

EXAMINATION OF OXYGEN FUNCTIONAL GROUPS ON CARBONACEOUS SOLIDS BY
LINEAR TEMPERATURE DESORPTION TECHNIQUES

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INTRODUCTION

It is important to understand the nature of carbon-oxygen complexes which exist on the surfaces of carbonaceous solids such as coal chars, activated carbons and carbon molecular sieves. The nature and concentration of the oxygen functional group will influence processes in which the carbon's surface is involved (1). As examples, wettability (2), adsorptive behavior (3,4), catalytic and electrical properties (5) are all affected by the chemical nature and extent of the oxygen-containing surface complex. In addition, oxygen chemisorption techniques have been used widely to estimate carbon "active site" concentration for various carbons and chars (6-9). These methods are used in attempts to correlate carbon reactivity with some fundamental property of the carbon. Of course, the surface complexes formed by this deliberate chemisorption of oxygen are the same as those produced by natural processes. Thus, a better understanding of carbon-oxygen complexes will be of value to practical and fundamental aspects of coal and carbon science and technology.

Highly porous carbonaceous solids, like coal chars, are mainly composed of relatively disordered carbon atoms. These materials, in general, demonstrate a high propensity for oxygen chemisorption because of large concentrations of edge carbon atoms. Once oxygen is chemisorbed onto these edge carbon atoms then carbon-oxygen complexes are formed. These surface functional groups can only be removed thermally as CO or CO₂. Complete thermal removal of the complexes requires temperatures of the order of 1250 K (6).

Direct analysis of the complexes has been performed (4) by a range of techniques. Unfortunately, many studies have produced conflicting results. This is probably a result of poorly defined carbons, poorly defined oxidation conditions and the use of widely different carbonaceous solids. In addition, it is understood that oxygen-carbon surface complexes do not behave necessarily in the same manner as do carbon-oxygen functionalities in simple organic compounds.

The principal purpose of this study was to examine oxygen complexes deliberately incorporated into a relatively pure, microporous carbon by using a Linear Temperature Programmed Desorption (LTPD) technique, in conjunction with chemical neutralization methods.

EXPERIMENTAL

Materials

A proprietary phenol-formaldehyde (PF) polymer was used to prepare the microporous char. The polymer was heated, in N₂, to 1275 at 10 K min⁻¹. The char was subsequently oxidized, to varying degrees, by (i) air oxidation performed in a fluidized bed over a range of reaction temperatures and times and (ii) treatment with concentrated HNO₃ solution for differing temperatures and oxidation times. Full details of these procedures (and others referred to in this paper) are given elsewhere (1).

Thermal Desorption Experiments

The LTPD experiments were generally carried out as follows. About 1 g of dried sample was heated in flowing N_2 at $5 K min^{-1}$ up to 1275 K. The evolved gases were continuously analyzed for CO_2 , CO, H_2 and H_2O vapor. Some experiments were performed in flowing H_2 , the procedure was identical to that using N_2 .

Selective Neutralization Technique

Small samples of char were immersed in separate solution of $NaHCO_3$, Na_2CO_3 , $NaOH$ and $Ba(OH)_2$. The amounts of acidic oxygen complexes neutralized by each solution were then calculated from titrations with HCl.

RESULTS AND DISCUSSION

Figures 1 and 2, respectively, present desorption profiles for the chars oxidized in HNO_3 (at 340 K, for 5 h) and in air (at 673 K for 3 h). As is to be expected, in both cases the principal gases evolved are CO and CO_2 . Essentially all the CO evolving complexes (CO-complex) and CO_2 evolving complexes (CO_2 -complex) are desorbed by 1275 K. It is important to note that each set of complexes (CO or CO_2 evolving) can be further divided into two categories depending on the temperature range of evolution. For example, in the case of the CO-complex, two evolution peaks are seen, one at about 900 K and one at 1100 K (Figures 1 and 2) for both samples. The CO_2 -complex on the HNO_3 treated char mainly appears at about 575 K (Figure 1), it then tails off with significant quantities of CO_2 being evolved up to 1000 K. On the other hand, the main CO_2 evolution for the air oxidized sample is around 900 K (Figure 2). This sample did evolve a small quantity of CO, in the lower temperature require (~ 550 K). For convenience sake we will refer to the four groups of complexes as lower and higher temperature, CO or CO_2 complexes. The main reasons for observing different evolution peaks for CO and CO_2 are that differing complexes will evolve the same gaseous species at various temperatures, and that the same oxygen complex may be formed at (and thus, desorbed from) energetically different carbon atoms in the zig-zag or armchair configuration.

