AN EPR SPIN PROBE STUDY OF THE EFFECTS OF SHORT TERM OXIDATION AND DEHYDRATION ON THE MOLECULAR ACCESSIBILITY IN ILLINIOS #6 COAL

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ABSTRACT

The effects of short term oxidation and dehydration on the structure and chemistry of the intercalation of potential catalysts into a coal structure during swelling was accomplished using the EPR spin probes 3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl (VI), TEMPAMINE (VII) and TEMPO (VIII) as guest molecules. Samples of Illinois #6 APCS coal were exposed to both oxygen and argon for time periods from 30 seconds to 50 minutes after removal from the sealed ampules. The results show that dehydration significantly affects the retention of spin probes with polar functional groups in as little as 30 seconds. It is also observed that structural changes upon exposure of the coal sample to air occur in under 5 minutes. The individual contributions of dehydration and oxidation are discussed.

INTRODUCTION

Exposure of coal to air before conversion has been a big concern in coal chemistry.[1] It has been suggested that the structure of coal can be altered in as little as two minutes exposure to air.[2] If so, this would make it difficult to carry out accurate structural studies on coal. The previous papers have shown that both dehydration and oxidation[3] change the physical and chemical structure in coal enough so that the molecular accessibility in coal is significantly altered. It is the goal of this paper to determine how quickly and to what extent oxidation or dehydration can affect the structure of coal using the EPR spin probe technique.[3-6] From the previous paper, it was determined that Illinios #6 coal would exhibit the greatest changes in structure upon dehydration and oxidation. Lower ranked coals are more affected by water removal, but do not show as much change during oxidation. A flow of dry oxygen over the coal would result in both loss of water and oxidation. A flow of argon, however, would result in only dehydration since it is inert. By comparing the difference in the effects of both gases on coal, the effects of oxidation alone can be determined. Argon was chosen as the inert gas because of its ability to cover the samples completely with far less difficulty than nitrogen or other inert gases commonly used. Toluene was chosen as a swelling solvent because it does not significantly open the structure of the coal yet allows for diffusion of the spin probes into the available structure. Pyridine was used because it completely opens up the structure and allows for examination of hydrogen bonding sites in coal. Spin probe VIII is a small spherically shaped molecule with no polar substituents. The intercalation of this spin probe simply measures physical changes in the coal structure. Spin probe VI has a carboxyl group and is a hydrogen bond donor with the ability to detect polar interaction in the coal. Spin probe VII has an amino group and is a hydrogen bond acceptor with a much stronger ability to detect polar interactions than spin probe VI. By comparing the retention data for all three spin probes, a more complete picture of the nature of the probe-coal interactions can be obtained.

EXPERIMENTAL

The vial containing the APCS coal[7] Illinois #6 was opened in a moisture free, pure argon environment and aliquots of coal immediately placed into an apparatus constructed to allow the flow of only pure argon or oxygen over the surface of the fresh coal. A sample of fresh coal was also swelled in each of the spin probe solutions to establish a point of no oxidation or dehydration. It should be noted that the coal was exposed to the argon environment for 10 to 15 seconds before it was placed into the swelling solvent. One aliquot of the coal was exposed to argon and the other to oxygen. A flow of approximately 40 mL per minute of each gas was maintained through the coal sample for 30 seconds, 5 minutes and 50 minutes. The coal was then swelled in a spin probe solution of toluene or pyridine for 18 hours. The swelling solvent was removed and the spin probe retention was measured by EPR. Samples were replicated so that some indication of reproducibility could be obtained.

The three spin probes used in this study are shown in figure 1. Spin probes 3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl (VI), TEMPAMINE (VII) and TEMPO (VIII), were chosen so that changes in both physical and chemical structure could be observed. All three have similar molecular volumes, but different chemical reactivities with the coal structure.

A detailed description of the experimental method for the intercalation of spin probes using swelling solvents has been previously published.[4-6]

RESULTS AND DISCUSSION

The effects of exposure of Illinois #6 swelled in toluene to both argon and oxygen on the retention of spin probe VI are shown in Figure 2(A). Dramatic effects are seen on the retention of spin probe VI after just 30 seconds. After 30 seconds, a decrease of over 1200 x 10^{15} spins per gram is observed for coal exposed to argon. The decrease in retention is somewhat less pronounced for exposure to oxygen. After 5 minutes of exposure to argon, the retention characteristic of Illinois #6 returned to that found for fresh coal. The increase for oxygen followed the same trend, but to a far less extent. At 5 minutes, the difference between dehydrated (argon only) and oxidized coal is significant. This difference becomes more pronounced after 50 minutes of exposure. In the first 5 minutes, oxidation seems to cause changes which counteract the effects of dehydration. Beyond 30 seconds, oxidation caused a decrease in the retention of spin probe VI, indicated by the increasing retention difference with exposure to oxygen as compared with argon. At 5 minutes or more, dehydrated coals (argon) have a much higher retention of spin probe VI than dehydrated and oxidized coal.

