

## Catalysis and Inhibition of the Carbon-Sulfur Reaction

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A reação de vapores de enxofre com carvão vegetal, coque e grafite puro foi estudada a 850-900 °C. A velocidade inicial de formação de sulfeto de carbono diminui na ordem carvão vegetal > coque > grafite, mas a reação é inibida e a conversão final de carbono diminui na mesma ordem. Os espectros XPS das amostras inibidas indicaram que o enxofre forma complexos superficiais, aparecendo como sulfeto orgânico. A comparação da conversão de carbono em CS<sub>2</sub> e o aumento da fração molar de enxofre mostraram que para grafite a formação de CS<sub>2</sub> é desprezível comparada à reação de complexação de enxofre. Para carvão vegetal a reação principal é a rápida conversão de carbono, enquanto a incorporação de enxofre é lenta. A espécie ativa do enxofre é provavelmente S<sub>2</sub> e propõe-se que este seja inserido na matriz do carbono de duas formas diferentes. Uma produz um complexo instável que se decompõe em CS<sub>2</sub>, e a outra produz um complexo estável, como sulfeto orgânico. O efeito de sais impregnados no coque, carvão vegetal e grafite é uma relação complexa entre o efeito do cátion, do ânion e do carbono. Titânio e níquel, provavelmente na forma de sulfetos, tem efeito catalítico muito pequeno. A ordem de atividade catalítica dos óxidos é Li < K < Na < Ca < Cs. A posição do cálcio depende de sua concentração na superfície. A atividade catalítica aumenta com a instabilidade dos correspondentes sulfetos e com a capacidade do cátion formar polissulfetos.

The reaction of sulfur vapour with coconut charcoal, coke and pure graphite was studied at 850-900 °C. The initial rate of formation of CS<sub>2</sub> decreases in the order charcoal > coke > graphite, but the reaction is inhibited and the final carbon conversion decreases in the same order. The XPS spectra of the inhibited samples indicated that the sulfur form surface complexes as organic sulfides. Comparison of the carbon conversion into CS<sub>2</sub> and the increase of molar fraction of sulfur in the carbon showed that for graphite the formation of CS<sub>2</sub> is negligible as compared to the sulfur complexing reaction. For charcoal the main reaction is the fast carbon conversion, while sulfur incorporation is a slow reaction. The active species of sulfur is likely to be S<sub>2</sub> and it is proposed that there are two types of insertions in the carbon matrix. One produces an unstable complex that decomposes into CS<sub>2</sub> and the other produces a stable complex as organic sulfide. The effect of salts impregnated in coke, charcoal and graphite is a complex relationship among cation, anion and carbon. Titanium and nickel, probably in the form of sulfides, have a very small catalytic effect. The order of catalytic activity of oxides is Li < K < Na < Ca < Cs. The position of calcium depends on the surface concentration. The catalytic activity increases with the instability of the corresponding sulfides and the capacity of the cation to form polysulfides.

**Keywords:** *carbon disulfide, catalysis, carbon-sulfur complexes*

### Introduction

The study of the reaction of carbon and sulfur has attracted the attention of many researchers because of its

similitude to the oxidation reaction C-O<sub>2</sub>, and lately because it is involved in the reduction of sulfur dioxide by carbon. This is an important reaction since it might be an alternative to flue gas desulfurization.

The C-S<sub>x</sub> reaction produces only carbon disulfide, but occurs parallel to the formation of sulfur surface complexes<sup>1,2</sup> and depends on the carbon forms<sup>3-10</sup>.

No important progress has been achieved in the understanding of the nature of the reaction of different forms of carbon and sulfur. In this work we compared the reactivity of a subbituminous coke with coconut charcoal, that contains carbon mainly in the amorphous form, and pure graphite. We observed the kinetics of carbon disulfide formation and sulfur incorporation into the carbon structure, and the concomitant total inhibition of the reaction before total carbon conversion. Finally, we also studied the effect of the addition of salts on the formation of CS<sub>2</sub>.