It should be noted that the fraction of oxygen existing as CO_2 complexes on the samples is quite different for the HNO_3 and air oxidized samples. For example, in all cases, the HNO_3 oxidized chars at least 50% of the total oxygen is present as CO_2 -complex. However, for the air oxidized samples (ranging from 473 K for 1 h up to 783 K for 50 min) the oxygen present as CO_2 -complex varies from 25% to 50%. Obviously, the HNO_3 samples contain much more CO_2 -complex than do the air oxidized ones.

A direct correlation exists between total acidity (from NaOH neutralization) and the concentration of CO_2 -complex for both the HNO_3 and air oxidized chars (Figure 3). No such correlation can be found for the CO-complex on any oxidized char (1). As can be seen, the slopes of lines on Figure 3 are quite different. For the HNO_3 oxidized chars the slope is near to unity, whereas, for the air oxidized samples the slope is about two. From this, and other evidence from samples exchanged with sodium, it is suggested that the principal acidic CO_2 -complex from the HNO_3 oxidized chars is carboxylic acids. For the air oxidized chars, the main acidic CO_2 -complex is a carboxylic anhydride, which in aqueous solution (as in the neutralization experiments) forms two carboxylic acids for each anhydride hydrolyzed.

In an attempt to determine further the nature of the acidic functionalities ion-exchange experiments were performed with $Ba(OH)_2$. Boehm (10) observed that if two carboxylic acid surface groups were adjacent, then both could be neutralized by one $Ba(OH)_2$; if they are not near to each other, then one $Ba(OH)_2$ is required for neutralization of each carboxylic acid (the extra positive charge on the surface is balanced by OH^-). Thus, by comparing neutralization data from NaOH and $Ba(OH)_2$ one

can speculate on the relative distance between the acid groups. Such data for our samples are given in Table 1. For the HNO_3 chars, one observes an almost 1:1 relationship between the CO_2 complex and the moles of NaOH required for neutralization. The ratio for the number of moles of $\text{Ba}(\text{OH})_2$, needed for neutralization and CO_2 complex concentration is about 2:1. For the air oxidized chars, it is seen that the observations are very different. That is, the number of moles of NaOH and $\text{Ba}(\text{OH})_2$ needed for neutralization are very similar, and about twice the number of moles of the CO_2 complex.

TABLE 1
Neutralization Data for NaOH and $\text{Ba}(\text{OH})_2$ on Air and
 HNO_3 -Oxidized Chars

Sample	$-\text{CO}_2$ Complex mmol/g	Neutralization (mmol/g)	
		NaOH	$\text{Ba}(\text{OH})_2$
Air Char			
648 K, 3 h	0.4	0.8	0.9
698 K, 11 h	1.5	3.2	3.1
HNO_3 Char			
340 K, 0.1 h	0.6	0.6	1.3
340 K, 5 h	1.8	1.9	3.2

These data indicate that for these samples the acid groups are adjacent for the air chars and nonadjacent for the HNO_3 oxidized chars. This observation fits in with the suggestion of carboxylic anhydrides are the dominant CO_2 complex for the air oxidized samples because on hydrolysis the anhydride will yield two adjacent carboxylic acid groups.

