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# Oxidation with Simon's reagent and $HNO_3/H_2SO_4$ of turbostratic graphitic carbon prepared catalytically by nickel particles (20nm) in a carbonized resin

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Four carbons, of heat treatment temperature 2800° C, were prepared from pure phenol formaldehyde resin (A-component), from this resin doped with nickel acetylacetonate ($T_s$-component), from a coal-tar pitch ($T_p$-component) and from the resin containing 30wt% nickel particles (50 $\mu$m) (G-component). These carbons are characterized by X-ray diffraction ($d_{002}$ and $L_c$), high-resolution phase-contrast electron microscopy, Raman spectroscopy and oxidation with Simon's reagent and mixed acid $HNO_3/H_2SO_4$. The X-ray diffraction patterns show that graphitization increased $A < T_s \leqslant T_p < G$. The Raman spectra, using the ratio $R = I\,(1355\,\text{cm}^{-1})/I(1575\,\text{cm}^{-1})$ indicate that the $T_s$-component has the least number of imperfections in the lattice. The $T_s$- and G-components react faster than other carbons in Simon's reagent but react slower in mixed acids. These faster rates are associated with lower activation energies. The Simon's reagent reacts preferentially with the more graphitic structures of the G-component unlike the $T_s$-component which appears to be structurally homogeneous. Rates of oxidation with mixed acid increase $G < T_p < T_s < A$.

## 1. Introduction

Metals are known to graphitize, catalytically, both isotropic and anisotropic carbons at elevated temperatures [1, 2]. Recently, the catalytic formation of a turbostratic graphitic carbon ($T_s$-component) was observed after heating a non-graphitizing carbon containing finely divided metals (Ni, Fe, Si, Al) [3–13]. The fine state of subdivision, about 20 nm particle size, was achieved by carbonizing a thermosetting resin which had been mixed homogeneously with an appropriate organometallic compound [12].

This $T_s$-component, as characterized by X-ray diffraction, has a *d*-spacing ($d_{002}$) of 0.340 to 0.344 nm and a crystallite height, $L_c$, of 8 to 16 nm, the variations occurring when different metals are used. The structure of this $T_s$-component remains almost unchanged on heating to 3000° C under atmospheric pressure [8, 14] or on heating to 2000° C under a pressure of 0.5 GPa [15]. The structure and mechanism of formation of this $T_s$-component have been studied previously using X-ray diffraction with optical and transmission electron microscopy [16]. The study of structure in the $T_s$-component is extended here to include oxidation behaviour in liquid oxidants [17, 18], Raman spectroscopy [19–22] and phase-contrast electron microscopy [23–28].

Raman spectra are correlated with structure within these carbons as determined by X-ray diffraction as well as phase-contrast high-resolution electron microscopy to produce fringe images of

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the constituent lamellae within the carbons [23–28]. Graphite gives a single Raman line at 1575 to 1580 $\text{cm}^{-1}$. Non-graphitized carbons give two Raman lines at 1575 to 1580 $\text{cm}^{-1}$ and at 1355 $\text{cm}^{-1}$. It is thought that the latter line is associated with a turbostratic carbon lattice [19]. Nakamizo and co-workers [20–22] indicate that the intensity ratio, $R = I(1355\ \text{cm}^{-1})/I(1575\ \text{cm}^{-1})$, is a measure of the extent of imperfection of order within the carbon, increasing with increased imperfection.

## 2. Experimental details

### 2.1. Carbon preparation

Non-graphitized carbon (A-component) was prepared from a phenolic resin (phenol formaldehyde, PF) [10], cured at 80° C for 1 day, by carbonization to 800° C and then to 2800° C, with a soak time of 1 h at each temperature. The turbostratic graphitic carbon ($T_s$-component) was prepared as follows [29, 12]. A solution of $Ni(CH_2COCH_2COCH_3)_2$ (Ni.AA) in a chloroform–ethanol mixture was added to the non-cured resin. After removal of solvent the doped resin was cured at 80° C for 1 day and then carbonized to 800° C, and 2800° C. The amount of Ni.AA added was such as to give 1 wt% nickel in the carbon of heat treatment temperature (HTT) 800° C.