## Experimental Details

### Carbon sources

The cokes were obtained from subbituminous coal at 1300 °C at "Carbonífera Criciúma" (Santa Catarina, Brazil) and had an ash content of 7.91% (CF-8) and 16.72% (CF-17). The specific surface of the CF-17 sample was 3.19 m<sup>2</sup>/g. This kind of coke is mainly graphitic<sup>11</sup>.

Charcoal from coconut shells was prepared by pyrolysis in an oven, heating at 300 °C, 500 °C and 1000 °C, for 2 hours at each temperature<sup>12</sup>. The charcoal had an ash content of 1.38% and the specific surface was 204 m<sup>2</sup>/g.

The 99.98% pure graphite was from Nacional de Grafite, and had a specific surface area of 21.94 m<sup>2</sup>/g.

The selected particle size for all carbons was - 28/+ 35 # Tyler (0.503 mm average diameter) except when otherwise indicated.

All reagents were of analytic quality.

### Methods

Specific surface was measured at room temperature using CO<sub>2</sub> and the Dubinin-Polanyi<sup>13</sup> equation.

Table 1. Analysis of cokes<sup>a</sup>.

Sample	CF-8	CF-17
Ash (%)	7.91	16.72
Volatiles (%)	1.90	1.50
Fix Carbon (%)	90.19	81.78
Humidity (%)	1.18	1.16
Total sulfur (%)	0.88	1.17
S	(4.90)	(5.23)
Fe	(26.95)	(11.77)
Si	(41.31)	(40.73)
Al	(12.27)	(19.22)
K	(6.62)	(9.05)
Ca	(-)	(1.35)
Ti	(7.94)	(12.65)

<sup>a</sup>Values in parenthesis are expressed in percent and were determined by X-ray scanning microscopy.

Analysis of cokes was performed by conventional methods, and the composition of ash was determined by an EG & ORTEC X-ray microscope (Table 1).

The chemical form of sulfur in inhibited carbons was determined by XPS in an ESCA 36 McPherson spectrometer, using an aluminium anode (AlK $\alpha$  = 1486.6 eV) and at a typical operating pressure of 4 x 10<sup>-7</sup> Torr.

Doped carbons were prepared by impregnation. To 6 g of carbon was added 200 mL of the salt aqueous solution, the water was evaporated in a rotatory evaporator at 60 °C, and the sample was dried at 100 °C. The amount of salt incorporated was calculated from the residue of salt left in the flask. Analysis of the particles by atomic absorption spectrometry gave essentially the same results.

Titanium oxalate was prepared from the reaction of the chloride salt and oxalic acid<sup>14</sup>.

### Reaction system

Figure 1 shows a scheme of the experimental system. Vapor from boiling sulfur was diluted in a stream of pure nitrogen and was passed through a quartz microreactor containing the sample of carbon, heated by an electric furnace. The temperature was kept constant by an automatic temperature controller. Two traps were connected to the outlet of the reactor, that were kept at 150 °C in order to collect the excess of sulfur. The reaction products were sent through stainless steel tubing to a gas chromatograph for analysis. Alternatively, carbon disulfide was condensed in a third graduated trap at 0 °C to measure the collected

