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TPD and XPS studies of O₂, CO₂, and H₂O adsorption on clean polycrystalline graphite

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Abstract

Temperature programmed desorption (TPD) and X-Ray photoelectron spectroscopy (XPS) studies on clean polycrystalline graphite under Ultra High Vacuum conditions are described. The same three strongly bound oxygenated species are formed after O₂, CO₂ and H₂O adsorption. They decompose to give CO at 973, 1093 and 1253 K. Small amounts of CO₂ are also produced after adsorption of these gases, with desorption temperatures at 463, 573, 693, 793 and 793 K. Attempts are made to ascribe these TPD features more precisely. After H₂O adsorption, some H₂ is evolved at *ca.* 1300 K. Hydrocarbons (C₁-C₆) are also produced, but in smaller amounts. A general mechanism is proposed for the gasification reactions of graphite with O₂, CO₂ and H₂O. Physical wetting of the clean graphite surface leads to a H₂O molecule reversibly bound to the carbon surface. According to XPS data, a hydrate type of bond is proposed. Considerations on the non-catalytic as well as on the catalytic steam gasification of graphite are made. It is suggested that in both cases the reaction is not only controlled by the desorption of the products, *i.e.* the decomposition of the surface intermediates, but also by the sticking probability of the H₂O on the graphite edges.

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1 Introduction

Elucidation of the structure and stability of the various surface species formed after adsorption of O_2 , CO_2 , H_2 and H_2O on graphite are very important for the understanding of the chemistry of graphite and its connection with processes leading to the stabilization of high surface area carbons or to carbon gasification. Although numerous studies have focused on the kinetic properties and the nature of the surface species formed after O_2 , H_2O or CO_2 oxidation, only a limited understanding has yet been achieved, owing certainly to the complexity of the system. These studies were conducted on various carbonaceous samples like graphite, carbon black, glassy carbon, coconut char and carbon fibers. Techniques such as gravimetric balances [1-5], reactor beds [6], pH measurements [7,8], Auger electron spectroscopy (AES) [9,10], infrared absorption (IR) [15-17], X-ray photoelectron spectroscopy (XPS) [15,16,17], ultra-violet photoelectron spectroscopy (UPS) [18], electron spin resonance (ESR) [19], transmission electron microscopy (TEM) [20], and temperature programmed desorption (TPD) [21-29] were employed and brought some useful informations about the nature of the graphite surface species. In particular, they showed that oxidation with O_2 led to dissociation of the molecule and formation of strongly bound oxo, or semi-quinone group which decomposes at temperatures above 900 K to yield CO. Subsequent O_2 adsorption on these semi-quinones leads to lactone groups which thermally desorb as CO_2 at lower temperatures. Other species like carbonates, phenols and carboxyls have also been mentioned as possible surface species.

The studies using XPS [15-17] and TPD [21-29] techniques were conducted

mostly on raw, or highly oxidized carbon samples, under not very well controlled atmospheres, therefore giving broad features, difficult to analyze. Our approach was to work under UHV conditions on a sample cleaned after degassing at high temperature. Except for H_2O adsorption, gases were dosed using leak valves which allowed to cover only a small amount of the sites on the surface. This procedure has turned out to give much better resolved and reproducible TPD features. Also the systematic use of isotopic derivatives labelled with ^{13}C and ^{18}O provided useful means in the determination of reaction mechanisms.

In a previous paper [30], we reported a study on the adsorption and interconversion of CO and CO_2 on the graphite surface. After exposure below 773 K, CO adsorbs molecularly, and desorbs in three distinguishable peaks at 393, 503 and 673 K. A small amount of the CO adsorbed (less than 10%) desorbs as CO_2 giving peaks at 443, 673 and 923 K. CO adsorption at temperatures above 773 K leads to surface species desorbing as CO at 973, 1093 and 1253 K. Most of the above mentioned species are also observed after CO_2 adsorption. These results could be justified by a reaction sequence involving two surface intermediates, semi-quinones and lactones. The first decomposes at high temperatures (> 1000 K) to produce CO , and the second decomposes at lower temperatures (< 900 K) to yield CO_2 .

In this paper the study of graphite surface species under UHV conditions is further pursued. TPD results obtained after H_2O , and O_2 adsorption will be compared to those previously reported for CO and CO_2 adsorption. XPS data obtained after H_2O , O_2 and CO adsorption will contribute to the assignment of the TPD peaks to plausible surface species.