The effects of dehydration and oxidation on the retention of spin probe VII in Illinois #6 coal swelled in toluene are shown in Figure 2(B). A decrease in spin probe retention of 2500 x 10^{15} spins per gram is observed upon exposure to either argon or oxygen for 30 seconds. This change represents an order of magnitude decrease in spin probe VII retention. This is followed by an increase in retention at 5 minutes of exposure, and then a more gradual decline in molecular accessibility for exposure up to 50 minutes. These results are similar to those obtained for spin probe VI in Figure 2(A) except that after 30 seconds, the coal exposed to oxygen shows improved retention over coal exposed to argon. This difference becomes less significant after 50 minutes of weathering. Again, the shape of each plot is very similar, indicating that the more severe changes are caused by dehydration rather than oxidation.

Structural changes in Illinois #6 coal swelled in toluene can be observed in Figure 2(C) by the retention of spin probe VIII. The plots generated are very similar to those shown in Figure 2(A) for spin probe VI. A decrease in retention is observed in the first 30 seconds, followed by an increase at five minutes and a gradual decrease in retention up to 50 minutes. The increase in spin probe retention exhibited at 5 minutes of exposure is much greater for coal exposed to argon than oxygen. The initial decrease in spin probe concentration is most likely due to a structural collapse or increased cross-linking, making the structure less accessible since the structure was likewise inaccessible to spin probes VI and VII. It also appears that the changes which occur due to oxidation counteract (to a limited degree) the changes brought about by dehydration in the first 5 minutes. Figure 2(C) shows that some of the effect seen in Figures 2(A) and 2(B) are due to changes in the physical structure since spin probe VIII has no reactive substituents, and shows similarly shaped plots. It is important to note that a retention of nearly 500×10^{15} spins per gram is observed after 30 seconds of exposure to argon. This figure is at least double any of the spin probe VIII concentrations found in Illinois #6 coal fresh, vacuum dried or weathered in air.

When Illinois #6 is exposed to oxygen and argon and then swelled in pyridine in the presence of spin probe VI, retention characteristics exhibit changes illustrated in Figure 3(A) which are similar to those shown for coal swelled in toluene. A decrease in spin probe retention is observed after 30 seconds of exposure to oxygen or argon. Although this decrease is quite small in comparison to those shown for polar spin probes in toluene, it does indicate that the inaccessibility of these spin probes at 30 seconds of exposure is not entirely due to changes in physical structure, since pyridine is capable of disrupting most polar interactions in coal. Again, after 5 minutes of exposure, the retention of spin probe VI is increased to a point which is considerably greater than the initial retention, more so for coal exposed to oxygen than argon. As the time of exposure is extended to 50 minutes, the retention of spin probe VI in dried (exposed to argon) coal increases slightly while the retention in oxidized (exposed to oxygen) coal decreases.

The results of changes in the retention of spin probe VII in Illinois #6 coal upon exposure to oxygen and argon are shown in Figure 3(B). As seen in the previous figures, a decrease in retention is observed for exposure to both oxygen and argon, but more so for oxygen. After 5 minutes in argon, the coal exhibits improved retention, far surpassing the accessibility of the fresh coal. Five minutes of exposure to oxygen does cause an increase in retention from the 30 second exposure, but the increase is still below the retention in the original fresh coal. After an exposure of 50 minutes, the retention of spin probe VII under both circumstances, increases (although to a greater extent in oxidized coal). It would appear that within the first 5 minutes, oxidational changes inhibit the accessibility of spin probe VII into the coal structure.

The retention of spin probe VIII in Illinois #6 coal upon exposure to argon and oxygen for up to 50 minutes is shown in Figure 3(C). Very little change in the structure is observed for 30 seconds of exposure. After 5 minutes of exposure, however, increase retention was observed for both dried and oxidized coal. This is particularly pronounced for oxidized coal. As the exposure time continues beyond five minutes, the retention of spin probe VII in coal exposed to oxygen decreases significantly, while the retention in coal exposed to argon increases. It is clear that oxidation has an effect on the physical structure of the coal which can suppress changes caused by water loss.

A comparison of Figures 2(A) to 2(C) and 3(A) to 3(C) shows that the retention characteristics of spin probe VI closely mirror those of spin probe VIII. This would suggest that changes in the physical structure of coal can influence the retention of spin probe VI as well. Also since oxidation produces an increase in retention of spin probe VII in coal swelled in toluene, but a decrease in the retention of spin probe VI, it would seem that oxidation causes an increase in active sights capable of being hydrogen bond donors.

CONCLUSION

It is clearly shown that significant structural changes in Illinios #6 can occur in as little as 30 seconds of exposure to a dry gas environment. This should be taken into consideration when the use of an experimental method to determine the structure of coal requires exposure to air for any length of time.