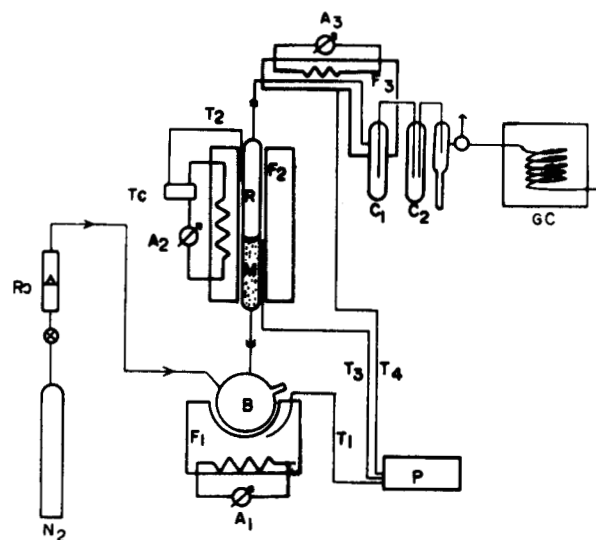


Figure 1. Reaction system; Ro, rotameter; A<sup>1</sup>, A<sup>2</sup>, A<sup>3</sup>, autotransformers; T<sup>1</sup> - T<sup>4</sup>, termocouples; P, multichannel pyrometer; R, reactor; M, mixing zone; B, sulfur boiler; F<sub>1</sub>, heating mantle; F<sub>2</sub>, furnace; F<sub>3</sub>, heater; TC, temperature controller; C<sub>1</sub>, C<sub>2</sub>, sulfur traps; C<sub>3</sub>, CS<sub>2</sub> trap; GC, gas chromatograph.

volume. Gas chromatography analysis was carried out using a Poropak-Q column.

The experiments were carried out by placing 5 g of carbon in the reactor and 200 g of sulfur powder in the flask. The flow of nitrogen was adjusted to 1.25 Nl/h, and the furnace was heated at 760 °C for 3 hours. Then the temperatures of the furnace and the sulfur boiler were raised to the final experimental condition. When the temperature of the sulfur boiler was kept at 600 °C, so as to maintain a proper flow of sulfur through the reactor, the flow of sulfur was 1.42 g/min, with the reactor behaving as a differential reactor.

### Kinetics

The initial rate of the reaction can be expressed by Eq. 1, where  $M_c^0$  is the initial mass of carbon,  $C_{CS_2}$  are the moles of carbon disulfide produced,  $P_s$ , the

$$\frac{1}{M_c^0} \left( \frac{dC_{CS_2}}{dt} \right) = k_s P_s^n \quad (1)$$

partial pressure of sulfur in the flow,  $k_s$ , the specific rate constant per unit mass of carbon, and  $n$ , the order of reaction with respect to sulfur. If  $P_s$  is kept constant the reaction will be zero order, and can be calculated from a linear plot of the amount of  $CS_2$  produced versus time. A typical plot of the reaction can be observed in Fig. 2.

### Results and Discussion

The reaction of the formation of carbon disulfide can be represented by Eq. 2, where  $y$  represents different carbon sources and  $S_x$  the active sulfur species.

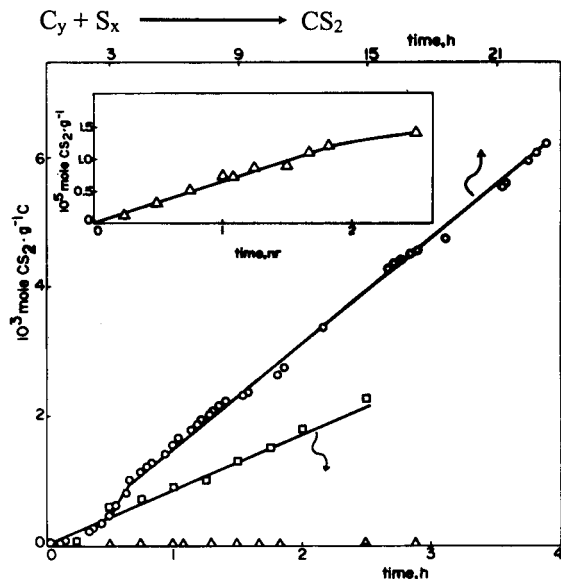
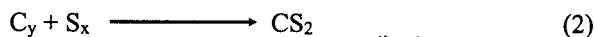


Figure 2. Typical plots of initial rate of formation of  $CS_2$  from different carbons;  $\square$ , coke CF-17, particle size - 28/+ 35 mesh Tyler, boiler at 600 °C, reactor at 850 °C;  $\circ$ , charcoal, particle size - 16/+ 35 mesh Tyler, boiler at 500 °C, reactor at 900 °C;  $\Delta$ , graphite, particle size - 28/+ 35 mesh Tyler, boiler at 500 °C, reactor at 900 °C.

