✓
MASTER

DNL 28342

C-2402

CONF-801125--1

A Study of Coal Oxidation by Charged Particle Activation Analysis

D. J. Schlyer and A. P. Wolf

Department of Chemistry

Brookhaven National Laboratory

Upton, New York 11973 USA

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

* Research carried out at Brookhaven National Laboratory under contract with the U. S. Department of Energy and supported by its Office of Basic Energy Sciences.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Introduction

It has been recognized for many years that exposure of coal to air can significantly alter the processing characteristics of the coal. This effect is more pronounced in lower rank coals and in fact some brown coals will undergo spontaneous combustion at or near ambient temperatures.

Both the initial oxidation and the effect this oxidation has on the processing characteristics of the coal have been an area of interest for many years.¹ In the last few years there has been a renewed interest in the oxidation of coal and several new analytical techniques have been applied to this problem^{2,3,4,5,6}. Several salient features of the process have been discovered including the chemical forms the oxygen takes when bound to the coal. It has been noted that the oxidation is not uniform throughout the particle as evidenced by the formation of a discoloration of the coal near the surface⁷. This "oxidation rim" is directly related to the behavior of the coal.

The purpose of this study is to apply the unique technique of Charged Particle Activation Analysis (CPAA) to distinguish the characteristics of the oxidation process from a different point of view and define parameters which can be uniquely determined by this technique. The parameters to be determined are (1) the kinetics of the adsorption of oxygen containing species, (2) the elemental composition of the oxide layer and how deeply it extends into the particle, and (3) the number of reactive sites on or in the surface.

Experimental

The technique of Charged Particle Activation Analysis (CPAA) for analysis of oxygen in coal has been described previously.⁸ In the experiments to study the adsorption of oxygen onto the coal, a slight modification of this procedure has been used. Small lumps of coal were transferred in an oxygen-free atmosphere to a spex mixer and ground so that the particle diameter ranged from approximately 45 microns (325 mesh) to 74 microns (200 mesh). The samples were then dried at 100°C under vacuum for 18 hours to remove moisture. Again all handling of the samples was done under an inert atmosphere. The samples were removed from the vacuum oven at room temperature and exposed to the air in flat shallow pans for a given period of time. After this exposure the samples were either sealed directly into a one mil (.025 mm) aluminum packet or returned to the vacuum oven, evacuated at 65°C for 3 hours and then sealed into the packets. The packets were then irradiated with He-3 at an energy of 10 MeV. The samples were then counted and analyzed as described previously to determine the oxygen to carbon ratio.

To measure the oxygen depth profile a range of particle sizes were needed. The coal sample was ground as usual. The particles were then sorted according to size by using standard sieves. In most cases this separation procedure was done in air. An exception to this was the procedure used to determine if the oxygen to carbon ratio varied in different size coal particles before exposure to air. In that case the sieving was done under an inert atmosphere. After sieving the

coal particles were exposed to the air for 60 days in a controlled humidity room (relative humidity 45%) and then sealed into the aluminum packets for irradiation. Standards to determine the nuclear reaction cross-section ratio for the oxygen depth profile experiments were "sandwiches" made from varying thicknesses of polyester and polyethylene films layered on top of one another. The standards consisted of a film of polyester of known composition followed by a polyethylene film followed by another polyester film representing the oxide layer, the central unoxidized coal, and another oxide layer. The "sandwiches" were sealed in the aluminum packets and irradiated and counted in a manner identical to that used for the coal samples.

