# Effect of Chemisorbed Oxygen on Char Reactivity

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Many workers have demonstrated that a substantial amount of oxygen can be chemisorbed to form oxide layers on carbon surfaces in the course of chemical oxidation reactions (Laine et al., 1963; Walker et al., 1965; Puri, 1970). This communication reports results of a set of experiments conducted to explore how such deposited oxygen affects the intrinsic reactivity and the pore enlargement in a series of bituminous chars.

The five char samples used in this study were prepared from a single coal under various pyrolysis conditions, following the procedures set forth by Su and Perlmutter (1984) and labeled as samples *B* to *F* in the earlier work. Air oxidation of each sample was carried out at 673 K. At desired conversion levels (15, 30, 45, 60 and 75%), reaction was terminated within 1 min by purging nitrogen through the TGA reaction chamber. After 10 min without any detectable further weight loss at 673 K, the temperature of the nitrogen purge was rapidly raised to 1,223 K within 3 min and held at that temperature for 10 min. Substantial weight loss was observed during this heat treatment, most of it occurring before the temperature reached 1,173 K. Greater weight loss was observed at greater conversion levels for all the chars tested.

## RESULTS AND DISCUSSION

To interpret these weight loss determinations in terms of oxygen chemisorption, it is useful to recall the findings of Sato and Akamatu (1954) and Laine et al. (1963) showing that, upon heating in vacuum, the chemisorbed oxygen can be released as CO and/or $CO_2$, but predominantly as CO at temperatures above 773 K. Assuming that all adsorbed oxygen was released as CO, the amount of the chemisorbed oxygen was calculated from the weight loss data. The results given as Table 1 show that oxygen deposition increases with conversion for all five char samples tested and accounts for 8 to 14 wt.% of the remaining char after 75% conversion.

The corresponding surface areas occupied by the chemisorbed oxygen are presented in Table 2, estimated on the basis of each oxygen atom occupying 8.3 $Å^2$ (Laine et al., 1963) and normalized with respect to the total surface area measured by physical adsorption of $CO_2$ at 273 K. The fraction of total surface area occupied by the deposited oxygen increases from 36 to about 100% as conversion proceeds from 15 to 75%. For chars at 75% conversion, the calculated oxygen-covered area even exceeded the total $CO_2$-based surface area in two cases. Apparently similar contradictions were reported by Taylor and Walker (1981), whereupon they suggested that the area normally taken for an atom of oxygen on a carbon surface is too large for chars. It is also possible that the oxygen deposited may have penetrated into the bulk carbon or that the oxygen is not limited to a monolayer on a char surface. In any case, the experiment results indicate that the coverage of the chemisorbed oxygen on the surface is quite extensive.

In their studies of the oxidation of Graphon, a highly graphitized carbon, Laine et al. (1963) and Walker and Janov (1968) found that the active surface area for reactions is only a very small fraction of the total surface area. Moreover, they suggested that all the deposited oxygen is chemisorbed on these active surface areas, acting to retard reaction. Laine et al. (1963) obtained rate constants based on the unoccupied active surface area. The results in Table 2 and those of Taylor and Walker (1981) indicate, however, that this is not the case for chars. Unlike Graphon, whose surface is composed mainly of unreactive graphite in basal planes with relatively few reactive edge sites, the char surfaces are much more

TABLE 1. WEIGHT PERCENT OF OXYGEN CHEMISORBED ON CHARS AT DIFFERENT CONVERSIONS

| Sample | Conversions, % | | | | |
|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 |
| *B* | 5.1 | 8.0 | 9.7 | 10.9 | 13.7 |
| *C* | 4.0 | 7.1 | 8.8 | 9.1 | 11.1 |
| *D* | 3.1 | 4.6 | 6.3 | 7.4 | 8.3 |
| *E* | 4.0 | 6.9 | 9.1 | 10.9 | 12.6 |
| *F* | 4.0 | 5.1 | 8.0 | 9.1 | 10.9 |