At high temperature (850-900 °C) more than 98% of the sulfur is in the diatomic form<sup>15</sup>. It has been shown that  $S_2$  is a powerful nucleophile that adds readily to the carbon-carbon double bond<sup>16,17</sup>, but at high temperature it is possible that activated elemental sulfur might also be the reactive species.

### Inhibition of the $C + S_x$ reaction

The reaction of sulfur vapor with carbon for an extended period of time shows complete inhibition of the formation of carbon disulfide with no carbon conversion. The final conversion decreases in the order charcoal > coke > graphite (Fig. 3), in the same order of reactivity measured by the initial rate. Also, the reactivity and final conversion of coke increases with ash content. The influence of ash content on the reactivity of carbons has been noted for such reactions as gasification<sup>18-21</sup> and sulfur dioxide reduction<sup>22,23</sup>.

The sulfur content in the coke CF-17 increased from 1.17 to 5.22% in the inhibited coke, and the final conversion was 11.4%. The chemical fixation of sulfur on carbon has been observed for active carbons<sup>4</sup>, coals<sup>5</sup>, carbon blacks<sup>6,7</sup> and charcoal<sup>8</sup>, and during the reaction with sulfur dioxide<sup>9,10</sup>.

Table 2 shows the XPS spectra of graphite, charcoal and coke, after the reaction with sulfur. The XPS  $C_{1s}$  region presented only one peak at 284.6 eV, that in the case of graphite also showed a satellite peak, characteristic of the crystalline component. In the region of  $S_{2p}$ , the graphite showed one peak at 164.2 eV that was assigned as organic sulfur in the form of sulfide ( $S^{2-}$ )<sup>24-26</sup>. Some disulfides also have a similar binding energy, but a disulfide insertion should be unstable at high temperatures because the S-S

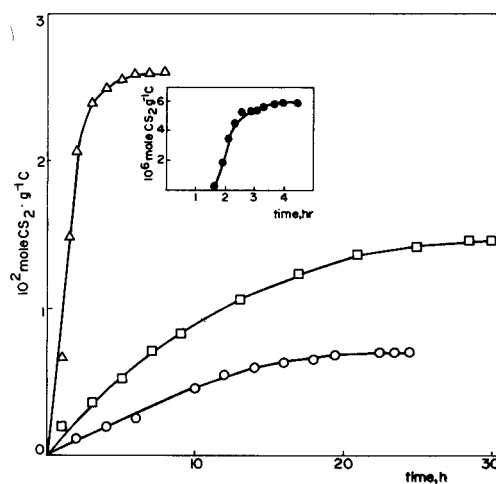


Figure 3. Inhibition of the reaction of formation of  $CS_2$  from different carbons at 850 °C, boiler at 600 °C;  $\Delta$ , charcoal;  $\square$ , coke CF-17;  $\circ$ , CF-8;  $\bullet$ , graphite.

**Table 2.** Peak positions of XPS spectra of different carbons after reaction with sulfur and percent surface atomic concentrations<sup>a</sup>.

	C <sub>1s</sub>		O <sub>1s</sub>		S <sub>2p</sub>	
		O <sub>I</sub>	O <sub>II</sub>	SO <sub>4</sub> <sup>2-</sup>	S <sup>2-</sup>	
Graphite <sup>b</sup>	284.6 (1.6)		532.7 (2.8)			164.2 (2.4)
% AC	97.1		2.3			0.6
Charcoal <sup>c</sup>	284.6 (1.7)	534.2 (2.7)	532.6 (2.7)	168.9 (2.7)		164.4 (2.7)
% AC	89.0	2.0	4.9	0.6		3.5
Coke CF-17 <sup>d</sup>	284.4 (2.0)	534.3 (2.5)	532.2 (2.7)	169.4 (2.8)		164.1 (2.8)
% AC	82.4	6.1	9.1	1.2		1.2

<sup>a</sup> Binding energy in eV (0.3 eV). Values in parenthesis are the width at midheight in eV; % AC: percent atomic concentrations; <sup>b</sup> Reaction at 900 °C for 9h; <sup>c</sup> Reaction at 900 °C for 44 h; <sup>d</sup> Reaction at 850 °C for 10 h.

bond would have a 0° torsional orientation which would maximize the S-S lone pair energy interaction<sup>17</sup>.