Next we address the CO complexes by a series of LTPD runs made in 4.05% H_2 (balance N_2). The evolution of CO_2 was not influenced by the change to this gas mixture. The CO_2 profiles are almost identical to those obtained in N_2 . However, in this H_2 containing gas the LTPD profiles for the CO evolution are changed. For both the HNO_3 and air oxidized chars there is a dramatic loss of the higher temperature CO complex, but the lower temperature CO complex is little altered. In the case of the HNO_3 char, a second H_2O evolution peak appears at high temperatures, around 950 K (see Figure 4). For the air char, a H_2O peak is also observed at about 950 K. It should be noted that in all these runs the oxygen balance was remarkably good. That is, the total amount of 'oxygen' evolved is identical in both N_2 and H_2/N_2 gas mixtures. The only difference is in the distribution of species which indicates that the 'loss' of high temperature CO complex is quantitatively accounted for by the appearance of a new high temperature H_2O peak. Figure 4 also shows the consumption of H_2 during these experiments. The consumption of H_2 seems to parallel the evolution of the lower-temperature CO complex. A series of experiments was performed in which the lower temperature CO complex was systematically removed by heat treatment in N_2 , prior to LTPD in 4.05% H_2 . Figure 5 shows the results. There is an apparent direct relationship between H_2 consumption and CO complex decomposed.

Experiments were also carried out in pure H_2 at atmospheric pressure (Figure 6). The evolution of CO_2 was not influenced by H_2 , however, the evolution of CO is markedly reduced. There is a relatively large quantity of CH_4 produced. A run made with a clean char (heated to 1275 K prior to H_2 treatment) also produces some CH_4 (Figure 6) but it is also evident from this figure that the presence of some CO evolving complex enhances CH_4 evolution. Figure 7 is a plot of CH_4 evolved versus the amount of lower temperature CO complex that decomposes as CO (in H_2 , up to 1000 K). This figure does indicate that CH_4 production can be related to the lower-temperature CO complexes, irrespective of char type. The slope of this line

is the same as that (0.75) seen in Figure 5. These data suggest, strongly, that CH_4 evolution originates from the chemisorption of hydrogen on to carbon atoms made available by decomposition of CO complex. Ultimately the carbon-hydrogen complex decomposes to evolve CH_4 .

CONCLUSIONS

It has been shown that a combination of LTPD techniques, in different gaseous atmospheres, with selective neutralization techniques can yield very valuable information on carbon-oxygen surface complexes or chars. Specifically, it is concluded that, for these samples;

- The oxygen complexes can be conveniently divided into four groups comprised of lower and higher-temperature CO and CO_2 evolving complexes.

- CO_2 evolving complexes are mainly responsible for acidic nature of the chars studied.

- The principal CO_2 complexes can be characterized as (i) lower-temperature CO_2 complexes are nonadjacent carboxyl groups formed at dangling edge carbon atoms; (ii) higher-temperature CO_2 complexes are carboxylic anhydrides, which on hydrolysis form adjacent carboxyl groups.

- Thermal decomposition of the lower temperature CO evolving complex generates highly reactive dangling carbon atoms. These atoms can either chemisorb H_2 or produce CH_4 in the presence of H_2 .

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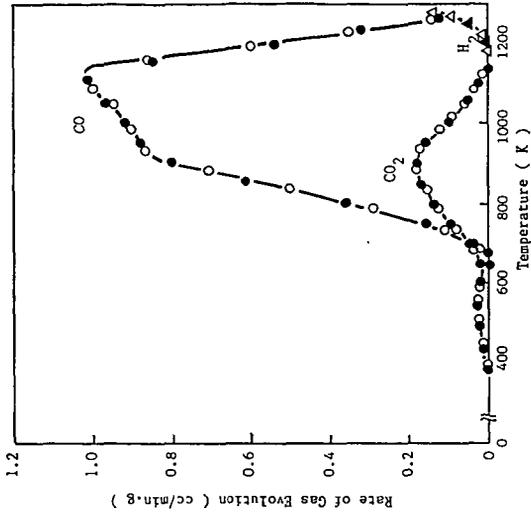


