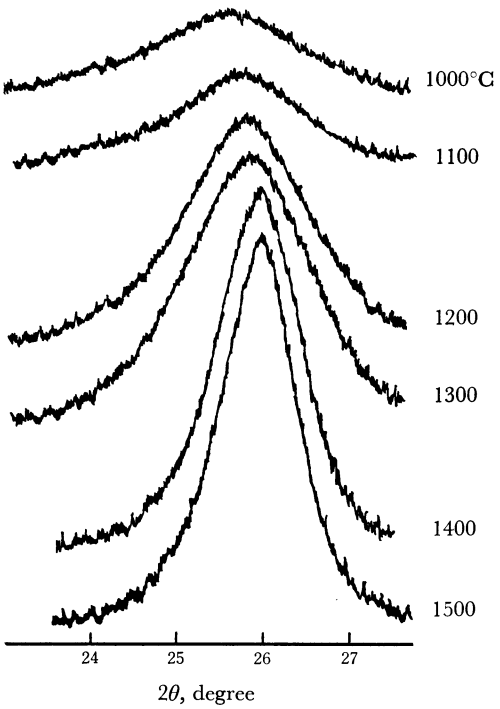
[5] H. C. Fischer, *J. Amer. Ceram. Soc.*, **38**, 245, 284 (1955).

[6] T. Noda, *Kogyo Kagaku Zasshi*, **40**, 195, 196 (1937).

[7] Y. Ono and T. Matsuoka, *Yogyo Kyokai Shi*, **59**, 284, 341 (1951).

[8] M. Inagaki, S. Hirano and H. Saito, *ibid.*, **76**, 264 (1968).

[*1] Suffix denotes these components were formed in the presence of a mineral.



c) in the presence of calcium oxide calcined at 1470°C for 60 min (CaO-15)

in the present experiment.

Changes of the profile of (002) diffraction line with HTT are shown in Fig. 1 a), b) and c). We see that there is a remarkable difference in the accelerating effect of the three kinds of calcium oxide on graphitization of carbon. In the presence of CaO-9, the graphitization of carbon began at about 1100°C and the profile for the graphitic component developed rapidly with the increase in HTT. The graphitization of the same carbon was found to begin at about the same HTT in the presence of limestone[1)] and calcium carbonate.[2)] In the presnece of CaO-10, the graphitic component G_M could be detected on (002) profile of the specimen heat-treated above 1400°C. In the presence of CaO-15, however, the graphitic component, an even hump at the corresponding diffraction angle, could not be detected in specimens heat-treated below 1500°C. From profiles of (004) line, the same results were deduced.

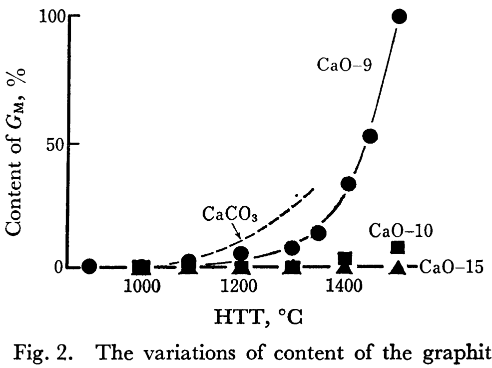


Fig. 2. The variations of content of the graphitic component G_M with HTT under 3.2 kbar for 60 min.
●: in the presence of CaO-9
■: in the presence of CaO-10
▲: in the presence of CaO-15

The variation of content of the graphitic component G_M is shown in Fig. 2 as a function of HTT. In the presence of the most reactive calcium oxide CaO-9, the graphitic component G_M increased very rapidly. The content of G_M turned out almost 100% at HTT of 1500°C. In the presence of less reactive CaO-10, however, only a small amount of the graphitic component G_M was found above 1400°C, and in the presence of CaO-15 no graphitic component G_M was observed at least up to 1500°C. The changes of c_0-spacing and crystallite size L_c with HTT are given in Figs. 3 a) and b), together with the results obtained in the presence of calcium

