PYROLYSIS MECHANISM AS STUDIED BY ELECTRON MICROSCOPY, DTA, IR AND ESR

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Carbon ability to graphitize first depends on its precursor chemical composition (hydrogen or oxygen rich) then on experimental pyrolysis conditions : reticulation by air, for instance, which changes carbon properties, is technologically important. The present work considers controlled pyrolysis of two materials : A material is relatively hydrogen rich and oxygen poor (sporopollenin H/C 1,56 O/C 0,34), B material is hydrogen poor and oxygen rich (lignite H/C 1,12 O/C 0,44). For both samples 140 mg have been packed in a covered graphite crucible and heat-treated in a N_2 flow at 4°/mn. Differential thermal analysis (DTA) was performed during heat-treatment. Samples corresponding to various representative points of the DTA curve were subjected to rapid quenching under inert gas out of the furnace. They have been used for weight loss measurements (WL), chemical analysis, infra red spectrometry (IR) electron-spin resonance (ESR) and electron microscopy (EM) studies. Carbonization paths of A (dashed line) and B (full line) materials are represented in the Van Krevelen patterns of fig. 1 (H/C atomic ratio is plotted versus O/C atomic ratio). The corresponding weight losses (WL) and rates of WL (DWL) as well as DTA curves are respectively represented in fig. 2, 3 and 4.

Visual observation as well as optical and scanning microscopy studies show that sporopollenin (A material) melts at 436° C (point n° 3) while B material (lignite) remains powdered. The large diffuse exothermic peak in the DTA curve of A followed by an exothermic plateau and the two diffuse peaks of B correspond to tar departure. For B they are shifted toward the lower HTT and the first maximum in DTA coincide with the maximum rate of tar departure (peak in DWL curve). On the contrary for A it is the beginning of the DTA plateau which coincides with DWL curve peak (after melting). Maximum WL for A material is much higher than for B (80 % as compared to 60 %).

Numbered samples on DTA curve were studied in dark-field (DF) high resolution EM. The incident beam is progressively tilted relatively to a small objective aperture set paraxial (diameter 0,18 $Å^{-1}$, Airy disc diameter $\simeq$ 7 Å) and the optical image is observed during tilting (1,2). Bright dots appear on a dark-field whenever a hkl scattered beam passes through the aperture. In all samples, bright dots less than 10 Å in size appear only when 00.2, 10 and 11 beams of turbostratic carbons are approximately paraxial and thus pass through the aperture. These dots have been verified to be real objects in using through-focus series and various apertures (3). Stacks of aromatic molecules containing 2 or 3 layers and less than 10 aromatic rings thus become obvious.

If the 00.2 beam is only used for DF imaging, the carbon layer stacks which appear as bright dots are those situated edge-on on the supporting film. For A material all samples heat-treated below 460° C (numbered from 1 to 5 on DTA curve) show bright dots homogeneously distributed in the particles. Since they are distributed as such, the stacks are thus at random in the material. In the n° 6 sample corresponding to the DTA plateau at 460° C the bright dots gather in clusters about 1.000 Å in size (fig. 5). For producing clusters, carbon layers of neighbouring stacks have to lay parallel. A molecular orientation has thus been developed in regions about 1.000 Å in size. Misorientation of the carbon layer stacks can be described by evaluating first their azimutal disorder (twist), then their deviation from the Bragg angle (tilt). Twist is approximated to the 00.2 ring portion intersected by the aperture ie 40°. Tilt is evaluated by using a goniometer stage ie ± 30°. For HTT higher than 460° C size of the stacks and extent of the molecular orientation remain constant. Therefore bright dot cluster contrast increases. Since neither twist nor tilt changes the contrast improvement should be due to a decrease in layer distorsions. It is probably related to the progressive disappearance of non aromatic molecules linked to the layers. For B material all the samples can be considered as containing aromatic layer stacks distributed at random (it is only above 1.000° C. that very small clusters of bright dots occur. the molecular orientation extent is in this case smaller than 50° A).

The A material (sporopollenin) has been treated 5h at 200° C in air (reticulation). The curves in dotted line in fig. 1 to 4 respectively represent its carbonization path, WL, DWL and DTA. It is noticeable that reticulated A sample is then absolutely comparable to B : carbonization path is slightly lower and weight loss as well. The two diffuse DTA peaks are reduced to one and it is shifted toward the low HTT. Molecular orientation characteristic of A sample (1000 Å in size) disappears and the material does not melt.

A material is extremely sensitive to experimental conditions. For instance, if a very small amount of sporopollenin (< 10 mg) is heated in an open crucible (4) under a nitrogen gas flow the material does not melt and the molecular orientation almost disappear (< 50 Å in extent).

