

# THE INTERPRETATION OF SECONDARY INTERACTIONS DURING TEMPERATURE PROGRAMMED DESORPTION OF OXYGEN COMPLEXES IN TERMS OF CHAR POROSITY MORPHOLOGY

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## INTRODUCTION

Our recent work [1] concerning temperature programmed desorption (TPD) of oxygen complexes from oxidized coal char surfaces has demonstrated that secondary interactions during the thermal desorption process can convolute the resultant spectra. Their effects are generally enhanced by the presence of inorganic mineral matter impurities and seem to be influenced by the nature of the char porosity [2]. However, the relationship between pore morphology and the behavior of these secondary interactions was not systematically explored in our previous work performed on coal chars at constant burn-off [1]. In the current communication we investigate the variation of the extent of secondary interactions with char burn-off in oxygen. As shown, the results of this work suggest that the behavior of secondary interactions during TPD exhibit some potential as a diagnostic technique for monitoring the variation and development of char porosity; perhaps as a complement to other methods such as gas adsorption.

We have identified two different types of secondary interactions [1]. One involves the reaction of desorbed "free" CO in the process of out-transport to the bulk gas phase with other oxygen surface complexes to produce CO<sub>2</sub>. This is primarily manifested as a reflection or satellite peak under primary CO desorption features, the largest of which is typically centered ca. 1000K. The other type of secondary interaction involves rechemisorption of "free" CO onto unoccupied active sites to form more stable complexes [1]. This is usually manifested as a high temperature peak or shoulder in TPD spectra, typically centered ca. 1200K. It will be demonstrated here that secondary CO<sub>2</sub> production appears to take place in the smaller pores of the char (i.e., the microporosity), while CO rechemisorption takes place primarily in the larger pores.

## EXPERIMENTAL

Samples of two precursor coals -- Wyodak and Pittsburgh #8 -- were obtained from the Argonne Premium Coal Sample Bank. The coals were pyrolyzed in ultrahigh purity helium at 1273K with a soak time of one hour. Care was taken to insure that the coals did not come into contact with

oxygen during handling.

The chars from this treatment of the two coals exhibit distinct pore morphologies. During slow carbonization, and in the complete absence of oxygen, Pittsburgh #8 passes through a fluid state during which most of its original microporosity is lost [3]. The resultant char has a very low surface area and develops porosity during subsequent gasification. Conversely, Wyodak is a subbituminous coal which does not proceed through a fluid phase upon carbonization. Consequently, much of the original porosity present in the coal is preserved or enhanced during carbonization. A number of studies indicate that the original porosity consists of a random network of pores with extensive "ink-bottle"-type restrictions and a significant amount of "closed" porosity [3,4]. Our conclusions support these observations. Therefore, gasification of the Wyodak coal char not only develops new porosity, but also tends to enlarge restrictions and render previously closed pores accessible.

Details of the TPD apparatus and the experimental procedures are described elsewhere [1]. The typical sample size was ~10 mg, and ultrahigh purity helium was used as the carrier gas. A heating rate of 100K/min was used for the experiments reported here because this gave good peak resolution [2] and reasonable gas desorption rates. Also, our results [2] suggested that this heating rate tended to maximize the effects of secondary interactions for a number of different coal chars. Char gasification was performed in a TGA apparatus in 0.1 MPa of O<sub>2</sub> at the selected temperature. The 77K N<sub>2</sub> isotherms were measured in a Quantachrome Quantasorb gas adsorption apparatus. No significant differences were observed between N<sub>2</sub> isotherms and CO<sub>2</sub> isotherms obtained at higher temperatures for these chars.

## RESULTS AND DISCUSSION

In a companion paper in this symposium [5], it is demonstrated that total oxygen TPD spectra from coal chars can be deconvoluted from secondary interactions by fitting the leading edge of the principal desorption feature to a Gaussian distribution. The residual spectrum, typically centered *ca.* 1200K, is believed to be primarily due to rechemisorbed CO. Typical total oxygen TPD spectra for Wyodak coal char gasified to varying extents are presented in Figure 1. The CO desorption spectra can also be fit to Gaussians in a similar fashion, since CO accounts for the majority of the total oxygen desorbed. For our purposes here, the resultant integral under the CO Gaussian will be termed "1000K CO," and that under the residual CO will be termed "1200K CO." Due to the relatively low amounts of primary CO<sub>2</sub> formed at the lower temperatures, all the CO<sub>2</sub> will be referred to as secondary CO<sub>2</sub>.

