POROSITY DEVELOPMENT *Via* TPD

L. Zhang and J.M. Calo
Chemical Engineering Program
Division of Engineering
Brown University
Providence, Rhode Island 02912

Introduction

Porosity and porosity development of carbons and chars can have a significant influence on the accessibility of fluid species to their internal surface area. This is of direct relevance to the rates of all heterogeneous interactions occurring within these materials. The most often used techniques for porosity characterization of these types of materials involves physical adsorption of gases. However, these well known methods can often be labor-intensive and time-consuming. Consequently, there is a continuing need for new methods to supplement or even replace some of these techniques.

In the current work, one such new approach is explored for the characterization of porosity and the study of porosity development during gasification or activation processes. This approach involves the interpretation of post-activation temperature programmed desorption (TPD) spectra. The results show that there exist both qualitative and quantitative relationships between porosity development and post-reaction desorption features of oxygen surface complexes formed during the activation process.

Experimental

The samples used in the current study were prepared from Wyodak subbituminous and Pittsburgh bituminous coal samples, obtained from the Argonne Premium Coal Sample Bank [1]. Carbonization was conducted in a tube furnace in flowing ultra-high purity helium for two hours at 1000°C. A smaller sample (on the order of 20-60 mg) from this larger char preparation was used for each run in the reaction/desorption system.

All the oxidations and thermal desorptions were carried out in the same TPD-MS/TGA apparatus without removing the samples and exposing them to the ambient environment. The samples were all gasified in 0.1MPa of oxygen at 420°C for Wyodak and 470°C for Pittsburgh #8, to varying extents. All the TPDs were carried out at a heating rate of 50K/min to 1200°C in ultra-high purity helium carrier gas, passing over the sample in downflow at a total pressure of about 20 torr. Detection of the desorbed species was performed using a quadrupole mass spectrometer (MS) which sampled a small portion of the total gas flow through a vacuum leak valve.

Adsorption isotherms of the various samples were obtained using a Quantachrome Quantasorb surface area analyzer with nitrogen at 77K.

Results and Discussion

The total specific surface area, external surface area, and micropore volume of the samples were determined from the nitrogen isotherm data using the so-called α-plot method [2]. This technique is based on a comparison of the shape of the adsorption isotherm of a sample with that of a standard reference material. The adsorption data is replotted as an α-plot using the standard material isotherm data expressed as values which represent the adsorbed amounts normalized by that adsorbed at a particular point on the isotherm (typically $p/p° = 0.4$); i.e., $\alpha = n/n_{0.4}$. The slope of the plot at low α provides the total surface area; the slope of the upper linear branch gives the nonmicroporous surface area; and the extrapolation of this branch of the curve to $\alpha = 0$ provides the total micropore volume.

α-plots were constructed for all the nitrogen adsorption isotherms for the current samples using data for the standard nonporous carbon proposed by Rodriguez-Reinoso *et al.* [3]. Corresponding surface areas and pore volumes were also obtained *via* comparison with the isotherm for the reference adsorbent given in this reference [3], following the data work-up procedures contained therein.

The resultant CO and CO_2 desorption spectra from post-reaction TPD experiments for both types of char samples were qualitatively similar, but differed quantitatively by substantial amounts. Both CO and CO_2 spectra exhibited two major desorption features which were analyzed by fitting them to Gaussian peaks.

Figure 1 presents a comparison of the specific gasification rate, the total amount of CO desorbed upon TPD (i.e., the integrals), and the specific surface area, as determined from the α-plot analysis of the nitrogen isotherms, as a function of burn-off for the Wyodak char samples. As shown, all three data sets exhibit similar trends with burn-off. That is, they all initially increase with burn-off, attain peak values in the range of 30 - 40% burn-off, and decrease thereafter as gasification proceeds. On the other hand, as shown in Figure 2, both the external surface area, as determined from the α-plot analysis of the nitrogen isotherms, and the total amount of CO_2 desorbed, increase monotonically with burn-off. The relationship between them is almost linear. The results for the Pittsburgh #8 char samples are qualitatively similar, although the surface areas and the porosity evolution history for these samples are substantially different than for the Wyodak samples.

These results suggest that the entire pore structure is involved in the formation of CO-evolving complexes during gasification, but that the CO_2-evolving complexes are formed primarily on the surfaces of the larger porosity. This result is consistent with the work of Otake and Jenkins [4], who have shown that high temperature evolution of CO_2 results from the thermal decomposition of large carboxylic anhydride complexes {O=(C)-O-(C)=O} which may not form in the smaller microporosity. Related carboxylic acid groups have also been identified using FTIR spectroscopy on the surfaces of the larger pores in other carbons [5].

Conclusions

The data presented demonstrate that a strong relationship exists between the pore structure of chars and the CO and CO_2 evolved during thermal desorption following burn-off in oxygen. This has been shown for two chars that exhibit significantly different porosity development histories. Work is proceeding to place these observations on a more quantitative footing, and to ascertain whether similar correlations result for other activating agents.

Acknowledgement

References

1. Vorres, K.S., *Users Handbook for the Argonne Premium Coal Samples*, ANL/PCSP-93/1, DOE, Argonne, Il, 1993.
2. Gregg, S.J., and Sing, K.S.W., *Adsorption, Surface Area, and Porosity*, 2nd ed., Academic Press, NY, 1982.
3. Rodriguez-Reinoso, F., Martin-Martinez, J.M., Prado-Burguete, C., and McEnaney, B., *J. Phys. Chem.* **91**, 515 (1987).
4. Otake, Y. and Jenkins, R.G., *Carbon* **31**, 109 (1993).
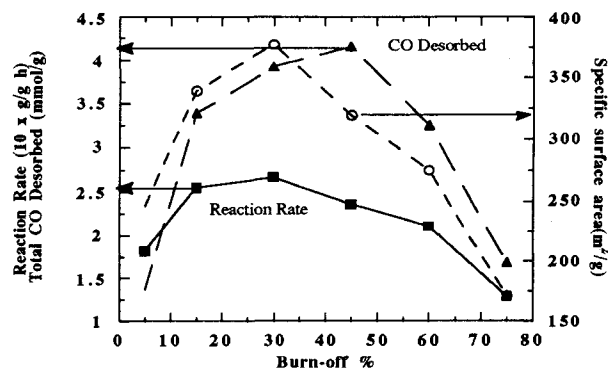5. Starsinic, M., Taylor, R.L., Walker, P.L., Jr., and Painter, P.C., *Carbon* **21**, 69 (1983).

Figure 1. Comparison of reaction rate, specific surface area, and total desorbed CO as a function of burn-off for Wyodak char gasified in 0.1MPa of oxygen at 420°C.
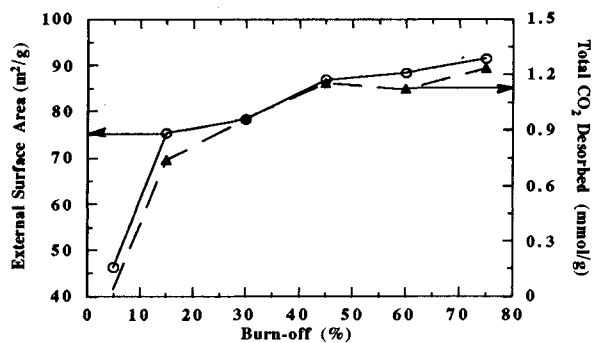

Figure 2. Comparison of external surface area and total desorbed CO_2 as a function of burn-off for Wyodak char gasified in 0.1MPa of oxygen at 420°C.