FIGURE 2. GAS EVOLUTION PROFILES FROM AIR CHAR (673 K, 5 H)

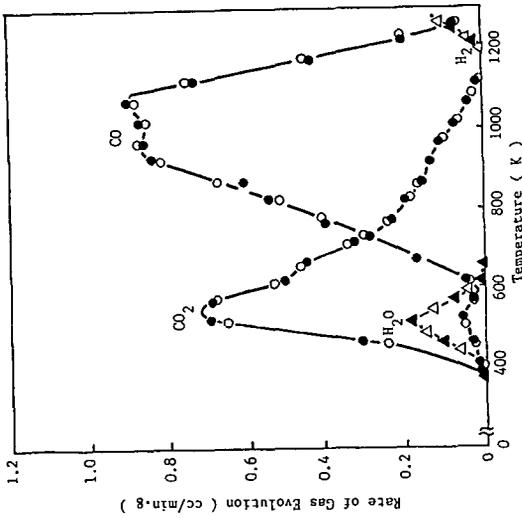


FIGURE 1. GAS EVOLUTION PROFILES FROM HNO₃ CHAR (340 K, 5 H)

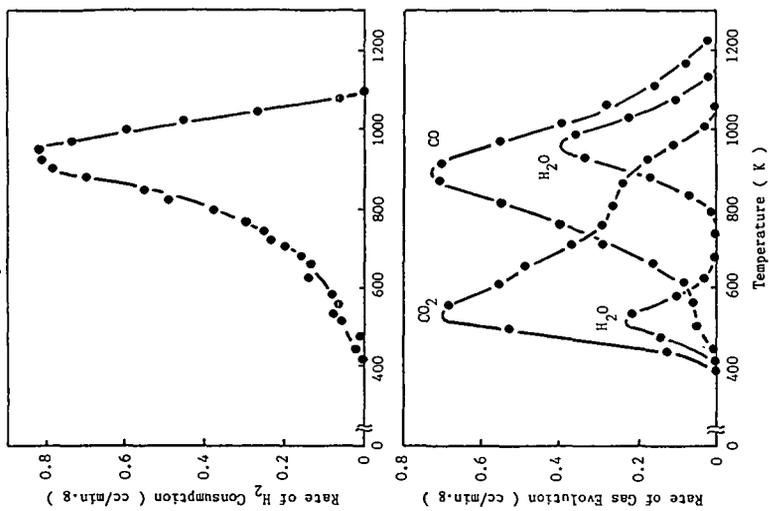


FIGURE 4. RATES OF GAS EVOLUTION AND H₂ CONSUMPTION ON HNO₃ CHAR (340 K, 5 H) DURING LTPD IN 4.05 Vol% H₂

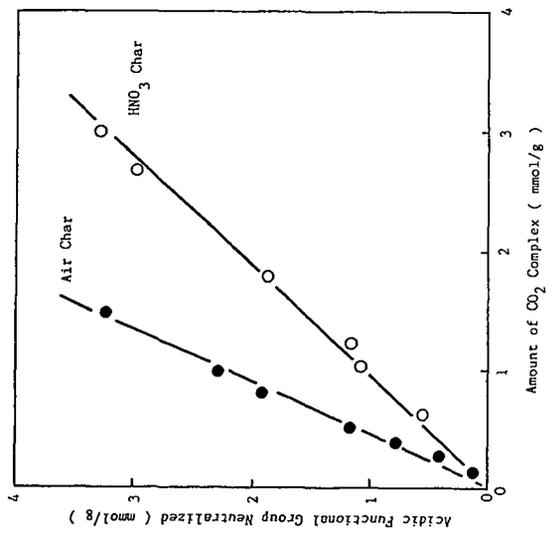


FIGURE 3. RELATIONSHIP BETWEEN TOTAL ACIDITIES MEASURED BY NaOH AND SITE CONCENTRATIONS OF CO₂ COMPLEXES PRESENT ON HNO₃ CHARs AND AIR CHARs