In the charcoal and coke samples, sulfur presented a doublet, at 169.2 and 164.2 eV, where the higher binding energy was assigned to oxidized sulfur in the form of sulfate (SO<sub>4</sub><sup>2-</sup>)<sup>24,25</sup>. The O<sub>1s</sub> peak is broad and resolved in two (O<sub>I</sub> and O<sub>II</sub>). The ratio O<sub>I</sub>/SO<sub>4</sub><sup>2-</sup> is 3.3 ± 0.6 for charcoal and 4.9 ± 0.9 for coke, the expected value for sulfate, within experimental error. Since there was no oxidized sulfur in the original sample of charcoal, in this sample sulfate might have been formed by air exposure after the reaction. We do not know the way O<sub>II</sub> is bound. The high difference in energy between the two lines of the sulfur doublet is characteristic of the sulfate-sulfide pair<sup>25,27</sup>.

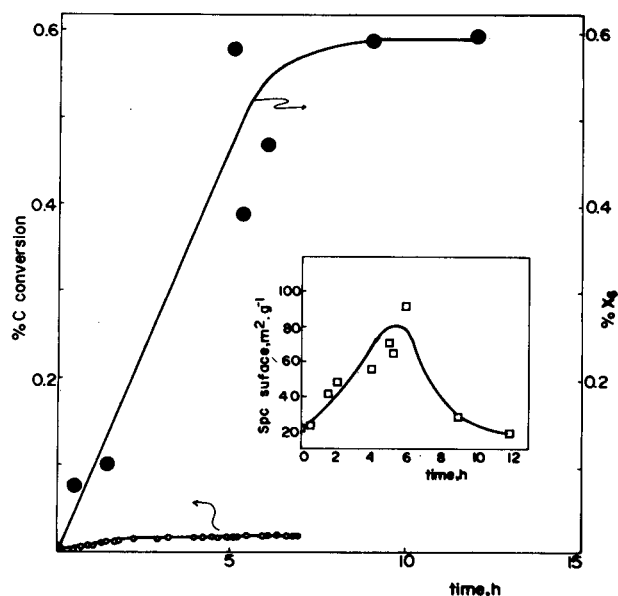
The increase of total sulfur content in the coke, after the reaction with sulfur is due to the increase of sulfur in the surface. The bulk atomic ratio C/S in the original sample was 186.4 which decreased to 37.0 after the reaction. From the surface atomic concentration, the ratio is 34.3, suggesting that in the original sample the sulfur surface concentration was about four times higher than that observed from bulk analysis, as has been found for some coals<sup>24</sup>. For coke the signal at 164.1 eV corresponds to organic and pyritic sulfur.

Therefore there are two types of insertions of the reactive species of sulfur, one producing an unstable intermediate that decomposes into carbon disulfide<sup>2,28</sup>, and other producing stable and unreactive surface sulfide.

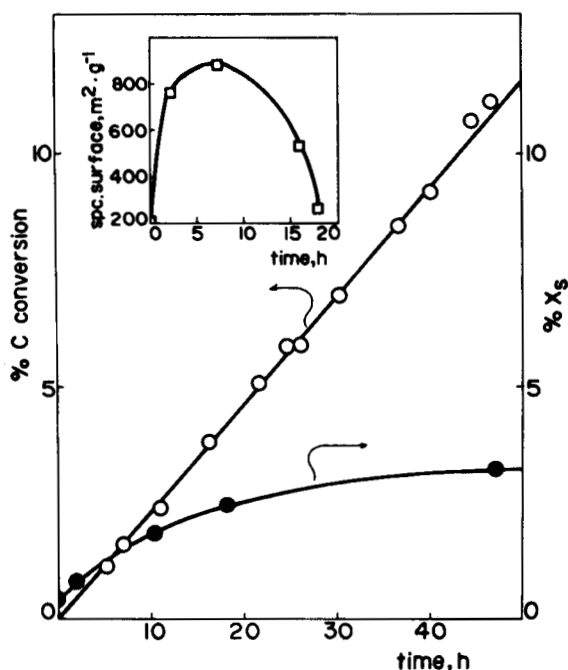
The relation between carbon conversion into CS<sub>2</sub>, change of the specific surface, and the change of molar fraction of the sulfur incorporated into the carbon with time, was studied using pure graphite and charcoal as the carbon source (Figs. 4 and 5). There is no apparent influence of the change of specific surface on the carbon conversion or sulfur incorporation of the two types of carbons, suggesting that the change of specific surface does not change the number of active sites. The concomitant change