Experiments on the sorption of oxygen radiotracers were performed in the following way. A column was prepared by filling a 1/4" stainless steel tube one foot long with coal of 100-220 mesh. This column was placed in a gas chromatograph equipped with both a thermal conductivity detector and a radiodetector so that both a mass trace and an activity trace could be obtained for each experiment. The column temperature was lowered to -40°C using a liquid nitrogen cooling system. After the sample was injected onto the column, the temperature was held at -40°C for two minutes at which point any unreacted oxygen had eluted. The temperature of the column was then raised linearly to a final temperature of 250°C . This temperature was held for 5 minutes. Two series of experiments were carried out using radioactive oxygen-containing molecules. A Pennsylvania Anthracite column of coal never exposed to air was prepared and

exposed to molecular oxygen labelled with a trace of oxygen-15 prepared from the $^{16}\text{O}(\text{p},\text{pn})^{15}\text{O}$ nuclear reaction. A column of North Dakota Lignite was prepared and injected with a mixture of labelled O_2 , CO_2 and H_2O . The oxygen-15 in these molecules was prepared from the $^{15}\text{N}(\text{p},\text{n})^{15}\text{O}$ nuclear reaction and thus the mixture contained only a trace of molecular oxygen. The tracer, with or without added carrier, was placed in a 5 cc gas syringe and injected onto the coal column.

Results

Kinetic experiments. The experimental curves for the uptake of oxygen-containing molecules versus time are shown in Figure 1 for three types of coal. The three types all follow the same general behavior in that they show a rapid uptake of oxygen followed by a more gradual uptake. In the case of the lower rank coal, this uptake lasts for a considerable amount of time. The lower curve in each case is the uptake of oxygen containing species after the sample had been placed in the vacuum oven at 65°C for 3 hours. In all cases a considerable amount of the oxygen can be pumped off. The anthracite shows essentially no increase in oxidation of after about 15 minutes. In the lignite the irreversible uptake lasts for a very long period of time. This is probably due to chemical oxidation of the coal.

Oxygen Depth Profile. When coal samples of different particle size which had never been exposed to air were analyzed for the oxygen to carbon ratio, it was essentially the same for all sizes. When the same analysis was carried out for coal exposed to air there was a definite increase in the oxygen to carbon ratio as the particle size decreased. This indicates that there is an oxide layer on the outside of the coal particle. In order to estimate the depth of the layer a model must be used. Three models have been explored in the attempt to estimate the depth of penetration. The first of these is a layer of constant composition which falls to the unoxidized value at a point within the sphere. The second is a linear decrease in the O/C from the outside of the particle towards the center and the third is an

exponential decrease in the ratio. The depth of the oxide layer is fairly insensitive to the model chosen but the oxygen to carbon ratio on the surface of the coal particle is extremely sensitive to the model. As a result it is possible to give meaningful numbers for the depth of the oxide layer but not for the oxygen content of the surface. The curves from the model are given in Figure 2. These have been corrected for the experimentally determined nuclear cross-section ratio. Figure 3 is the data from the activation of New Mexico Sub-bituminous compared to the model curves. The values obtained for the oxide layer depths for the three types of coal are given in Table 1.

Labelled Oxygen Adsorption. When a few milliliters of oxygen labelled with a trace of O-15 were injected onto the Pennsylvania Anthracite, about 5% was retained on the column at low temperature. All of this oxygen was desorbed during the heating cycle. When a mixture of labelled O₂, CO₂ and H₂O in proportions of 80:15:5 in 5 cc of nitrogen was injected onto the column with no added carrier (approximately 10¹⁴ molecules of O₂ due to ppm impurities of O₂), all of the activity was retained on the column. When 1 cc of O₂ was added to the mixture only activities which corresponded to CO₂ and H₂O were retained on the column. When CO₂ and O₂ were added only about 5% of the activity was retained on the column. This activity probably corresponds to the water activity.

Discussion

Several salient features have emerged from work done in other laboratories on the low temperature oxidation of coal. These are listed below:

- (1) The adsorption of oxygen onto most types of coal follow Elovich kinetics i.e. a rapid uptake followed by a much more gradual uptake⁹
- (2) The oxygen adsorbed by low rank coals can form phenolic-OH or carbonyl groups^{10,11,12}. The phenolic groups can split out H₂O to form ether linkages.
- (3) Water sorption isotherms on low rank coals have a standard type II sigmoid shape typical of porous adsorbents.⁴
- (4) The heat of desorption for macroscopic amounts of water off most coals is very near that of the heat of vaporization of water.⁴
- (5) The apparent activation energies for oxidation are very low.