Figures 2 and 3 show how the three contributions to total oxygen desorption -- "1000K CO," "1200K CO," and "secondary CO<sub>2</sub>" -- vary as a function of burn-off for Wyodak and Pittsburgh #8 coal chars, respectively. These figures reveal some interesting behavior. Consider for example the analysis of these data presented in Figure 4. As shown, the "1200K CO/secondary CO<sub>2</sub>"

ratio increases continuously with increasing burn-off for the Wyodak char, while it remains essentially constant for the Pittsburgh #8 coal char. This will be shown to be consistent with the expected porosity development for these chars with burn-off.

The available evidence suggests that the 1200K oxygen complexes arise primarily from "free" CO rechemisorbed during the TPD process, and not from just chemically different (i.e., from the 1000K complexes) oxygen complexes formed during steady-state gasification/oxidation. If these complexes did arise from the latter source, their population would tend to *increase* relative to the "low temperature" complexes with exposure under gasification conditions, rather than *decrease*, as generally observed. In fact, for both Wyodak and Pittsburgh #8, the 1200K CO shoulder actually decreases at high burn-off. Product CO formed during isothermal, steady-state gasification is not appreciably chemisorbed because CO chemisorption has been shown to be a highly activated process with a low sticking probability [6]. As a consequence, at the relatively low temperatures used for oxygen gasification, the rate of rechemisorption of product CO is too low to occupy the high energy sites available under gasification conditions. Moreover, any sites that may be accessible under these conditions would react preferentially with oxygen, which is present in considerably greater amounts and exhibits much greater reactivity towards the formation of stable complexes. During TPD, however, the high temperatures experienced during the nonisothermal heating process in the absence of oxygen serves provides the conditions necessary to "fix" a certain fraction of the desorbed CO.

The available evidence suggests that secondary CO<sub>2</sub> formation is a phenomenon associated with the smaller pores (e.g., the micropores) rather than the larger pores. For example, it has already been shown in Figure 4 that the "1200K CO-to-secondary CO<sub>2</sub>" ratio is a minimum for zero burn-off Wyodak, which exhibits a "Type I" N<sub>2</sub> adsorption isotherm (as shown in Figure 5), characteristic of microporous materials. Further evidence derives from other oxidation studies where, for example, it has been reported that, due to the large size of the nitrate ion, nitric acid does not oxidize the surface within the microporosity, but rather only that accessible in the meso- and macroporosity, as well as the external surface [7]. TPD spectra on such nitric acid oxidized chars exhibit no secondary CO<sub>2</sub> in comparison to gas oxidized chars [7]. We obtained similar results from hydrogen peroxide-oxidized chars [8]. If secondary CO<sub>2</sub> production did take place appreciably in the larger pores, then significant amounts of secondary CO<sub>2</sub> would be expected from such chars. On the other hand, significant, discernible 1200K CO, which is believed to be due to CO rechemisorption, was evident upon TPD for both nitric acid and hydrogen peroxide-oxidized chars [8]. The reasons for this behavior are still a matter for speculation, but it may be that secondary CO<sub>2</sub> production takes place primarily in micropores for the same reason that a normal distribution of bond energies occurs [5]; that is, the low temperature, less stable complexes would also tend to be more reactive towards attack by "free" CO as they would be towards desorption. In a similar fashion, there is as yet no definitive evidence as to whether CO rechemisorption can occur in micropores to an appreciable extent. However, it is noted that the zero burn-off Wyodak which is known to have significant microporosity does not exhibit any

1200K CO. It may be that CO rechemisorption cannot compete with the more favorable secondary CO<sub>2</sub> production in the micropores. In any case, any CO that might be rechemisorbed in micropores may also participate in secondary CO<sub>2</sub> formation, and thus may not survive to desorb in the higher temperature peak *ca.* 1200K.

In summary then, it is hypothesized that secondary CO<sub>2</sub> formation takes place primarily in the more restrictive porosity, such as the microporosity, whereas CO re-chemisorption is favored in the larger pores. Therefore, the two secondary interactions are in a sense complementary and sensitive to different aspects of the char porosity. In this manner, the decrease in the relative magnitudes of both secondary interactions at high burn-off for Wyodak, as indicated in Figure 2, is consistent with a reduction in total porosity as a result of pore collapse at high burn-off.