TABLE 2. FRACTION OF TOTAL SURFACE AREA COVERED BY CHEMISORBED OXYGEN

| Sample | Conversions, % | | | | |
|---|---|---|---|---|---|
| | 15 | 30 | 45 | 60 | 75 |
| *B* | 0.45 | 0.68 | 0.69 | 0.77 | 1.07 |
| *C* | 0.36 | 0.56 | 0.69 | 0.70 | 0.91 |
| *D* | 0.45 | 0.51 | 0.63 | 0.74 | 0.79 |
| *E* | 0.41 | 0.55 | 0.74 | 0.85 | 1.08 |
| *F* | 0.42 | 0.44 | 0.65 | 0.75 | 0.88 |

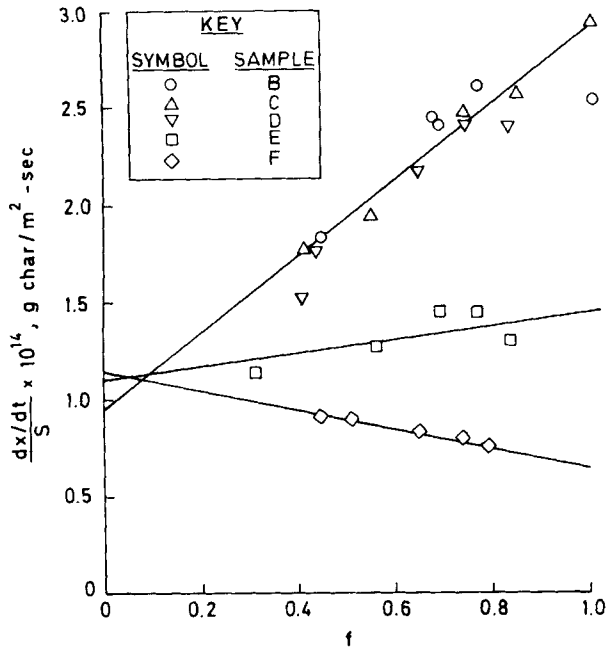


**Figure 1. Effects of oxygen coverage on intrinsic oxidation rates.**

disordered. The large levels of oxygen coverage on the surface shown in Table 2 support the view that all the surfaces are active for reaction. Further, the oxygen deposited on the char surface did not retard reaction as suggested by Laine et al. (1963); i.e., the reaction did not cease completely at 75% conversion when virtually all the surfaces were covered by oxygen complexes.

## ADSORPTION-REACTION SEQUENCE

Noting that the oxygen complexes are stable at reaction temperature (673 K) under a nitrogen atmosphere but decompose if exposed to oxygen suggests the following schematic sequence for carbon-oxygen reaction on a char surface:

$$C + O_2 \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} [\text{C-O complex}] \tag{1}$$

$$[\text{C-O complex}] + O_2 \xrightarrow{k_d} CO, CO_2 \tag{2}$$

with Eq. 2 as the rate-controlling step. In addition, Karsner and Perlmutter (1982) suggested that besides the oxygen adsorption-desorption reactions, the carbon can also be gasified by direct burnoff on those surfaces unoccupied by oxygen; i.e.

$$C + O_2 \xrightarrow{k_b} CO, CO_2 \tag{3}$$

The intrinsic oxidation rate on a char surface may thus be formulated as the combination of first-order direct burn-off and adsorption-desorption reactions by

$$r = k_s C_0 = (k_d C_0 - k_b C_0) f + k_b C_0 \tag{4}$$

where $f$ is the fractional coverage of the deposited oxygen.

An experimental intrinsic rate can be obtained directly by dividing the measured reaction rates by the measured total surface areas at different levels of conversion. For reactions at 673 K, such results are presented in Figure 1 with respect to fractional coverage of the deposited oxygen. The best fit straight lines can be identified with the prediction of Eq. 4 to extract both the direct burn-off reaction rate $k_b C_0$ and the oxygen complex decomposition rate $k_d C_0$. Such results are summarized in Table 3 with corresponding 90% confidence intervals and together with overall reaction rates and intrinsic rates obtained earlier (Su and Perlmutter, 1984) from the random pore model. It is particularly interesting to note that chars prepared at different pyrolysis temperatures (samples *C*, *B*, and *D*) have essentially the same direct burn-off rates. Their differences in intrinsic rates are almost completely attributable to the differences in the oxygen complex decomposition rate, and the overall rates are further affected by differences in pore structures. For chars generated at different heating rates but at the same pyrolysis temperature (samples *B*, *E*, *F*,), direct burn-off rate, oxygen complex decomposition rate, and therefore the intrinsic rate are all the same. The differences in overall rates are affected only by pore structures.