A weakly graphitizing carbon ($T_p$-component) was prepared from a coal-tar pitch by bubbling through it an air/chlorine mixture at 500° C followed by carbonization to 800° C and 2800° C.

A graphitic carbon (G-component) was prepared by carbonizing a doped PF resin containing 30 wt% nickel particles (size about 50 $\mu$m) to 800° C and then to 2800° C.

### 2.2. Structural analyses

Raman spectroscopy was undertaken by the method of Nakamizo *et al.* [20]. The phase-contrast high-resolution transmission electron microscopy of powdered carbons was undertaken according to Tomizuka and Watanabe [28]. For each of the above four carbons, X-ray diffraction studies [8] measured interlayer spacing, $d_{002}$/nm, and apparent crystallite size, $L_c$/nm, from the diffraction angle and broadening of the (0 0 2) diffraction profile, respectively.

### 2.3. Carbon oxidation

The carbons described above were reacted with Simon's reagent which is reported to react preferentially with the more graphitic of the components within the carbon [17]. The mixed acid $HNO_3/H_2SO_4$, conversely, reacts predominantly with the less graphitic of the components within the carbon [30].

Simon's reagent was prepared as a solution of 5 g silver dichromate in 25 $\text{cm}^3$ concentrated sulphuric acid. The oxidation was carried out in the apparatus shown in Fig. 1. 15 mg carbon, (150 to 250 $\mu$m) was mixed with 7.5 $\text{cm}^3$ reagent at the following temperatures of boiling liquids: ethanol 78° C; isopropyl acetate 89° C; water 100° C; toluene 111° C. The carbon dioxide evolved was measured in a gas burette after passing it over heated reduced copper to remove traces of oxygen.

In the oxidation with mixed acids, 300 mg carbon (250 to 550 $\mu$m) was added to 30 $\text{cm}^3$ $HNO_3/H_2SO_4$ (5:1 volume ratio) and heated in the temperature range 90 to 120° C. Extents of oxidation were monitored as losses in weight from the carbon.

## 3. Results and discussion

### 3.1. Structural analyses

The X-ray parameters and Raman intensity ratios, $R$, for carbons, HTT 2800° C, of A-, $T_s$-, $T_p$- and G-components are given in Table I. The interlayer spacings and crystallite heights indicate that the components increase in extent of graphitization in the order $A < T_s \leqslant T_p < G$. The values of $R$ in Table I show two unusual features. The lowest value of $R$ is for the $T_s$-component which according to $d_{002}$ and $L_c$ values is certainly not a graphitic carbon. The G-component has a $d_{002}$ value approaching that of graphite and has a large value of $L_c$. Yet the reported value of $R$ is higher than that for the $T_s$- and $T_p$-components

Atomic spectral analysis indicates that these four carbons contain < 100 ppm nickel.

Fig. 2a to e are micrographs of fringe images of structure within the four carbons of Table I. The structure of the A-component (Fig. 2a) is of small crystallites (3 to 4 nm thick) forming a three-dimensional network [31, 32] possibly of hollow shells such that the cross-sections of Fig. 2a indicate ribbon-like crystallites.

Fig. 2a and b of the $T_s$-component show that the nickel from Ni.AA has changed the structure to be more ordered than that in the A-component. The crystallites are larger (10 to 15 nm thick) and