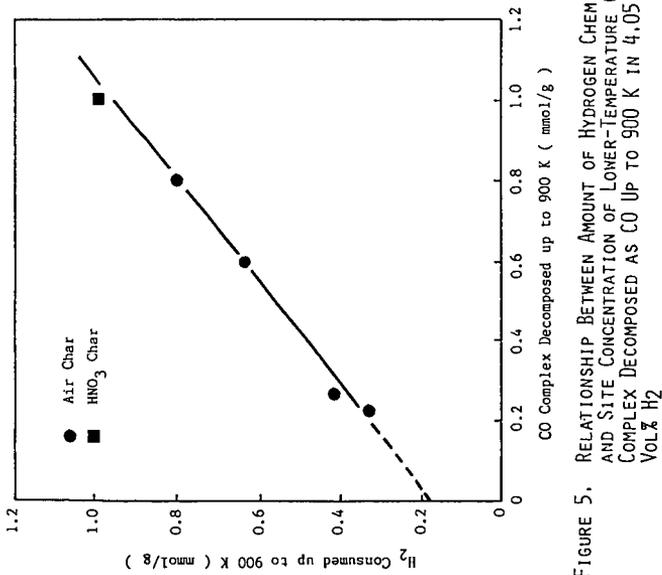


FIGURE 5. RELATIONSHIP BETWEEN AMOUNT OF HYDROGEN CHEMISORBED AND SITE CONCENTRATION OF LOWER-TEMPERATURE CO COMPLEX DECOMPOSED AS CO UP TO 900 K IN 4.05 VOL% H₂

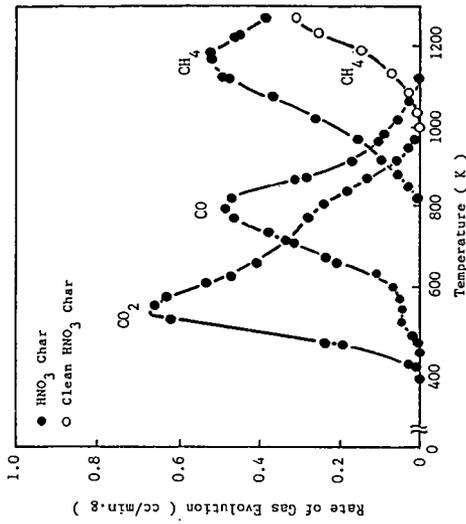


FIGURE 6. RATES OF GAS EVOLUTION FROM HNO₃ CHAR (340 K, 5 H) DURING LTPD IN ATMOSPHERIC PRESSURE H₂

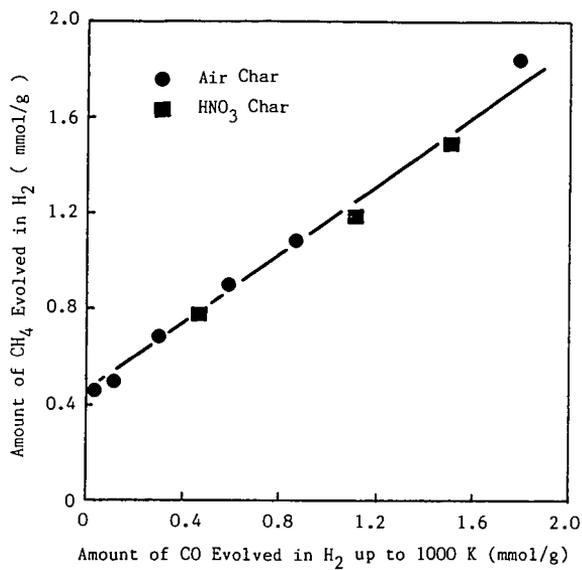


FIGURE 7. RELATIONSHIP BETWEEN AMOUNT OF CH₄ EVOLVED AND SITE CONCENTRATION OF LOWER-TEMPERATURE CO COMPLEXES DECOMPOSED AS CO UP TO 1000 K IN ATMOSPHERIC PRESSURE H₂