2 Experimental

Details of the apparatus have been published in a preceding paper [30]. In short, it consists of a stainless steel UHV chamber equipped with a high pressure cell for adsorption of gases at pressures higher than 10^{-4} Torr, leak valves for adsorption below this pressure, quadrupole mass spectrometer for TPD measurements, X-ray source with a Mg anode and a double pass cylindrical mirror analyzer for XPS measurements.

The sample was prepared by coating a Ta foil with a film of a polycrystalline graphite suspension in water. It was mounted on a X-Y-Z- θ manipulator and heated resistively. A linear heating ramp in the whole temperature range (290-1400 K) is indispensable to obtain reproducible TPD results. Redhead [31] has demonstrated that the peak position and intensity of the TPD features are function of the heating rate. In our case, a linear and reproducible rate of 50 K/min was achieved by using a power supply, whose output is controlled by a sample-temperature feedback. A chromel-alumel thermocouple in intimate contact with the foil allowed temperature measurements. Cleaning of the sample was performed by degassing at 1400 K for five minutes in UHV. The XPS C_{1s} peak was recorded at a pass energy of 40 eV, and the weaker O_{1s} signal at 80 eV pass energy.

Graphite wetting by H_2O was carried out under the following conditions: degassing under UHV, taking the sample out via the high pressure cell, wetting first with ethanol and then with water, drying with a heat gun and replacing in the UHV chamber via the high pressure cell. The wetting of the clean sample directly with water could not be achieved because of its high hydrophobicity. We checked

with XPS that no significant adsorption of ethanol occurs when the sample is only wetted with ethanol, and then dried.

3 Results

3.1 O₂ adsorption

Figure 1 shows the TPD spectra of mass 28 amu obtained after exposing the clean graphite surface to various doses of O₂ at 523 K. Two maxima at 1093 and 1253 K and a shoulder at 973 K are observed. High exposures (> 150 L) are necessary to obtain a measurable adsorption signal. O₂ chemisorption can be enhanced by raising the adsorption temperature (figure 2), with the 1093 K TPD peak increasing the most. Some CO₂ (mass 44 amu) is also evolved. Figure 3 shows two maxima at ca. 463 and 693 K and a tail around 900 K. The scales in the intensities are expanded by a factor of 20 compared to figures 1 and 2. Raising the adsorption temperature allows one to observe at least three other peaks at 573, 793 and 923 K (figure 4), so that a total of five different chemisorbed species yielding CO₂ are isolated. The adsorption of a mixture of 47% ¹⁸O₂ and 53% ¹⁶O₂ produces TPD features of masses 44 amu (C¹⁶O₂), 46 amu (C¹⁶O¹⁸O) and 48 amu (C¹⁸O₂) (figure 5). Like for CO₂ adsorption [30], total scrambling occurs, since the intensities are respectively 33, 19 and 48% and 31, 24, and 45% for the peaks at 433 and 693 K. Theoretical values for the total isotope mixing are 28, 22 and 50% respectively. Similar isotopic ratios were measured for the other TPD features at 573, 793 and 903 K, and are not reproduced here.

The O_{1s} XPS signal after high O₂ exposure (250 Torr of O₂ for 5 min at 803 K) is shown in figure 6a. The peak is centered around 532 eV, and it is similar to that

obtained after CO chemisorption, although more intense. No change in the C_{1s} signal is observed after this treatment, compared with clean graphite. In agreement with the TPD results (figure 1), oxygen on the surface desorbs thermally and the clean surface is recovered after flashing the graphite sample to 1080 K as shown by the decrease in the O_{1s} signal (curves b to d in figure 6). Variations in the position of the maximum with temperature are within experimental error.

3.2 CO₂ adsorption

Under UHV conditions, CO₂ chemisorption leads to the same TPD features as after adsorption at high pressures [30] (figure 7). Again, the 28 amu TPD signal shows a maximum at 1093 K, which can be enhanced by raising the adsorption temperature. A shoulder near 1223 K becomes the prominent feature of the spectrum, when adsorption is carried out at 973 K. Finally, the 973 K shoulder observed after high pressure exposure or after O₂ adsorption is hardly detectable. Similarly to the case of O₂ adsorption, low temperature (<773 K) CO₂ desorption peaks are observed and the total amount is less than 10% of the amount of CO evolved. These spectra are not reproduced here.

