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Catalytic Formation of Graphite from Benzene on Iron Powder

There have been many investigations (*1*–*3*) on the deposition of carbons from CO and hydrocarbons on heated transition metal surfaces such as Fe, Co, and Ni, and a variety of morphologies have been reported in the temperature range 400–1000°C. These include graphite flakes or platelets, lamellar graphitic coatings or films on the metal surfaces, clusters or islands of less graphitic crystallites, and filamentous-type deposits of poor crystallinity. Among them, graphite flakes or platelets are most interesting in the sense that graphite can be produced at considerably lower temperatures than the usual graphitization temperatures 2500–3000°C. None of the previous works, however, reported high yields of such products. In the present work an attempt has been successfully made to produce graphite powder from benzene by using iron powder as a catalyst.

Thermal decomposition of benzene was carried out in a flow system at atmospheric pressure, using a 25-mm-id quartz tube reactor. The catalyst used was electrolytic iron powder of 100 mesh from Wako Pure Chemicals Industries. The BET surface area from nitrogen adsorption was 7.9 $m^2 \cdot g^{-1}$. The 2.0 g of iron particles was placed in a mullite boat and loaded in the reactor. The catalyst was heated up to a desired reaction temperature of 400–1150°C at a rate 10°C $\cdot$ min^{-1} in flowing hydrogen. Then a mixture of benzene and hydrogen was passed over the catalyst at a flow rate 40 $cm^3 \cdot min^{-1}$ (25°C, 1 atm) for a certain period up to 3 hr. The concentration of benzene was fixed at 14.2%, which was chosen from our preliminary observation that the optimum concentration was approximately 5 to 20% in hydrogen for graphitic carbon formation. After the feeding of benzene had been stopped, the system was maintained for 20 min more at the reaction temperature and then cooled down in flowing hydrogen. The amount of carbonaceous products was measured as a weight gain. The nature of the products was examined by a transmission electron microscope, and by the usual X-ray diffraction technique using silicon as an internal standard.

Carbonaceous product was obtained mainly as a soft bulky mass of powder form on the iron particles. Figure 1 shows the amount of the product obtained during the decomposition for 3 hr as a function of the reaction temperature. The ordinate is also indicated by "yield" based on the amount of carbon fed as benzene (3.02 g). Other forms of carbon such as blacks, films, or coatings were also obtained on the walls of a quartz tube and a boat, but only in negligible amounts in most cases. These minor products are not included in Fig. 1. The exit gases contained a small amount of methane as a main gaseous product (*4*), as well as unreacted benzene. In addition some high-molecular-weight hydrocarbons condensed into tars or brown substances in the exhaust tubing of the reactor. The amounts of these by-products, however, were not determined. In Fig. 1, it is noted that the temperature dependence of the yield is characterized by two regions; a lower-temperature peak having a maximum (about 40%) at 600°C, and an increase above 700°C. The yield in the latter region reached about 80% at 1100°C, and then abruptly decreased to nearly 0% at 1150°C.

First of all, it should be noted that the formation of carbons was ascribable neither to the precipitation of dissolved carbon

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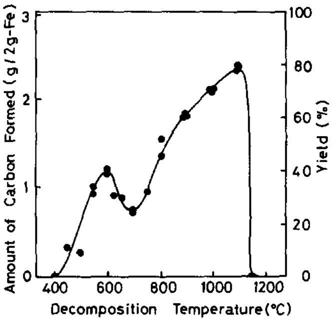

FIG. 1. The amount and yield of carbon powder obtained in the thermal decomposition of benzene on iron particles.

in iron on cooling (*5, 6*), nor to the decomposition of carbides such as Fe_2C and Fe_3C on cooling (*7–9*), because the amounts of carbons observed were much larger than those expected for such cases. For example, stoichiometric formation of Fe_3C from 2 g of iron would leave only 0.14 g of carbon. Thus it is unambiguous that the carbons have been produced by some catalytic action of iron. This point was confirmed from the results of Fig. 2, where the formation of carbon was examined as a function of reaction time at 600, 800, and 1100°C. Similar results were also obtained at other temperatures. The linear increases with time strongly support that the formation of carbon is really catalytic. In addition the data may suggest the existence of an induction period in Fig. 2. However, the initial deviation from the linear correlation is probably caused by a time lag until the concentration of benzene reaches the desired level.