of porosity also suggests that the active sites are external to the pores or mainly related to large diameter pores. If diatomic sulfur S<sub>2</sub> is the active species (see below) the large diameter of the sulfur atom might preclude reaching the small diameter pores.

However the behavior of graphite and charcoal with respect to those processes is quite different. Carbon conversion of graphite into CS<sub>2</sub> is negligible as compared to the sulfur complexing reaction (Fig. 4), which shows a saturation curve with a plateau at about 0.6 per cent of sulfur molar fraction. On the other hand, for charcoal the main reaction is the fast carbon conversion, while sulfur incorporation occurs by a slower reaction, that eventually determines the maximum carbon conversion at the inhibi-



**Figure 4.** Reaction of graphite and sulfur at 900 °C, boiler at 500 °C; ○, % carbon conversion; ●, molar fraction of sulfur in carbon; □, surface area.



**Figure 5.** Reaction of charcoal and sulfur, at 900 °C, boiler at 500 °C; ○, % carbon conversion; ●, % molar fraction of sulfur in carbon; □, surface area.

tion point. These results support the mechanism where sulfur insertion occurs in two different forms. The fact that the formation of CS<sub>2</sub> from charcoal is reversible<sup>2</sup> suggests that those insertions occur in two different active sites.

#### Catalysis by salts

The effect of salts impregnated in coke CF-17 was studied at 850 °C, setting the sulfur boiler at 600 °C with increasing concentrations of salts of alkaline metals and some metals of the first long period (Table 3). The samples were submitted to a pretreatment at 760 °C for 3 hours under nitrogen. Under these conditions titanium oxalate and nickel nitrate decompose to the oxides<sup>29</sup> and react with sulfur forming the corresponding sulfides. The tendency of sulfur to adsorb chemically in transition metal oxides<sup>30-33</sup> is well known. The catalytic effect of these sulfides is very small.

Calcium nitrate shows a stronger catalytic effect than others alkaline salts, as can be observed in Fig. 6. The catalytic effect of the salts studied shows a complex relationship among cation, anion and carbon. LiNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> inhibit the reaction, KNO<sub>3</sub> has a small catalytic effect, and NaNO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> catalyze the reaction. A simple mechanical mixture of coke and K<sub>2</sub>CO<sub>3</sub> did not change the rate of the reaction. For carbonates, the order of the catalytic effect is Na < K << Cs. The decomposition temperatures of sodium and potassium carbonates are 1000 and 950 °C respectively<sup>34</sup>, and did not decompose into oxides during the pretreatment at 760 °C, although in the presence of carbon the temperature of decomposition is