3.3 H₂O adsorption

Under similar conditions, the amount of H₂O on clean graphite is much lower than those of adsorbed O₂ or CO₂. Exposures to high H₂O pressures (> 1 Torr) are necessary to detect the desorption products in TPD experiments. The TPD signal at mass 2, 28 and 44 amu, corresponding to the desorption of H₂, CO and CO₂ after exposure to 20 Torr of H₂O for 60 sec are reproduced in figure 8. H₂ is evolved at high temperatures (ca. 1300 K). CO desorption spectra shows the usual shape

centered around 1093 K, with a shoulder at lower temperatures and a small peak near 1300 K. Two other peaks at mass 28 amu and around 450 and 650 K are also observed. These peaks are not present after O_2 or CO_2 chemisorption, and are likely due to C_2 hydrocarbons. Other hydrocarbons are also produced. Figure 9 shows the TPD spectra taken after H_2O adsorption (20 Torr for 60 sec), for masses corresponding to C_1 (15 amu), C_2 (26-30 amu), C_3 (39-41 amu) and C_8 (78 amu) hydrocarbons. The scale in figure 8 is expanded by a factor of 10 as compared to figure 8. The integrated intensity of the H_2 peak is slightly less than one third of the total CO produced, while the low temperature CO_2 massif, not well resolved, corresponds to less than one tenth of the CO signal.

In an attempt to increase the amount of H_2O adsorbed, physical wetting of the clean graphite sample was carried out. The utilized procedure is described in the experimental section. In figure 10 it is reproduced the O_{1s} signal of the wetted surface, compared to the one exposed to 20 Torr H_2O vapor for 60 sec. It is immediately apparent that the wetted surface contains much more oxygen than the one exposed only to H_2O vapor. The binding energy of the O_{1s} signal after H_2O wetting (533 eV) is higher than that observed after O_2 chemisorption (532 eV). The C_{1s} XPS signal shows, after physical wetting, a tail located in the higher binding energy region (figure 11). The difference between wetted and clean sample shows a maximum at *ca.* 287 eV, i.e. 2 eV higher than for clean graphite. This shift is characteristic of weakly oxidized carbon atoms [16]. The integrated intensity of this difference is about 20% of the one for the clean surface. The thermal decomposition of the wetted surface occurs around 650 K (figure 12). The decomposition product is mostly H_2O as observed by the TPD spectrum (mass 18 amu) which is not

reproduced here. After flash at 663 K, the O_{1s} signal weakens considerably, and shifts to 532 eV. This signal is, however, still larger than that observed after exposure to 20 Torr H_2O vapor. It eventually vanishes after heat treatment above 1000 K.

4 Discussion

It is clear that adsorption of O_2 , CO_2 or H_2O gives CO as prominent decomposition product. All three yield the same TPD features, composed of peaks around 973 (shoulder), 1093 and 1253 K. (Figures 1, 7 and 8). Similar TPD features were observed after CO adsorption at high temperature as well [30]. These temperatures are only approximate, since slight variations are sometimes observed.

In a preceding paper [30], it was suggested that these TPD features can be ascribed to semi-quinone groups, which are known to be very stable in the series of polycyclic aromatic compounds [32]. The existence of these surface-reaction intermediates has been suggested earlier by various authors [6,12-15,25] but, to our knowledge, none of them has isolated three different types, according to activation energies for desorption of 57, 64 and 74 kcal/mol respectively, according to Redhead's calculations [31]. Also, it was not clear before whether the same chemical surface species could be created on the graphite surface after adsorption of the four different gases. The assignment of a specific kind of semi-quinone to each TPD peak, however, is still an open question. In particular, the knowledge of which type of edge site (zig-zag, arm-chair, or even more complicated structures) corresponds to which desorption temperature would be of great interest.

As for sticking probabilities, figure 1 shows that they are not constant with coverage. This confirms earlier studies and in particular two recent publications by

Kelemen and Freund [9,10]. The variation of the coverage with temperature, for a given exposure, could lead, in principle, to activation energies of adsorption for each site, but the uncertainty in intensity measurements in a spectrum of broad overlapping peaks makes it difficult. It is interesting to note, however, that the 1253 K peak, which remains almost temperature insensitive for O₂ adsorption (figure 2), is the most prominent feature after CO₂ exposure at high temperature (figure 7).