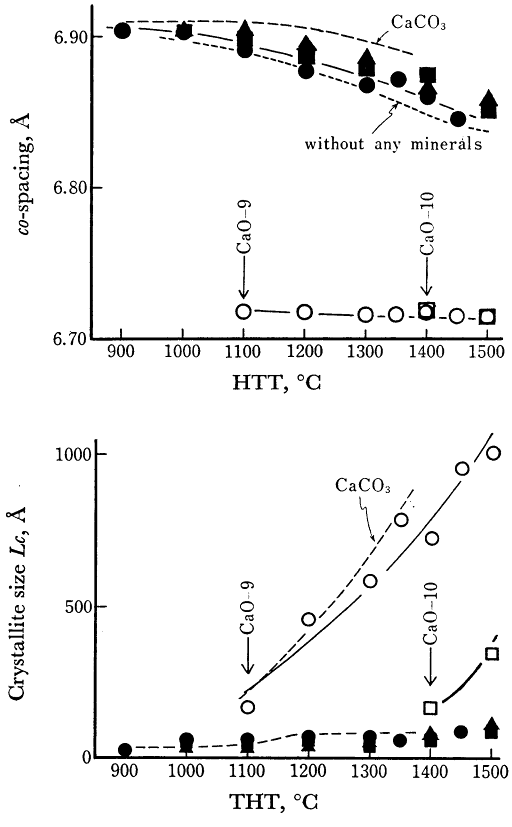


Fig. 3. Changes of c_0-spacing and crystallite size Lc of carbon (PV-7) with HTT, which was heat-treated under 3.2 kbar.

Turbostratic component A_M	Graphitic component G_M	
●	○	in the presence of CaO-9
■	□	in thejpresence of CaO-10
▲	△	in the presence of CaO-15

carbonate and without any coexisting mineral.[2] The c_0-spacing of the graphitic component G_M was almost constant at 6.72 Å as in the cases of coexistence of limestone or calcium carbonate and without any mineral.[2,3] The crystallite size L_c of G_M increased with the increase in HTT, and became larger than 1000 Å at 1500°C in the case of CaO-9. The c_0-spacing of the turbostratic component A_M decreased gradually and its crystallite size L_c increased only silghtly with the increase in HTT.

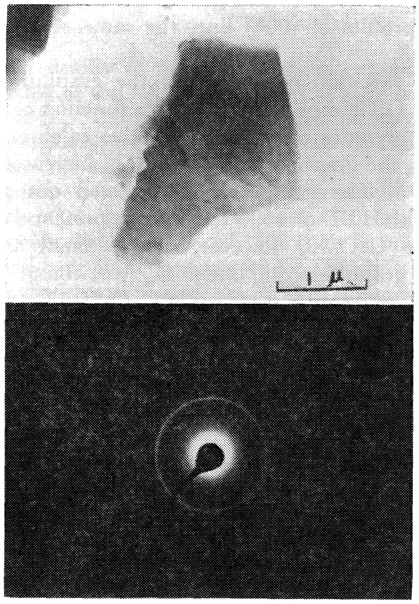


Fig. 4. Bright-field electron micrograph and selected area electron diffraction pattern of turbostratic particle under 3.2 kbar in the carbon specimen heat-treated at 1100°C for 60 min under 3.2 kbar in the presence of calcium oxide CaO-9.

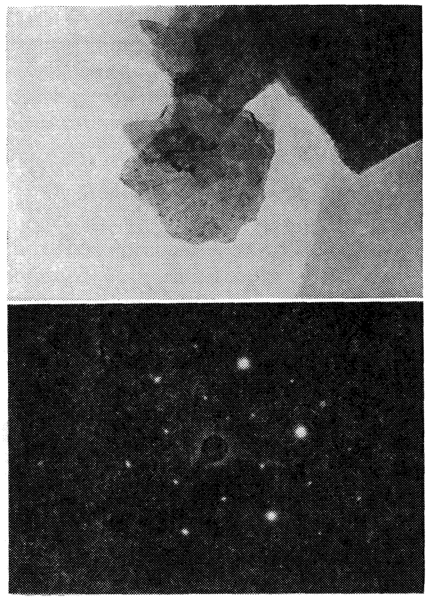


Fig. 5. Bright-field electron micrograph and selected area electron diffraction pattern of graphitic particle in the carbon specimen heat-treated at 1100°C for 60 min under 3.2 kbar in the presence of calcium oxice CaO-9.

In the specimens heat-treated above 1100°C in the presence of CaO-9 and those heat-treated above 1400°C in the presence of CaO-10, well-crystallized flaky particles having the same six-fold diffraction pattern as graphite single crystal were found under an electron microscope, besides the particles having continuous diffraction rings (Figs. 4 and 5).

The distribution of the graphitic component G_M in the caked specimens was examined by taking samples from different parts. The change of profiles and the distribution of the content of G_M in the specimen heat-treated at 1400°C in the presence of CaO-9 are shown in Fig. 6 as an example. The part closer to calcium oxide disk was found to have a larger content of G_M. The distribution of calcium element was measured by using an electron microprobe analyzer. In Fig. 7, the distribution of calcium across the thickness is shown on the specimen heat-treated at 1400°C in the presence of CaO-9. It is shown that the closer to calcium oxide disk, the larger the content of calcium.