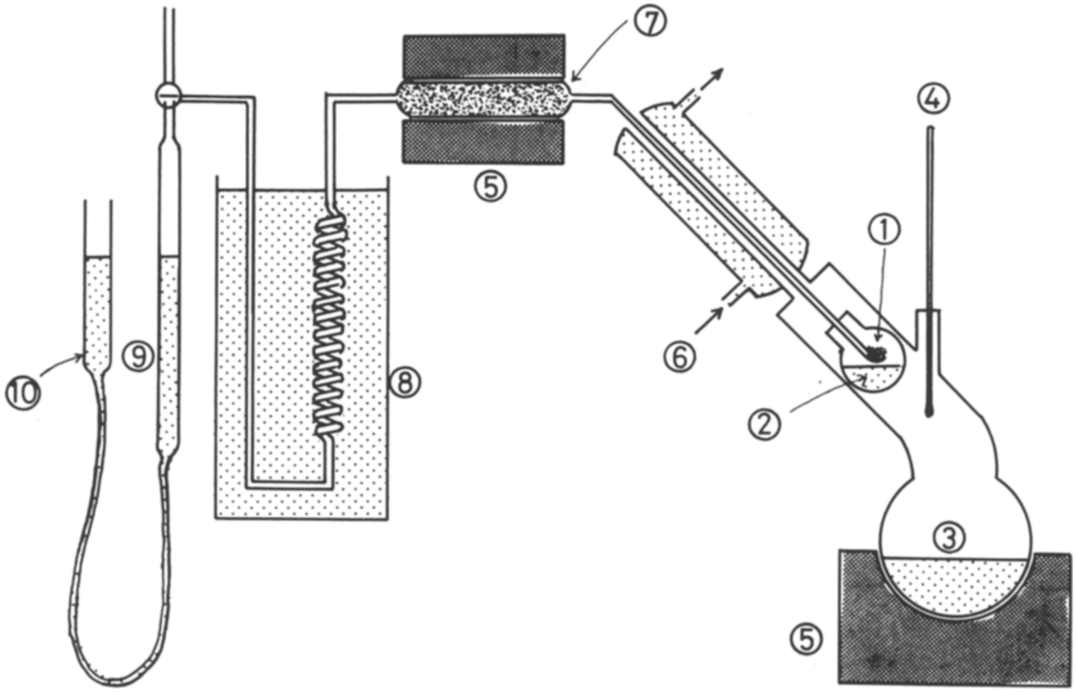

*Figure 1* Apparatus for oxidation using Simon's reagent. (1) Carbon sample, (2) Simon's reagent, (3) solvent, (4) thermometer, (5) electrical furnace, (6) water, (7) reduced copper, (8) thermostat, (9) gas burette, (10) water saturated with NaCl.

more obvious. The sphere structure of Oberlin [32] may not have survived the action of the finely divided nickel, and randomly orientated crystallites may have resulted. The catalytic action of the nickel in the $T_s$-component has produced crystallites similar in size to those found in the carbon (2800°C) from pure pitch, $T_p$-component (Fig. 2d).

The low-magnification micrographs of the G-component show Moiré patterns of a three-dimensional graphite crystallite and a "spotted" diffraction profile.

## 3.2. Carbon oxidation

Fig. 3 shows the variation of volume of gas evolved with reaction time, using Simon's reagent at 89° C for the four carbons. Oxidation rates are relatively high for the $T_s$- and G-components, but relatively low for the A- and $T_p$-components.

TABLE I X-ray parameters and $R$-values of the 2800° C-carbons

| Carbon sample | Interlayer spacing, $d_{002}$ (nm) | Crystallite height, $L_c$ (nm) | $R$-value |
|---|---|---|---|
| A | 0.343 | 3.6 | 1.40 |
| $T_s$ | 0.3415 | 12.0 | 0.23 |
| $T_p$ | 0.3422 | 12.5 | 0.51 |
| G | 0.3356 | > 100 | 0.90–1.05 |

The rates of these reactions increased with increasing temperatures of reaction. The variations of $\log K$ ($K$ = reaction rate, i.e. linear initial portions of Fig. 3) with $T^{-1}/K^{-1}$ are shown in Fig. 4. Activation energies from Fig. 4 are given in Table II, for oxidations with Simon's reagent and with mixed acids. For the Simon's reagent, the relatively fast oxidations of $T_s$- and G-components are associated with low activation energies (23 and 34 kJ mol$^{-1}$, respectively). However, for the mixed acid, rates of oxidation decrease with extent of graphitization $A < T_s < T_p < G$ (Fig. 5). The Arrhenius plot of this reaction is shown in Fig. 6, and the activation energies are given in Table II showing that the oxidation of $T_s$- and G-components is associated with relatively high activation energies (40 and 41 kJ mol$^{-1}$, respectively).