CO₂ is evolved at lower temperatures than CO after O₂ and H₂O adsorption (figures 3, 4, 5 and 8). Whereas only three desorption temperatures at 443, 673 and 923 K were observed after CO adsorption [30], five peaks can be distinguished at 463, 573, 693, 793 and 903 K after O₂ adsorption. These various peaks can be attributed to desorption of the same type of species from different chemisorption sites. In agreement with other authors [6,8,13,25] we propose that this chemical species which we can consider as a CO₂ precursor, is a lactone group. Our experiments allow the isolation of five different types, corresponding to activation energies for desorption of 26, 33, 39, 46 and 53 kcal/mol respectively. H₂O exposure does not show such well resolved peaks. Instead, a broad continuum from 400 to 800 K is observed (figure 8), which is likely to originate, however, from the same kind of species. Structural information concerning these groups is not possible without the help of spectroscopic evidence.

The O_{1s} XPS signal after O₂ or CO adsorption shows the same maximum at a binding energy of 532 eV, although they originate from two different species, presumably semi-quinones and carbonyls [30] respectively. The peak position at 532 eV is lower than that reported for covalent non-polarized oxygen bonds (534 eV) [33],

but higher than that reported for compounds containing O^- (531 eV) [33]. This is in agreement with the formation of a polarized carbon-oxygen covalent bond like an oxo group which is present in both carbonyl and semi-quinone surface species.

The higher intensity of the O_{1s} signal after O_2 adsorption, compared with the CO case, is an indication of the relative higher O_2 sticking probability. In both cases, however, only a small fraction of the surface atoms are oxidized, since even after high O_2 exposures no change in the C_{1s} XPS peak is detected (not reproduced here).

As previously discussed, H_2O adsorption gives the same kind of oxygenated species (mostly semi-quinones and some lactones) on the graphite surface than CO_2 and O_2 adsorption. Figure 8 also shows that H_2 desorbs at high temperature, close to 1300 K in agreement with the findings of Matsumara *et al.* [28]. Also similar to their results, the integrated intensity for H_2 production amounts for less than one third of the total amount of CO produced. A possible explanation for this loss of hydrogen is that H_2O chemisorption, leading to the CO precursor, yields two hydrogen atoms which either recombine (higher probability event) or form a C-H bond on the surface (lower probability event), which then decomposes around 1300 K.

Although proposed earlier by several authors [12,13,15-17], hydroxyl or phenol groups do not appear to be good candidates for surface species after H_2O adsorption, based on our TPD results. The great similarities of the CO desorption signal, after exposures to either O_2 , CO_2 or H_2O is a good indication that the same species are produced, as Kelemen and Freund pointed out [10]. The keto-enolic equilibrium, totally displaced towards the ketonic form for polycyclic aromatic compounds of

high order [32] is another argument in favor of the non-existence of phenol groups on the graphite surface.

Since the hydrocarbon evolution after H_2O exposure occurs between 400 and 700 K, it probably only involves the breaking of carbon-carbon single bonds, rather than highly more stable aromatic bonds. To account for such behavior, we must postulate the existence of aliphatic fragments like $-\text{CH}_2-$, $-\text{CH}_3$ or even $-\text{C}_2\text{H}_5$. Thermal decomposition would lead to radical formation, which would yield hydrocarbon molecules after recombination. The origin of the the two different maxima around 500 and 700 K (figure 9) remains unexplained.

Based on the results presented in this paper and in our preceding publication, a general scheme for the desorption products after adsorption of O_2 , CO_2 , H_2O and CO is proposed (figure 13). In all the cases studied, the desorption of CO at high temperatures is the main feature in the TPD experiments. It is then proposed that the main pathway for adsorption of the reactants is the formation of the CO precursor species, probably a semi-quinone. The activation energy for adsorption depends on the molecule itself, the site on which it adsorbs, and the coverage. O_2 dissociates to give two CO precursors, CO_2 yields a CO precursor and a gaseous CO molecule, and H_2O produces two hydrogen atoms which can either recombine (more probable event) or form CH bonds (less probable event). The latter bonds can be benzenic-like and desorb as H_2 at *ca.* 1300 K, or aliphatic to yield hydrocarbons at lower temperatures.