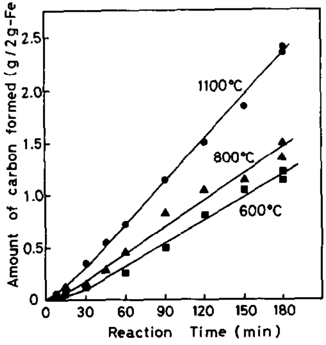

FIG. 2. The amount of carbon powder obtained as a function of reaction time at 600, 800, and 1100°C.

The results of Fig. 1 suggest different mechanisms or different catalytic species for the two temperature regions. The appearance of the lower-temperature peak has been often observed and argued in relation to the formation of carbidic intermediates (*10–12*). Our X-ray diffraction analyses also identified the formation of cementite, which was maximum at 600°C. On the other hand, γ-Fe seems to be responsible for the formation of carbon in the higher-temperature region, since the lowest α–γ transition point in the system Fe–C coincides well with the starting temperature of this region. The abrupt decrease in the yield at 1150°C was caused by melting of all the iron particles into a single mass. At this temperature most of the benzene was converted into soot, which was carried away from the reactor, probably through its homogeneous decomposition. Under such conditions it may be expected that iron dissolves some carbon or reacts with carbon to form cementite, and hence that about 0.1 g of carbon is left on cooling. But the result at 1150°C showed a much smaller amount of carbon. Therefore it is apparent that the iron sample does not have enough surface to decompose benzene on it after the sample melts.

The morphologies of the products were appreciably different according to their formation temperature, although they were obtained apparently in powder form in every case. In particular, a drastic change was observed between 700 and 800°C, corresponding to the transition between the two regions mentioned above. The morphologies at 500–700°C were mainly filamentous as reported by many authors (*2, 3, 8, 11–13*), while those at the higher temperatures were platelets. The size of the platelets was mostly smaller than 0.3 μm at 800°C, but increased markedly with the temperature. Figure 3 illustrates large plate-like crystals obtained at 1000 and