**Table 3.** Effect of salt impregnation of coke CF-17 on the rate of carbon disulfide formation<sup>a</sup>.

Salt	10 <sup>3</sup> at.g cation/g coke	10 <sup>4</sup> k <sub>obs</sub> , mole.h <sup>-1</sup> /g coke
None	—	8.80 <sup>b</sup>
LiNO <sub>3</sub>	9.78	3.88
	17.00	0.84
NaNO <sub>3</sub>	1.69	3.90
	1.69	13.20
Na <sub>2</sub> CO <sub>3</sub>	5.69	18.20
	0.80	6.99
KNO <sub>3</sub>	2.97	2.65
	3.19	1.16
	0.68	8.85
K <sub>2</sub> CO <sub>3</sub>	1.19	9.22
	2.66	10.16
	0.52	14.87
Cs <sub>2</sub> CO <sub>3</sub>	0.95	16.90
	2.13	21.12
	2.66	21.62
Ca(NO <sub>3</sub> ) <sub>2</sub>	5.32	8.78 <sup>c</sup>
	0.37	14.46
	0.79	31.40
Ti(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub>	1.25	38.28
	1.08	10.17
Ni(NO <sub>3</sub> ) <sub>2</sub>	2.54	13.18
	3.93	26.78
	6.58	30.58
	1.56	8.37
	2.63	8.88
	0.81	10.97
	1.92	12.19

<sup>a</sup>At 850 °C, boiler at 600 °C, pretreatment at 760 °C for 3h under nitrogen; <sup>b</sup> Average of three runs; <sup>c</sup> Mechanical mixture.

lower than the thermodynamic dissociation<sup>35-37</sup>. Cesium carbonate and all the nitrates studied decompose into the oxides at temperatures lower than 760 °C. The order of catalytic activity is Li < K < Na < Ca < Cs. The position of calcium depends on the superficial concentration of the cation (Fig. 6). The inversion of sodium and potassium might be due to rather important differences in the cubic expansion coefficient of the sodium oxide (10<sup>-6</sup> Δv. °C<sup>-1</sup>) compared to potassium oxide (8.5 × 10<sup>-7</sup> Δv °C<sup>-1</sup>). As a consequence a more active catalytic site might be formed when NaNO<sub>3</sub> is added.

At 850 °C, most of the sulfur vapor is in the form of singlet sulfur S<sub>2</sub><sup>38</sup>, which is a powerful nucleophile<sup>16</sup>.

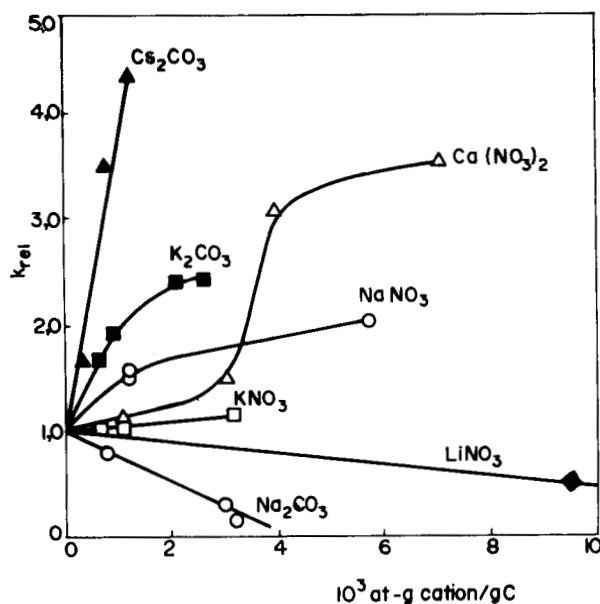
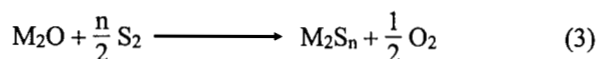


Figure 6. Relative rates of formation of carbon disulfide at 850 °C, from coke CF-17 impregnated with salts. Reference rate in the absence of salt.

Sulfur and oxygen show many similar reactions that differ because of the stabilities of the products. For example, alkaline metal oxides react with sulfur to form sulfides and polysulfides<sup>14</sup>, and similarly metal oxides form peroxides<sup>36,37</sup> (Eq. 3).



The stability of simple alkaline sulfides decreases from lithium to cesium. The ability to form polysulfides increases in the same direction which might be a more active catalytic species. Accordingly, calcium sulfide decomposes before melting, and lithium does not form polysulfides<sup>14b</sup>. The former is an active catalyst while the latter inhibits the reaction.

It is also possible that the catalytic process consists of the reduction of the cation to free metal that would make the sulfide into an intercalate in the carbon structure<sup>39</sup>.