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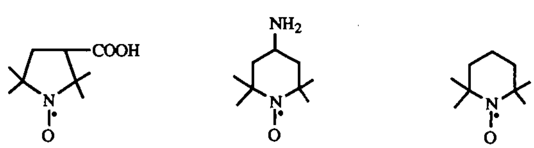

VI VII VIII

Figure 1. Spin probes VI, VII, and VIII

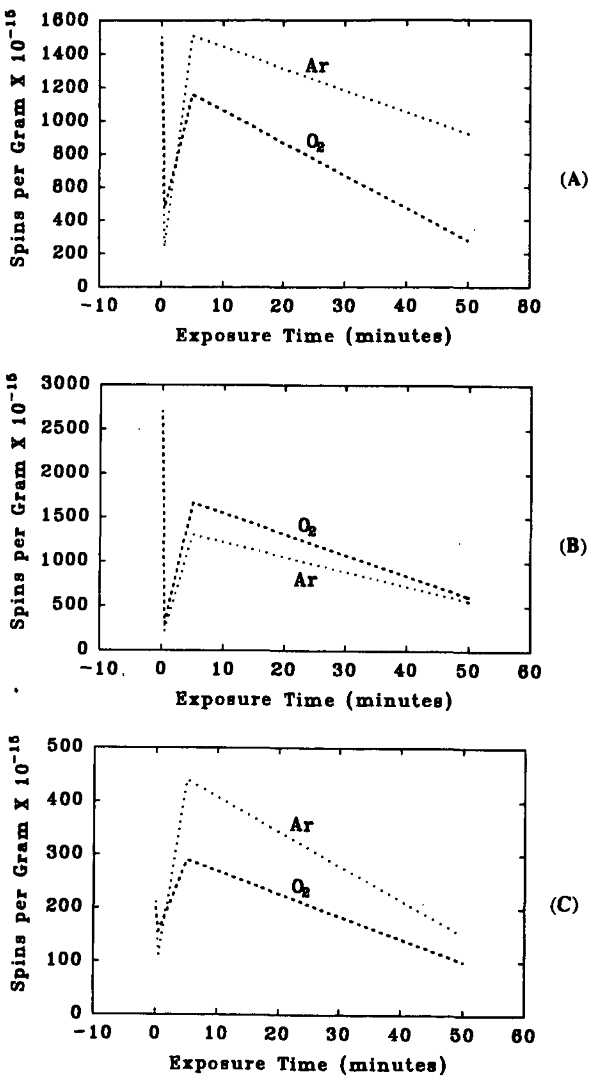

Figure 2. The retention of spin probes (A) VI, (B) VII and (C) VIII in Illinois #6 APCS coal swelled in toluene versus exposure to oxygen or argon in minutes.

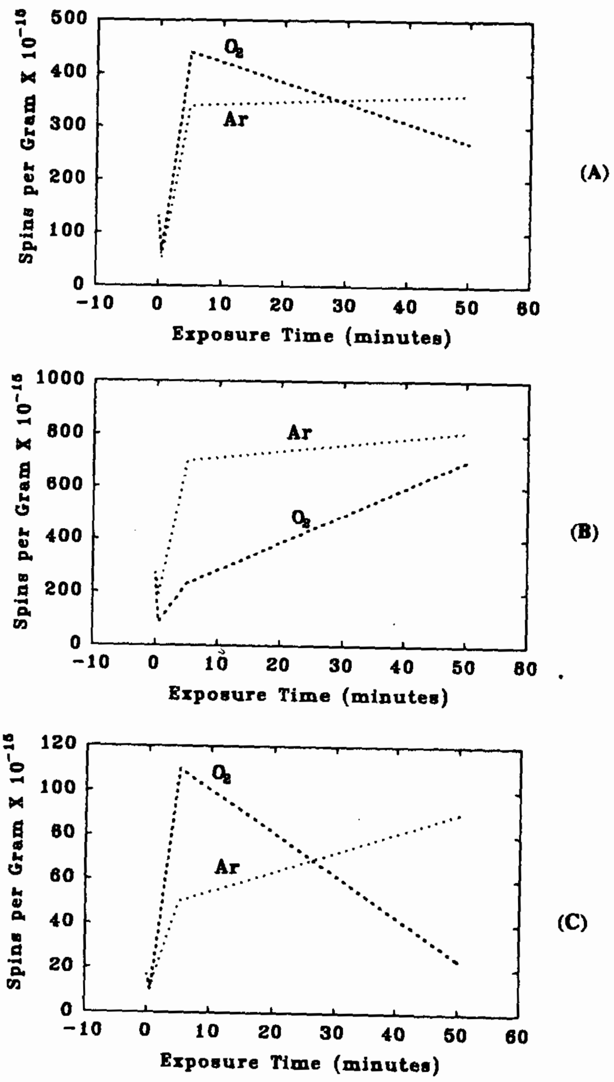

Figure 3. The retention of spin probes (A) VI, (B) VII and (C) VIII in Illinois #6 APCS coal swelled in pyridine versus exposure to oxygen or argon in minutes.