If the temperature is low, say below 900 K, thermal decomposition of the CO precursor cannot occur, and only the formation of a second surface species, involving a second reactant molecule is possible. It is suggested that this species is a

lactone group, based on our results and those of other authors. Its decomposition gives CO_2 as major component, and the total oxygen scrambling observed after O_2 and CO_2 adsorption can be explained by an equilibrium between the CO precursor, and the CO_2 precursor in the presence of the reactant gas. Since in our TPD experiments, the amount of CO desorbing is much higher than the amount of CO_2 this equilibrium is probably shifted to the formation of the more stable CO precursor.

More spectroscopic data is now necessary in order to support our assignment of the CO and CO_2 precursors to a semi-quinone and lactone groups respectively. Vibrational techniques such as infrared, Raman or High Resolution Electron Energy Loss Spectroscopy (HREELS) under UHV conditions might bring very fruitful indications in that respect.

The physical wetting of clean graphite by liquid H_2O favors the formation of different surface species than the adsorption of H_2O vapor. After physical wetting, the amount of H_2O adsorbed is much higher. This is clearly shown by the appearance of a shoulder at 287 eV in the C_{1s} XPS signal, which amounts to 20% of the carbon signal (figure 11). In contrast, the signal obtained after H_2O vapor adsorption is the same as that of clean graphite, indicating that in this case a very small fraction of the carbon atoms interact with H_2O . The position of the shoulder after physical wetting (287 eV) is characteristic of slightly oxidized carbon atoms in compounds such as alcohol or ethers. The O_{1s} signal (figure 12) shows a large peak centered at 533 eV. This value is 1 eV higher than that observed after O_2 and CO adsorption.

The desorption at rather low temperatures (623 K) (figure 12), giving H_2O as the main component, suggests again a weakly bound type of species. Phenolic groups can be ruled out since they would show an O_{1s} signal at lower binding

energies (531 eV), and the recombination of a C-OH and C-H groups to recover the H₂O molecule, should occur at much higher temperatures, since it involves the breaking of a benzenic like carbon-hydrogen bond. The proposed species is a solvate between a H₂O molecule and an edge carbon atoms with bond energies of about 35 kcal/mol, as given by the desorption temperature [31]. After heating above 700 K, the O_{1s} binding energy shifts toward 532 eV. This indicates that a fraction of the chemisorbed H₂O is able to dissociate and form CO-precursor type species on the surface. The intensity of this signal is higher than that observed after H₂O vapor adsorption, and shows that physical wetting increases the water dissociative chemisorption.

The reaction of H₂O on graphite is of great interest for the steam gasification of carbon solids. The high temperature non-catalyzed reaction to give CO and H₂ proceeds probably following the high temperature route of figure 13, that is via the formation of the CO precursor formed by its thermal decomposition and H₂ recombination. To lower the temperature required to run this process, one must find ways to facilitate the formation of the CO₂ precursor and its further decomposition. Also of great importance, and probably related to the previous argument, is the accessibility of the H₂O molecule to the active sites on the graphite edges. XPS studies clearly show that the H₂O vapor, at least at room temperature, cannot significantly chemisorb on the surface, whereas physical wetting with water covers at least 20% of the total number of sites (figure 11). One must therefore find a way to increase the surface reactivity (sticking probability) by decreasing the activation energy for adsorption. There is no doubt that KOH, which is the prototype catalyst for most of the gasification reactions on graphite, apart from other possible catalytic properties

can provide such an action, owing to its hydrophilic properties. Additional TPD and XPS measurements must be systematically undertaken on the graphite/KOH system for a better understanding of the catalytic reaction mechanism. Preliminary experiments we carried out on this system tend to demonstrate that the catalyst does not change the decomposition temperatures but it enhances dramatically the intensities of the TPD peaks. In other words, the chemistry and the surface species are the same, and only the sticking coefficient of H_2O increases. If confirmed, these observations would be of great interest.