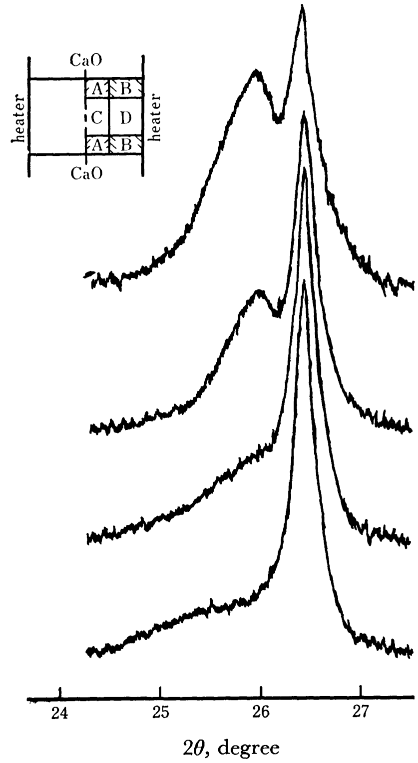


Fig. 6. Change of profiles of (002) diffraction line and distribution of content of graphitic component G_M in the specimen heat-treated at 1400°C for 60 min under 3.2 kbar in the presence of CaO-9.

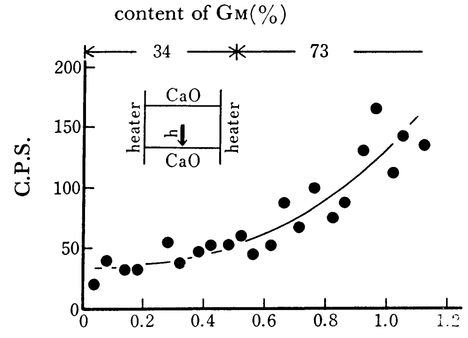


Fig. 7. Relation between distribution of calcium across the thickness and content of graphitic component *G*M in the specimen heat-treated at 1400°C for 60 min under 3.2 kbar in the presence of CaO-9.

Generally, the part having the larger content of calcium has the larger content of the graphitic component G_M. The same relation between calcium content and content of G_M was observed in the specimens obtained by heat treatment in the presence of calcium carbonate under 3.2 kbar.[9]

It is suggested that the formation of the graphitic component in the presence of calcium compounds under pressure proceeds by the mechanisms explained below. The fact that calcium carbide was detected above around 1300°C, in the part where the carbon specimen contacted the calcium oxide disk, suggests that the intermediate formation and subsequent decomposition of calcium carbide may mainly lead to the formation of the graphitic component in the carbon specimen:

$$CaO+3C\ (\text{amorphous}) \rightarrow CaC_2+CO \qquad (1)$$

$$CaC_2+CO \rightarrow CaO+3C\ (\text{graphite}). \qquad (2)$$

Calcium oxide distributed in the carbon specimen must be the decomposition product of calcium carbide according to Eq. (2). The content of graphitic component should vary with the content of calcium oxide in the carbon specimen. This was in good accordance with experimental results.[9] On the other hand, the fact that calcium carbide was not detected below 1200°C in the specimen and the difficulty of the decomposition of calcium carbide under such condition make it impossible to explain the formation of the graphitic component at lower temperatures below 1300°C by the same mechanism as that above 1300°C. In this case, the formation of the graphitic component may proceed through the following reaction:

$$CaO+C\ (\text{amorphous}) \rightarrow Ca+CO \rightarrow CaO+C\ (\text{graphite}). \qquad (3)$$

The results[11] concerning heat treatments of carbon in the presence of magnesia, alumina and silica under pressure also support this mechanism. The formation of the graphitic component by this mechanism is also possible for high temperature process. The driving force of the graphite formation through the intermediate formation of calcium carbide or calcium metal is the difference in the free energy between amorphous carbon and graphite, *viz.*, disordered and ordered graphite.[12]

The more reactive calcium oxide reacts with carbon more easily at lower temperature.[10] This was verified by the fact that carbide was detected in the carbon specimen heat-treated at 1300°C in the presence of CaO-9 and at 1400°C in the presence of CaO-10. This low reaction temperature of active oxide is closely related to the low temperture formation of the graphitic component in the presence of reactive oxide. When calcium carbonate (limestone) or calcium hydroxide was used as the coexisting mineral, nascent oxide formed during the heat treatment may have reacted with carbon to form calcium metal.

An apparent close association[1] of recrystallization and melting of coexisting calcium carbonate and hydroxide with the acceleration of graphitization is mainly due to the increased rate of reaction of the coexisting minerals with carbon at temperatures where recrystallization of minerals becomes vivid, or when the minerals melt.

The authors are indebted to Dr. T. Noda, President of Mie University, for many helpful suggestions and discussions on this work.

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[9] S. Hirano, H. Saito and M. Inagaki, This Bulletin, **43**, 2624 (1970).

[10] T. Mukaibo and Y. Yamanaka, *Kogyo Kagaku Zasshi*, **56**, 232 (1953).

[11] S. Hirano, M. Inagaki and H. Saito, unpublished.

[12] E. Fitzer and B. Kegel, *Carbon*, (Oxford), **6**, 433 (1968).