It is of interest to compare these observations with information available from adsorption isotherms. 77K N<sub>2</sub> adsorption isotherms for gasified Wyodak and Pittsburgh #8 coal chars are presented in Figures 5 and 6, respectively. Examination of Figure 5 shows that at zero burn-off, the Wyodak char exhibits a classical "Type 1" isotherm [9], characteristic of a microporous material. Figure 2 shows that the secondary CO<sub>2</sub> is relatively high, and that there is virtually no 1200K CO for this char. Therefore the interpretations of both isotherm and TPD spectra are consistent for this char. At 15.2% burn-off, the isotherm appears to have evolved into something in between a "Type 1" and "Type 2". This suggests that at this stage micropores are still a significant part of the Wyodak porosity, but that larger porosity is also developing with burn-off [9]. Again, this is consistent with the increase in the relative amount of 1200K CO to secondary CO<sub>2</sub>, as shown in Figure 4. At 48.6% and 61.8% burn-off, the isotherms appear to more closely approach "Type 2" behavior, indicative of larger porosity, and, consistently, secondary CO<sub>2</sub> decreases and 1200K CO increases significantly in this range. The corresponding N<sub>2</sub> surface area goes through a maximum between 15.2% and 48.6% burn-off. Following the maximum, the general tendency is for microporosity to be lost at the expense of larger pores.

For the Pittsburgh #8 char, the isotherms shown are similar for all degrees of burn-off, with some definite "Type 2" behavior characteristic of materials with significant mesoporosity. This is consistent with the even maintenance of the relative contributions of the two different types of oxygen over the entire burn-off range, as shown in Figure 4.

Proper interpretation of the TPD spectra may give additional insight into the nature of the porosity. For example, the isotherms for Wyodak burned-off to 61.8% at 623K and Pittsburgh #8 burned-off to 46% at 723K in Figures 5 and 6 are quite similar in shape, except that the Wyodak isotherm is about a factor of two greater in amplitude. Therefore, if one were to draw conclusions on the pore morphology based upon this evidence alone the conclusion would be that they were chars of similar pore structure. However, Figure 4 reveals that for the 61.8% gasified Wyodak, the ratio of 1200K CO to secondary CO<sub>2</sub> is 1.47, compared to 0.36 for the 46% gasified Pittsburgh

#8. This suggests that a much higher proportion of the surface area is present in restrictive porosity for the Pittsburgh #8 coal char in this particular case.

At this point it should be noted that integral measures of the various contributions to desorbed oxygen may not be a good indicator of total surface area or pore volume. This is especially evident for the Pittsburgh #8 coal char for which the total oxygen coverage increases steadily with burn-off in Figure 3, whereas the  $N_2$  surface area goes through a maximum between 25 and 46% burn-off (cf. Figure 6). It has been well established that total surface area, as measured by gas adsorption techniques, is generally not as good an indicator of char reactivity as is active surface area, as measured by oxygen chemisorption. The oxygen complexes that give rise to secondary interactions are obviously more related to active surface area and thus may behave in a similar fashion. However, it has also been shown that for some chars the amount of oxygen adsorbed under chemisorption conditions can be a fraction of that adsorbed under gasification conditions [10], and also that the amount of chemisorbed oxygen can yield larger apparent surface areas than the total surface area measured by gas adsorption [11]. Therefore, it is not clear at this stage exactly how the integrated amounts of the three contributions to desorbed oxygen are related to the absolute amount of macro-, meso-, and microporosity. In any case, the principal point to be made here is that the *relative* magnitudes of these contributions seem to be related to the char porosity morphology, and, moreover, seem to be quite sensitive to morphological changes during gasification.

## CONCLUSIONS

The kinetics of secondary interactions during thermal desorption processes are not yet sufficiently well understood to allow a more quantitative treatment of pore morphology at this time. However, we have demonstrated that the *relative* magnitudes of secondary interactions appear to be sensitive to pore morphology. Although the total amount of surface complex may not be a good indicator of total surface area, the *relative* extents of secondary interactions can reveal information about the pore morphology that is difficult to derive from adsorption isotherm analysis. Thus, the two methods are complementary.