5 Summary

O_2 , CO_2 and H_2O chemisorptions on polycrystalline graphite yield the same CO precursors on three different sites, decomposing at 973, 1093 and 1253 K. These species have been tentatively assigned to semi-quinone functional groups. CO_2 and H_2O give gaseous CO and H_2 respectively, as the by-products of the CO-precursor formation. H_2O chemisorption leads also to the formation of carbon-hydrogen bonds, involving either aromatic or aliphatic carbons. The first kind decomposes at 1300 K to produce H_2 , and the second type produces hydrocarbons below 800 K. CO_2 is also produced after chemisorption by these three molecules and thermally evolve in five TPD peaks at 463, 573, 693, 793 and 903 K. Lactone groups of various kind and/or located on different sites (zig-zag, arm-chair...) have been proposed to account for these CO_2 surface precursors. The amount of CO_2 produced is always less than 10% of the amount of CO, even following CO_2 adsorption. Physical wetting of the clean graphite surface leads to a different kind of surface species. In this case, H_2O is reversibly bound to the surface and desorbs at *ca.* 650 K. A hydrate type

of bond can account for such a weak bonding.

Analysis of our data allowed us to propose a simple mechanism for the gasification reaction of graphite by O_2 , CO_2 , and H_2O . Finally, the kinetics of the non-catalytic as well as the catalytic steam gasification of graphite appear to be controlled not only by the decomposition of the surface species, but also by the surface wettability, that is the sticking probability for H_2O adsorption.

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Table I: Desorption temperatures and activation energies for desorption of CO and CO₂ after adsorption of CO₂, O₂ and H₂O.

Adsorption gas	Adsorption temp (K)	Desorption product	Desorption temp (K)	E_{des}^a (kcal/mol)	Assignment
CO ₂	room temp	CO	973-1253	64-83	Semi-quinones
O ₂	500-900				
H ₂ O	room temp				
CO ₂	room temp	CO ₂	423	27	Lactones
O ₂	500-950		463-923	28-60	
H ₂ O	room temp		400-900*	21-51	

* One broad feature.

Figure captions

Figure 1: TPD spectra mass 28 amu after exposing a clean graphite surface to various doses of O₂ at room temperature.

Figure 2: TPD spectra mass 28 amu after exposing a clean graphite surface to 1500L (5×10^{-5} Torr for 30s) of O₂ at various temperatures.

Figure 3: TPD spectra mass 44 amu after exposing a clean graphite surface to various doses of O₂ at room temperature.

Figure 4: TPD spectra mass 44 amu after exposing a clean graphite surface to 900L (6×10^{-5} Torr for 15s) of O₂ at various temperatures.

Figure 5: TPD spectra after exposing a clean graphite surface to 900L (6×10^{-5} Torr for 15 s) of an O₂ isotopic mixture (53% ¹⁶O₂, 47% ¹⁸O₂) at room temperature.

Figure 6: a) XPS spectra (O_{1s}) of the graphite surface oxidized by exposure to 250 Torr of O₂ at 803 K for 5min; and after flashing at b) 993 K, c) 1113 K, d) 1353 K.

Figure 7: TPD spectra mass 28 amu after exposing a clean graphite surface to 48000L of CO₂ (8×10^{-4} Torr for 60s) at various temperatures.

Figure 8: TPD spectra masses a) 44 amu, b) 28 amu and c) 2 amu after exposing a clean graphite surface to 20 Torr of H₂O for 60 sec at room temperature.

Figure 9: TPD spectra after exposing a clean graphite surface to 20 Torr of H₂O for 60 sec at room temperature. The scale is expanded by 10 compared to figure 8.

Figure 10: XPS (O_{1s}) spectra of a graphite surface. a) Surface wetted with H₂O, and b) surface exposed to 20 Torr of H₂O for 60 sec.

Figure 11: XPS (C_{1s}) spectra of a graphite surface. a) Clean surface, b) surface

wetted with H_2O and dried, and c) difference spectrum.

Figure 12: XPS (O_{1s}) spectra of a graphite surface wetted with H_2O . a) Non flashed, and flashed at b) 523 K, c) 593 K, d) 663 K, e) 803 K, and e) 1013 K.

Figure 13: General schematic mechanism for graphite gasification reactions. The ordinate unit is arbitrary and the relative energy levels of the surface intermediates are not respected. RO represents the gas reactant, and R the by-product of the lactone and/or semi-quinone formation. The semi-quinone formation and further desorption as CO (solid lines) is more probable than the lactone formation and CO_2 desorption (broken lines).

Figure 1

Figure 2

Figure 3

Figure 4

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Figure 5

Figure 6

Figure 7

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Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

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