A comparison between charcoal and graphite with respect to the effect of nitrates and sulfides, gives extra insight into the catalysis. Addition of nitrates or sulfides (Na, K, Ca) to charcoal and graphite produces quite different effects (Table 4). The rate constant for the formation of CS<sub>2</sub> from charcoal is about 30 times faster than that from graphite, in the absence of salts. For graphite, addition of these salts inhibits completely the formation of carbon disulfide, except for KNO<sub>3</sub>, where a small increase in the rate constant was detected. The addition of stable sulfides to charcoal such as Na<sub>2</sub>S and K<sub>2</sub>S has no effect on the rate constant, but the addition of the unstable CaS shows an increase. Nitrates of sodium, potassium and calcium decompose during the pre-

treatment, and the oxides react with sulfur in the presence of carbon to form a more reactive active site, because there is a consistent increase in the rate constants as compared to those obtained by directly using the corresponding sulfide. The higher reactivity of the active site generated when the sulfide is formed *in situ* from the oxide might be due to the concomitant loss of a carbon atom as CO<sub>2</sub>.

Catalysis of the C + O<sub>2</sub> reaction can be explained through two mechanisms. The first suggests that during the oxidation the active species facilitates the electron transfer to and from the carbon structure, producing a redistribution of the π bonds, a weakening of the C-C bond and a strengthening of the C-O bond<sup>40,41</sup>. The second mechanism assumes that the catalysis enhances the oxygen transfer from gas phase to carbon surface<sup>42,43</sup>. The transfer would depend on the possibility that different oxidation states could exist<sup>44,45</sup>, especially for those peroxides from strongly electropositive bulky metal ions such as potassium, cesium and calcium. The latter two can easily form superoxides (K<sub>2</sub>O<sub>3</sub>, Cs<sub>2</sub>O<sub>3</sub>)<sup>46</sup>. Considering the similarity between O<sub>2</sub> and S<sub>2</sub>, the activation step of the catalyzed reaction C + S<sub>x</sub> might be the formation of sulfides and polysulfides, because the same metal ions are active catalysts in both reactions. The catalyzed formation of CS<sub>2</sub> would occur through two complementary effects: softening the electronic carbon structure and feeding the active sites with sulfide and/or polysulfides ions.

#### The model system

The carbon forms in coke vary from amorphous to graphite. The degree of graphitization is a result of the carbonization conditions and can change depending on the time, temperature and atmosphere of the reaction<sup>47,48</sup>. The

Table 4. Effect of salt impregnation of charcoal and graphite on the rate of formation of carbon disulfide<sup>a</sup>.

Salt <sup>b</sup>	Charcoal 10 <sup>4</sup> k <sub>obs</sub> <sup>c</sup>	Graphite 10 <sup>6</sup> k <sub>obs</sub> <sup>c</sup>
None	2.08	6.70
NaNO <sub>3</sub>	2.29	NR <sup>d</sup>
Na <sub>2</sub> S	2.10	NR <sup>d</sup>
KNO <sub>3</sub>	2.26	7.59
K <sub>2</sub> S	2.09	NR <sup>d</sup>
Ca(NO <sub>3</sub> ) <sub>2</sub>	2.54	—
CaS	2.31	NR <sup>d</sup>

<sup>a</sup>At 850 °C, boiler at 600 °C; <sup>b</sup>1.19 × 10<sup>-3</sup> at.g cation/gC; <sup>c</sup>mole. h<sup>-1</sup>/g C; <sup>d</sup>no reaction.

calorific value of carbon in coke also shows that it is composed of amorphous carbon and graphite<sup>49</sup>.

It is known that in general graphite is significantly less reactive than amorphous carbon. The kinetics of graphitization are a function of the carbonization conditions and the nature of the coals employed<sup>46</sup>, and consequently the reactivity of cokes varies accordingly.

The above results show clearly that the reactivity of charcoal from coconut, composed mainly of amorphous carbon, is quite different from that of graphite, with respect to the reaction with sulfur. The reactivity of coke can be studied in comparison to a model system of a mixture of amorphous and graphitic carbon.

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