X-ray diffractions were obtained of the G- and $T_s$-components after oxidation with Simon's reagent (Fig. 7). For the G-component the diffraction angle shifted to a lower value (increase in $d_{002}$) and became considerably broader (decrease in $L_c$), as in Fig. 7a and b. However, no significant change could be detected in the diffraction profiles

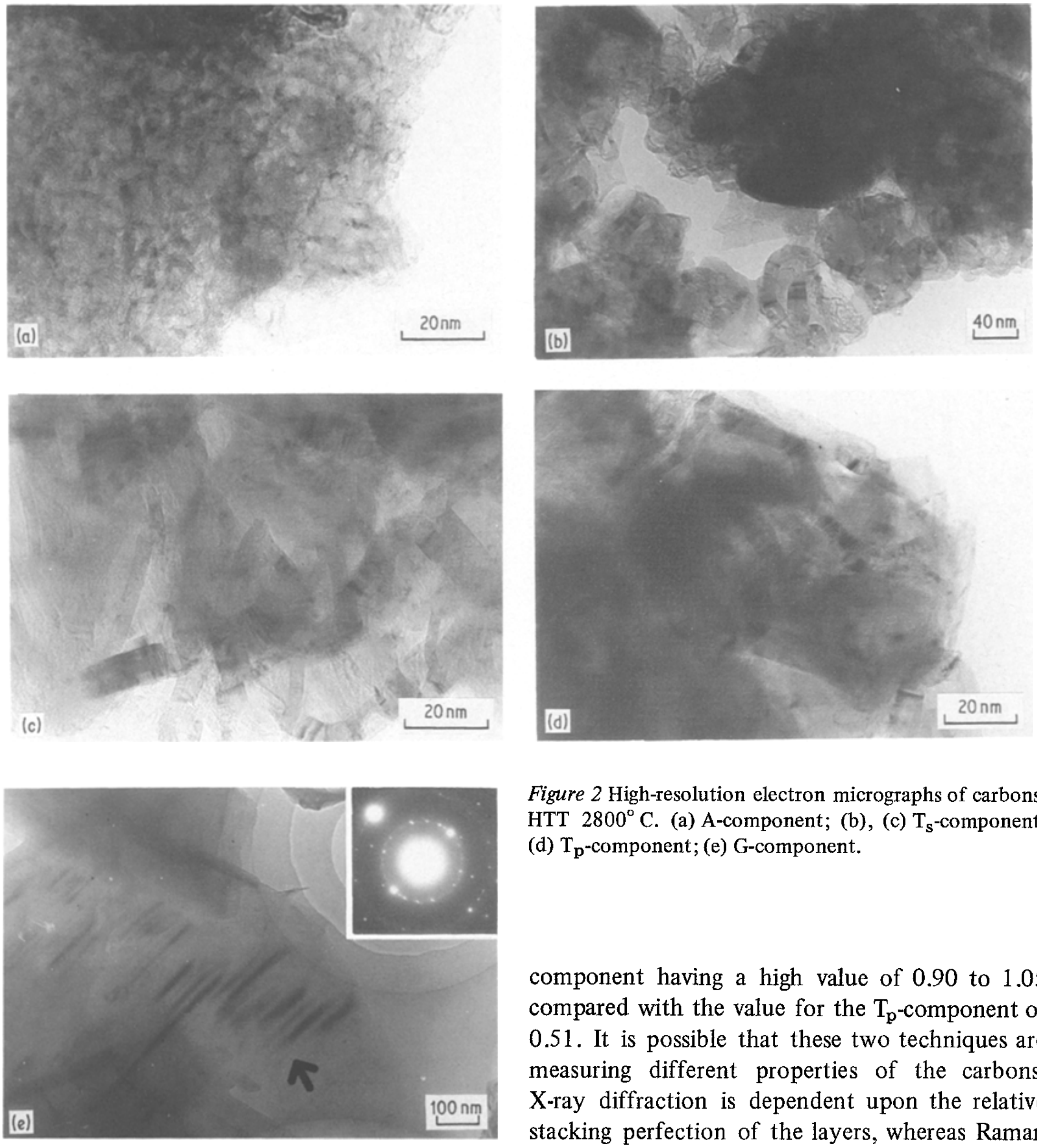

*Figure 2* High-resolution electron micrographs of carbons, HTT 2800° C. (a) A-component; (b), (c) $T_s$-component; (d) $T_p$-component; (e) G-component.

of the $T_s$-component even after 40% weight loss (Fig. 7c to e).