These data can be correlated to IR spectra (5) obtained on all the samples indicated by a representative point on WL curves (fig. 2). For A material heated in a covered crucible (dashed line DTA curve) molecular orientation occurence coincides with the extremum of aromatic CH groups, after OH, carbonyl

and carboxyl groups have practically disappeared and when aliphatic CH groups have reached a low value. This occurs slightly before the maximum spin concentration as measured by ESR (6,7).B material is quite different from A : OH groups are more numerous in B and their number decreases very slowly during heat-treatment. Aliphatic CH groups are less numerous and their number decreases faster while aromatic CH are both much less numerous and more stable when heat-treated. New groups C-O-C not present in A material occur in B and remain remarkably stable for a HTT as high as 600°C. Reticulation of A material or even heat-treatment of A in an open crucible changes the amount of various groups so as to increase OH groups and to decrease aliphatic CH groups and aromatic CH groups.

Chars issued from A or B materials may be considered as built-up of a few aromatic rings molecules (4-10 rings) piled up by 2 or 3. They are connected by non aromatic structures. If the latter are mainly aliphatic tar yield is large. First melting then occurence of a local molecular orientation are favoured. They are also favoured by all the factors which lead to tar retention. Molecular orientation occurs after melting when the rate of tar departure is maximum producing a maximum of mobility of the aromatic molecule stacks. Molecular orientation is reduced or inhibited when oxygen content increases and when tar percentage decreases which corresponds to a linkage between stacks of aromatic molecules. This can be related to the C-O-C groups which appear in B material. Finally reticulation mechanism should be first related to a combination of oxygen and aliphatic carbon groups (8) which produce water and is responsible for OH increase and aliphatic CH decrease in IR spectra. Then melting and consequently molecular orientation should be inhibited by linkage due to C-O-C bonding developing in A material after reticulation.

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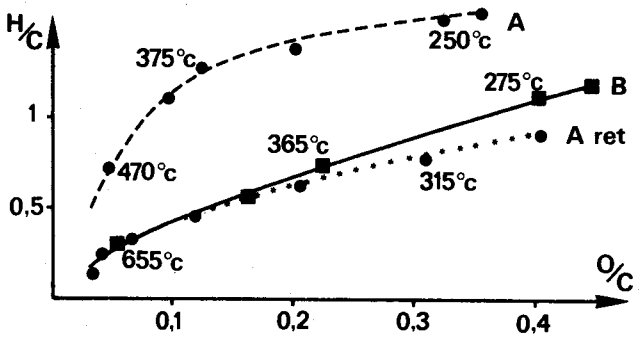

Figure 1

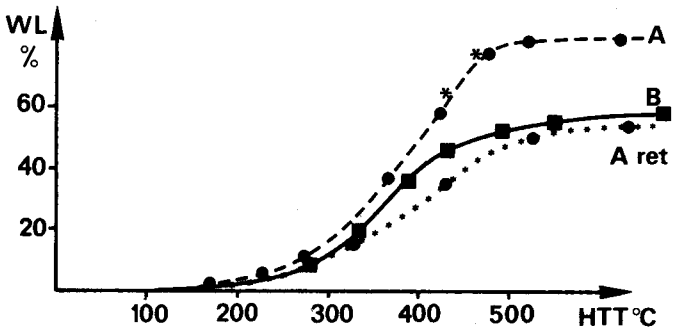

Figure 2

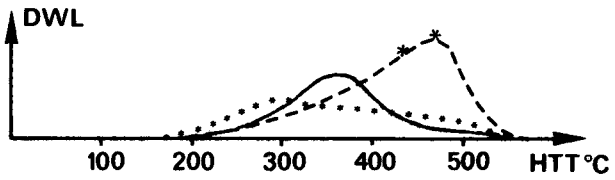

Figure 3

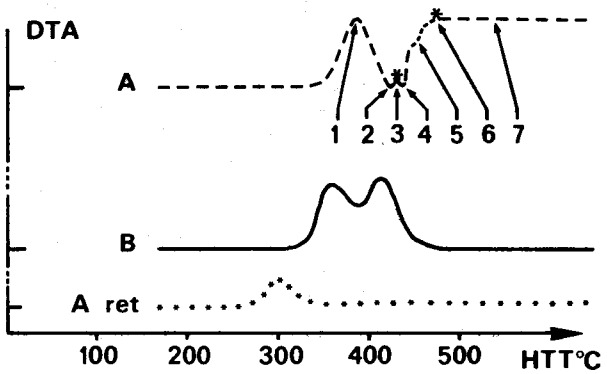

Figure 4

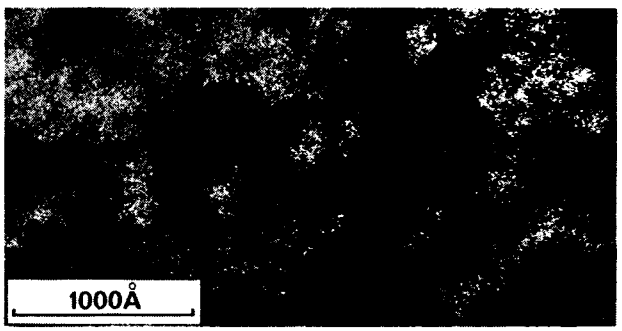

Figure 5