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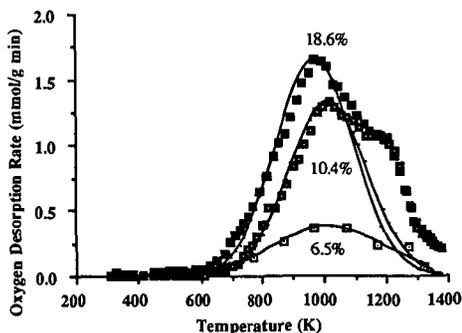


Figure 1. 100K/min TPD spectra total oxygen desorption spectra from Wyodak coal char gasified to varying extent in 0.1MPa oxygen at 573K and their Gaussian fits.

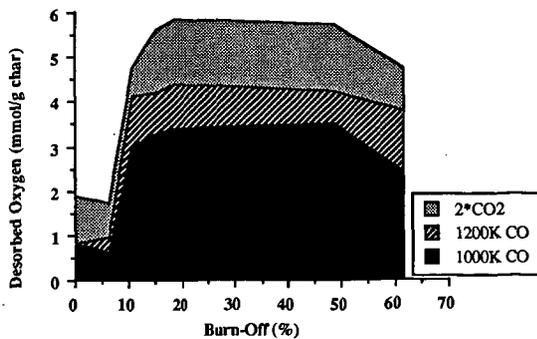


Figure 2. Desorbed oxygen distribution vs. burn-off for Wyodak coal char.

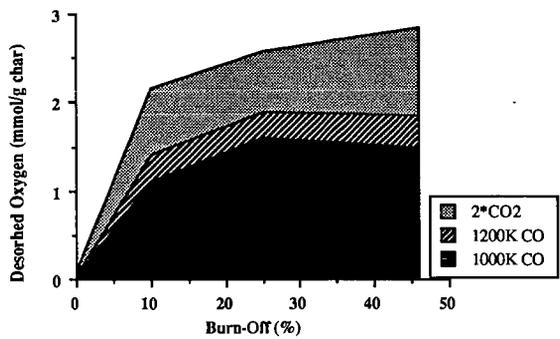


Figure 3. Desorbed oxygen distribution vs. burn-off for Pittsburgh #8 coal char.

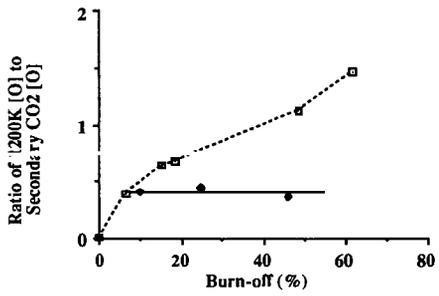


Figure 4. Variation of the ratio of [O] from 1200K CO to [O] from secondary CO<sub>2</sub> production as a function of char burn-off. --- Wyodak coal char; — Pittsburgh #8 coal char.

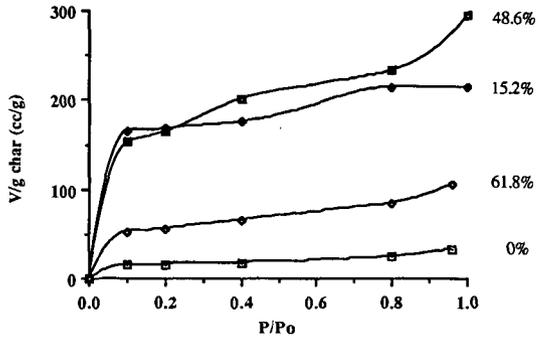


Figure 5. 77K nitrogen adsorption isotherms for Wyodak coal char gasified to varying extents in 0.1MPa O<sub>2</sub> at 623K.

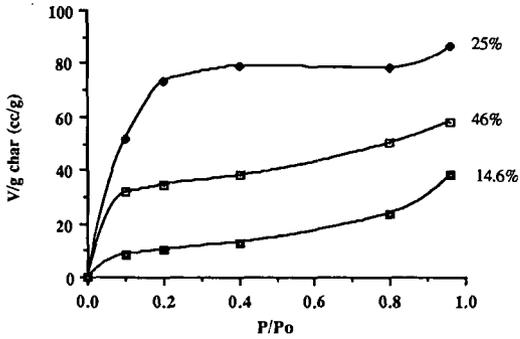


Figure 6. 77K nitrogen adsorption isotherms for Pittsburgh #8 coal char gasified to varying extents in 0.1MPa O<sub>2</sub> at 623K.