## 4. Conclusions

X-ray diffraction and electron microscopy studies of the four carbons indicate that the A-component is the least graphitic, the G-component is the most graphitic with the $T_s$- and $T_p$-components being intermediate and showing close similarities. The Raman spectra, however, although also indicating that the A-component is the least graphitic, suggest that the $T_s$-component with the lowest value of $R$ of 0.23 contains least imperfections, with the G-component having a high value of 0.90 to 1.05 compared with the value for the $T_p$-component of 0.51. It is possible that these two techniques are measuring different properties of the carbons. X-ray diffraction is dependent upon the relative stacking perfection of the layers, whereas Raman spectroscopy is dependent upon the perfection of atomic arrangement within the layers. This suggests that the finely divided nickel responsible for the $T_s$-component produces graphitic layers which are more perfect than those in the G-component which is based on larger sized particles of nickel.

TABLE II Activation energies of oxidation reactions

| Carbon sample | Simon's reagent (kJ mol$^{-1}$) | $HNO_3/H_2SO_4$ (kJ mol$^{-1}$) |
|---|---|---|
| A | 84 | 26 |
| $T_s$ | 23 | 40 |
| $T_p$ | 87 | 35 |
| G | 34 | 41 |

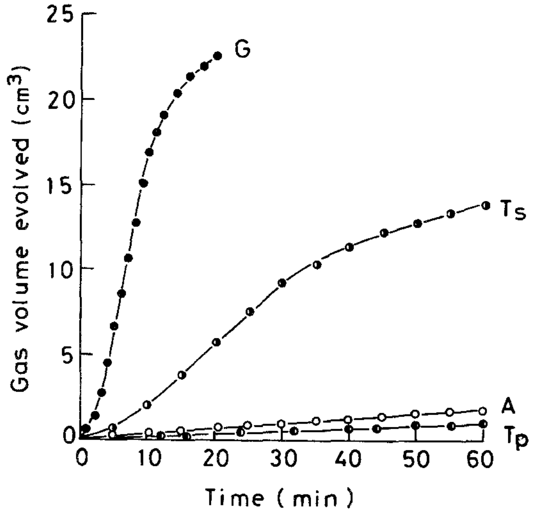

*Figure 3* Evolved gas volume plotted against reaction time for oxidation of carbons using Simon's reagent at 89°C.

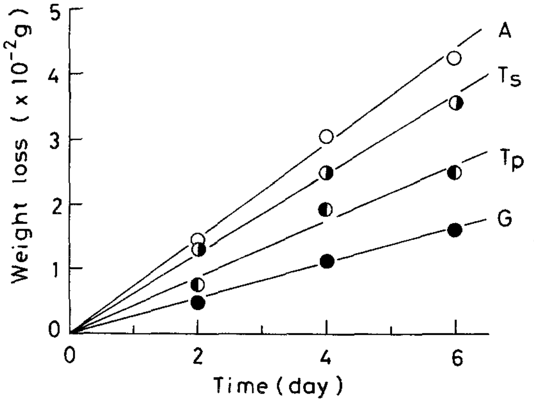

*Figure 5* Weight loss plotted against reaction time for oxidation of carbons using $HNO_3/H_2SO_4$ mixed acid at 110°C.

As predicted, Simon's reagent reacts relatively faster with the more graphitic carbons (based on X-ray analysis) with the mixed acids reacting relatively faster with the less graphitic of the carbons. The faster rates have also the lowest activation energies. The Simon's reagent reacts probably by a process of formation of intercalation compounds [6], with the mixed acids oxidizing surfaces without forming intercalation compounds. The activation energies reflect, respectively, the ease of formation of intercalation compounds and ease of oxidation of carbons of different degrees of graphitizability. Marsh and Taylor [33] similarly have found an increase in the activation energies of the reactions of oxygen and carbon dioxide with carbons of increasing degrees of graphitization.