After thermal decomposition of the oxygen complex, the surface areas of the chars were again measured by $CO_2$ adsorption at 273 K. Since some carbon was also removed during the heat treatment process, the chars after thermal decomposition were at a higher conversion level than before and a slightly higher surface area was to be expected. Taking this into account, no significant affect of the chemisorbed oxygen on pore structure could be identified in the experimental results.

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## NOTATION

$C_0$ = ambient concentration of gas reactant, mol/m$^3$
$f$ = fraction of the char surface covered by chemisorbed oxygen, dimensionless
$k_a$ = rate constant for oxygen adsorption on char surface

TABLE 3. DIRECT BURN-OFF RATES AND OXYGEN COMPLEX DECOMPOSITION RATES AT 673 K

| | Reaction rate × 10$^6$, g of char/s-m$^2$ surface | | | Overall oxidation rate at 40% conversion |
|---|---|---|---|---|
| | Direct Burn-off Rate | $O_2$ Complex Decomp. Rate | Intrinsic Oxidation Rate | |
| Sample | $k_b C_0$ | $k_d C_0$ | $k_s C_0$ | $\frac{dX}{dt} \times 10^4$, 1/s |
| *B* | 0.94 ± 0.15 | 2.90 ± 0.27 | 1.74 ± 0.84 | 6.80 |
| *C* | 1.11 ± 0.18 | 1.43 ± 0.32 | 1.07 ± 0.47 | 2.75 |
| *D* | 1.13 ± 0.04 | 0.66 ± 0.07 | 0.83 ± 0.27 | 1.65 |
| *E* | 0.94 ± 0.15 | 2.90 ± 0.27 | 1.51 ± 0.51 | 5.65 |
| *F* | 0.94 ± 0.15 | 2.90 ± 0.27 | 1.68 ± 0.70 | 4.73 |

$k_a'$ = rate constant for reversible oxygen desorption on char surface
$k_b$ = rate constant for direct carbon burn-off on char surface
$k_d$ = rate constant for oxygen complex decomposition on char surface
$k_s$ = intrinsic rate constant for char oxidation
$S$ = surface area per unit weight of reacting particle, $m^2/g$
$t$ = reaction time, s
$X$ = conversion, dimensionless

## LITERATURE CITED


Karsner, G. G., and D. D. Perlmutter, "A Model for Coal Oxidation Kinetics," *Fuel*, **61**, 29 (1982).

Laine, N. R., F. J. Vastola, and P. L. Walker, Jr., "The Importance of Active Surface Area in the Carbon-Oxygen Reaction," *J. Phys. Chem.*, **67**, 2,030 (1963).

Puri, B. R., "Surface Complexes on Carbons," *Chemistry and Physics of Carbon, Marcel Dekker, New York*, **6**, 191 (1970).

Sato, H., and H. Akamatu, "Formation and Thermal Decomposition of Surface Oxide on Carbons," *Fuel*, **33**, 195 (1954).

Su, J. L., and D. D. Perlmutter, "Effect of Pore Structure on Char Oxidation Kinetics," *AIChE J.*, **31**, 973 (June, 1985).

Taylor, R. L., and P. L. Walker, Jr., "Formation of Stable Oxygen Complex During the Gasification of Char in Air at 648 K," 15th Biennial Conf. on Carbon, *Abstracts*, 437 (June, 1981).

Walker, Jr., P. L., L. G. Austin, and J. J. Tietjen, "Oxygen Chemisorption Effects on Graphite Thermoelectric Powder," *Chemistry and Physics of Carbon*, Marcel Dekker, New York, **1**, 237 (1965).

Walker, Jr., P. L., and J. Janov, "Hydrophilic Oxygen Complexes on Activated Graphon," *J. Colloid Interface Sci.*, **28**, 499 (1968).



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