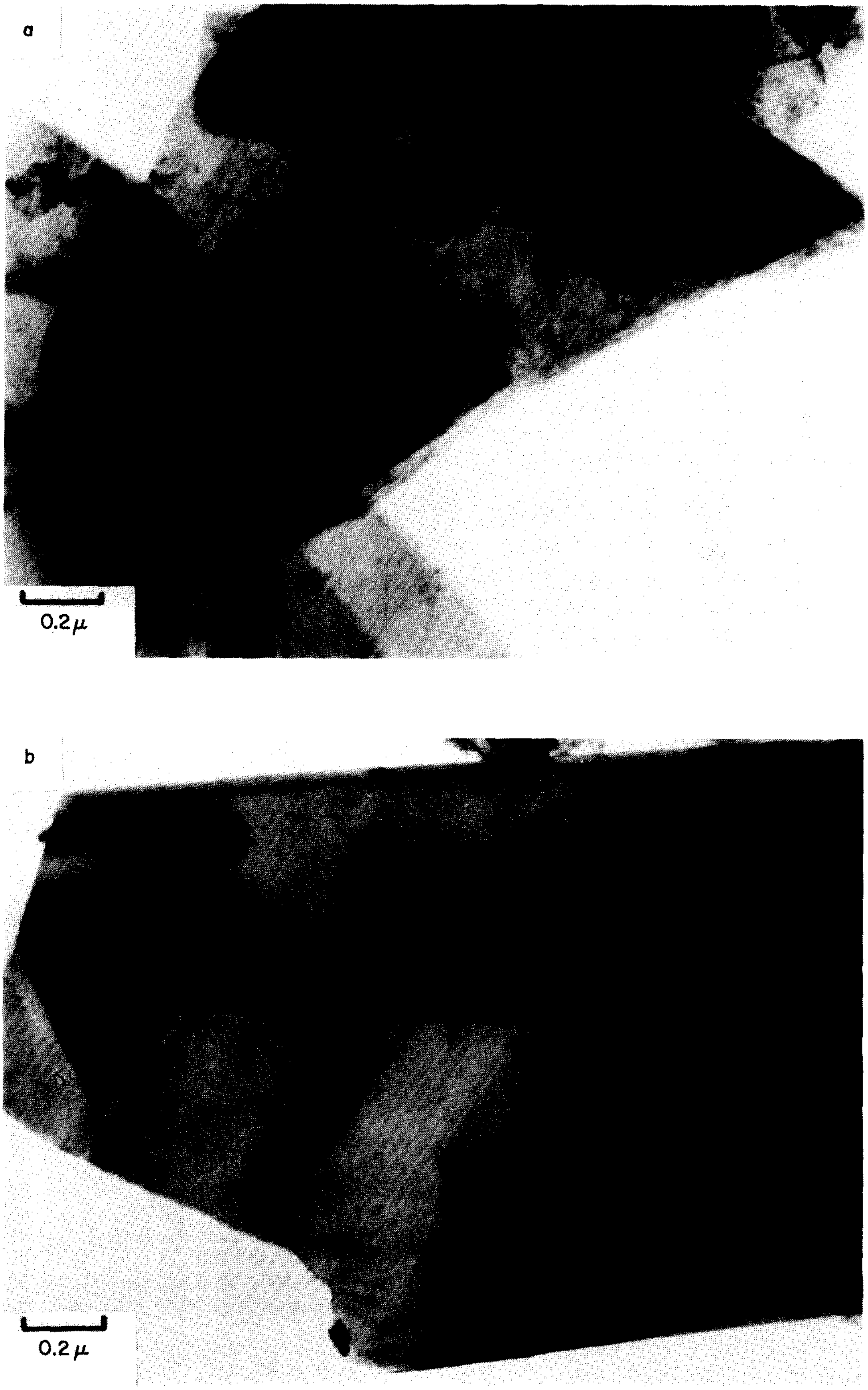

FIG. 3. Transmission electron micrographs of the graphitic carbons formed at (a) 1000 and (b) 1100°C.

TABLE 1

X-Ray Crystallographic Parameters of the Products

Formation temp. (°C)	Interlayer spacing d_{002} (Å)	Ratio of graphitization g^a	True diffraction broadening β (°)	Average crystallite size L_c (Å)	Relative intensity of (002) line[b]
600	3.383	0.663	0.758	120	73
700	3.379	0.709	0.659	138	79
800	3.377	0.733	0.446	204	77
900	3.374	0.767	0.256	360	70
1000	3.365	0.872	0.132	690	63
1100	3.358	0.953	0.085	>1000	82
Lonza KS-15[c]	3.355	0.988	0.082	>1000	100

[a] $g = (3.44 - d_{002})/0.086$ (*16*).

[b] Measured on the sample treated with a conc. HCl solution in order to remove iron particles incorporated into the products.

[c] A commercial graphite sample from Lonza Ltd., Switzerland.

1100°C. These crystals exhibited well-defined electron diffraction patterns characteristic of graphite. In addition the presence of spherical carbon black particles was not microscopically identified in any sample.

Some crystallographic parameters are listed in Table 1 and compared with those of a commercial graphite sample Lonza KS-15. With the increase of formation temperature, the interlayer spacing d_{002} and the average crystallite size L_c became progressively closer to those of graphite. The values of d_{002} are much smaller than those for nongraphitic or less graphitic carbons: 3.61 to 3.70 Å for dispersed carbons (*14*), 3.49 to 3.90 Å for glassy carbon (*15*), and 3.46 to 3.54 Å for pyrolytic surface carbon (*14*). A smaller value of d_{002} corresponds to a higher degree of graphitization, as proposed, for example, by Méring and Maire (*16*). Furthermore the 1000 and 1100°C products exhibited distinct (101) and (112) diffraction lines with intensities comparable to those of the graphite sample. From these results, it is concluded that the products are graphitic in nature, and that they are essentially three-dimensionally ordered graphite at 1000 and 1100°C. A semiquantitative estimate of the content of such graphitic carbon may be provided from the relative intensity data on (002) diffraction lines, although the intensities are greatly dependent upon the shape of the sample crystals, especially for the plate-like ones like graphite.

In conclusion, the present work revealed that graphite powder could be produced in good yield by decomposing benzene on iron powder at 1000–1100°C.

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