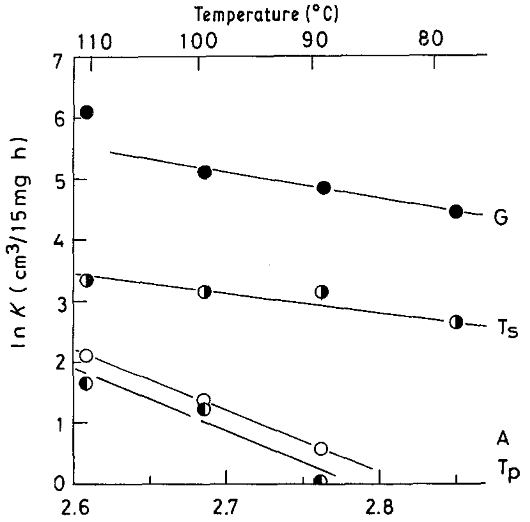

*Figure 4* Arrhenius plots for oxidation of carbons using Simon's reagent.

The X-ray diffraction studies of the oxidized $T_S$-component indicate that the Simon's reagent is not reacting preferentially with one structural component at the expense of other components. It would appear that the $T_S$-component is structurally homogeneous. However, for the G-component, the resultant line-broadening following oxidation suggests that selective removal of more ordered structures is occurring and possibly that residues of incomplete oxidation of these less-ordered structures contribute to line-broadening. Either selective removal of more ordered structures is ocurring or the oxidation processes creates less ordered structures from the more ordered crystallites.

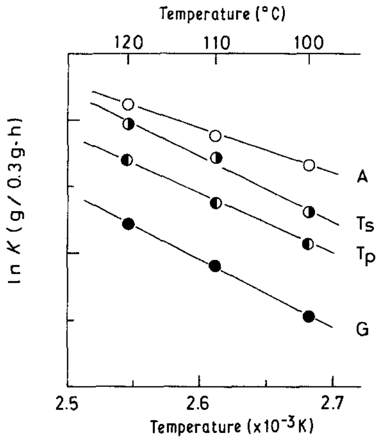

*Figure 6* Arrhenius plot for oxidation of carbons using $HNO_3/H_2SO_4$ mixed acid.

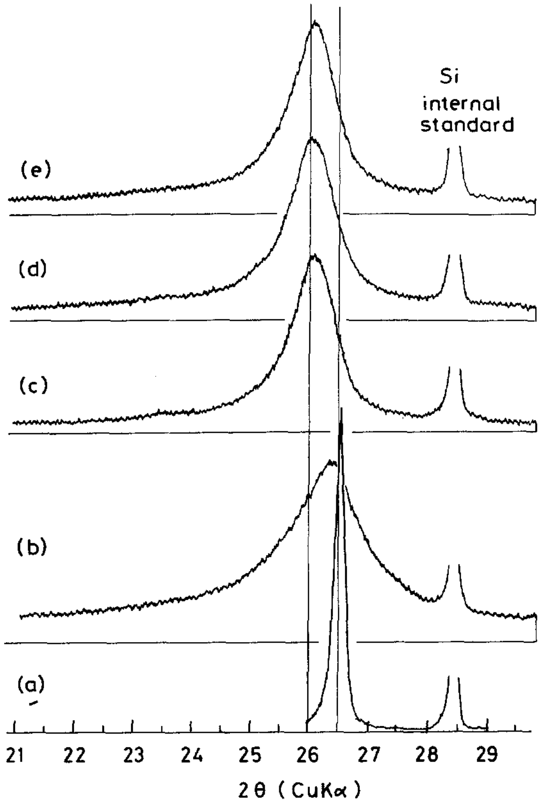

*Figure 7* Changes of (0 0 2) diffraction profiles following oxidation with Simon's reagent. G-component: no reaction (a), after 25% weight loss (b); $T_S$-component: no reaction (c), after 15% weight loss (d), after 40% weight loss (e).

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