The current studies using radiochemical techniques are in agreement with these findings. The adsorption of oxygen-containing species onto the coal follows Elovich-type kinetics. Recent modelling studies have demonstrated the equivalence of Elovich kinetics with diffusion and adsorption in microporous solids^{13,14}. These studies tend to support the idea of solid state diffusion with the fairly low

activation associated with these processes as a rate limiting step in the coal oxidation. The depth of penetration of the oxygen seems to be directly related to the porosity of the coal. In the cases studied here the anthracite showed the least penetration while the lignite showed the deepest. It has been possible to demonstrate that for the lower rank coals that there are very few (more than $10^{14}/g$ but less than $10^{19}/g$) reactive sites for strong oxygen adsorption. From the data collected we wish to propose the following mechanism for the low temperature oxidation.

Oxygen is adsorbed weakly onto the surface of the coal. This adsorbed oxygen can then migrate across the surface or into the interior of the coal particle to a reactive site at which point it becomes chemically bound. The form of this chemical bond is phenolic-OH, carbonyl or peroxide type moieties. As the surface layers become saturated the oxygen will diffuse deeper into the particles through pores and crevices to react with sites within the coal particle. This is the second slower part of the adsorption process. At some point the chemical potential against diffusion into the particle becomes great enough that the oxidation from the exterior of the particle ceases. This point will be determined by the porosity of the coal and the temperature at which the oxidation is carried out. As temperature is increased the oxide layer will extent deeper into the coal particle.

References

1. See for example Dryden, I. G. C. in Chemistry of Coal Utilization, Supplementary Volume (Ed. H. H. Lowry) Wiley, New York, 1963, Ch. 6, p. 272.
2. Painter, P. C., Snyder, R. W., Pearson, D. E., Kwong, J. FUEL, 59, 282 (1980).
3. Bouwman, R. and Freriks, I. L. C. FUEL, 59, 315 (1980).
4. Bhattacharyya, K. K. FUEL, 50, 214 (1971).
5. Avison, N. L., Winters, R. M., and Perlmutter, D. D. AIChE Journal 25, 773 (1979).
6. Swann, P. D., Allardice, D. J. and Evans, D. G. FUEL, 53, 85 (1974).
7. Dugan, P. and Moran, V. J. FUEL, 49, 415 (1970).
8. Schlyer, D. J., Ruth, T. J. and Wolf, A. P. FUEL, 58, 208 (1979).
9. Newman, J. O. H. et al. Nature 240, 280 (1967).
10. Ignasiak, B. S., Clugston, D. M., Montgomery, D. S. FUEL, 51, 76 (1972).
11. Swann, P. D. and Evans, D. G. FUEL, 58, 276 (1979).
12. Ignasiak, B. S., Szaldow, A. J. and Berkowitz, N. FUEL, 53, 229 (1974).
13. Harris, J. A. and Evans, D. G. FUEL, 54, 277 (1975).
14. Yang, R. T. and Wong, C. J. Phys. Chem. 84, 678 (1980).

Table 1
Oxide layer depths

<u>Coal type</u>	<u>Depth in microns</u>
Anthracite	4
Sub-bituminous	7
Lignite	10

FIGURE CAPTIONS

Figure 1 Uptake of oxygen by selected coal versus time.

● represent no heat or pumping. ▲ heated at 65°C
under vacuum.

Figure 2 Volume of oxide layer divided by the total volume
of the particle versus particle diameter for model.

Figure 3 Comparison of experimental data with model for New
Mexico Sub-bituminous.

UPTAKE OF OXYGEN BY SELECTED COALS

NEW MEXICO SUB-BITUMINOUS