THE ROLE OF MICROPOROSITY IN CARBON OXIDATION REACTIONS

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Introduction

The role of microporosity in carbon oxidation has been debated for many years. Most detailed studies conclude that it cannot be utilized, even under nominally Zone I conditions. Many empirical studies still normalize rates using micropore dominated surface areas. This study examines the utilization and development of micropore area in NO gasification, drawing upon results from several different oxidation reactions.

Experimental

The char reactivity measurements were performed in an Online Instruments TG-Plus thermogravimetric analyzer. The reactions were performed in a flow of helium and oxidizing gas (e.g., NO) with a gas flow rate of 230 cc/min. Further details of the procedures are available elsewhere [1]. Two carbons were selected for study. Wyodak coal char samples were prepared by pyrolysis in inert gas at 1173 K for two hours. The other sample was polycrystalline graphite. Nitrogen isotherms and specific surface areas were determined in an automated volumetric gas adsorption apparatus at 77 K. Pore size distributions were determined using the method proposed by Barrett, Joyner and Halenda [2] (the BJH method).

Results and Discussion

We earlier presented results illustrating that the reaction of NO with a char derived from Wyodak coal can exhibit Zone II (pore diffusion-limited) reaction behavior [2]. The Arrhenius plot for reaction of the char with 0.82 kPa of NO partial pressure is shown as Figure 1. The well-established two-regime reaction behavior is seen at low temperatures [3]; these regimes both involve intrinsic kinetic control, i.e., Zone I. The highest temperature regime has been hypothesized to involve transition to Zone II. The Dubinin-Radushkevich micropore volume is shown in Figure 2 as a function of burn-off. Nitrogen was used as the adsorbate, so the well-known phenomenon of opening up initially inaccessible microporosity is clearly seen at low burn-offs. The early porosity development in Zone I suggests that there exists

a significant amount of marginally accessible porosity in the raw char which is opened at the start of the gasification process. This microporosity is gradually lost through pore widening at high burn-offs, as shown in Figure 3. The pattern is similar in the case of the Zone II gasified char, except that the amount of porosity opened
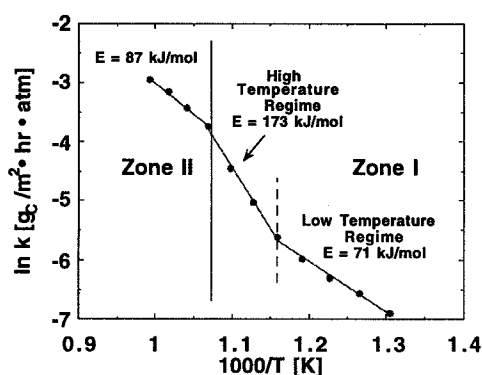

Figure 1. Reaction rate of NO with Wyodak char, presented as a rate per BET surface area.
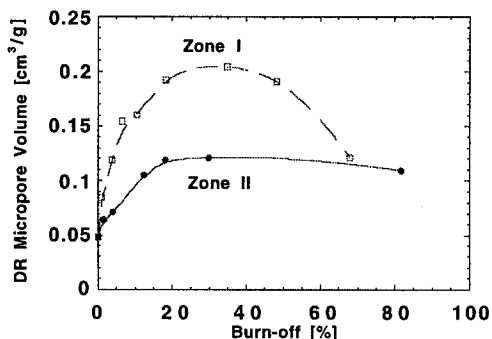

Figure 2. Micropore volume development in Wyodak char with burn-off in NO (Zone I-911K, Zone II-1027K)

is somewhat smaller, and the loss of microporosity is not observed. The lower development of microporosity can presumably be attributed to an inability of the reactant NO to fully penetrate the larger scale pores that

lead to the microporosity. The larger pores characteristic of gasification of this char in NO develop much more slowly with burn-off in Zone II. It can be noted that the microporosity per gram in Zone II is constant and considerably lower than that under Zone I conditions.
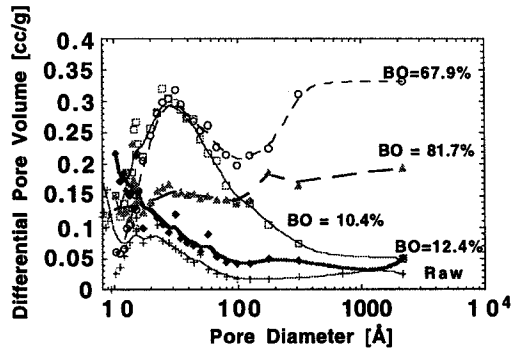

Figure 3. BJH pore size distribution for Wyodak char gasified under Zone I conditions (open points, thin lines) and Zone II conditions (solid points, heavy lines). Also shown as crosses are raw char data. BO = burn-off.

This is is suggestive of a process in which, after an initial period of significant micropore opening, the easily accessible surface uniformly recedes, exposing as yet unpenetrated surface. The surface recession must occur on a scale much smaller than the particle diameter. The char reactivity shows, in this Zone II case, a transient peak up to 20% burn-off, and then very constant reactivity up to 80% burn-off, consistent with the above porosity results.

The above results are interpreted as suggesting that NO penetrates meso-scale pores, and reacts early in the process with their surfaces to open initially covered micropores. It may be crudely inferred from Figure 2 that the accessibility of mesopores under the Zone I conditions is twice that under Zone II conditions, which is also roughly consistent with the extrapolation of the Zone I kinetics to the Zone II temperature (this gives a factor of two difference between predicted and actual). Since there is virtually no increase in micropore volume after the initial opening takes place, it does not appear that internal micropore surface is itself involved in reaction (at least until quite high burn-offs under Zone I conditions). This does not necessarily mean that micropore surface cannot be involved at all in the reaction; micropore openings might well act as active sites for reaction. Under Zone II conditions, the reactions developing the mesopores are clearly hindered, relative to Zone I conditions. This again suggests that this is the relevant size scale defining the Zone I to Zone II transition.

Figure 4 shows adsorption isotherm results for gasification of a polycrystalline graphite sample in three different oxidizing gases- NO, CO_2 and O_2. The material is initially extremely non-porous, exhibiting a BET surface area of just over 1 m^2/g. All of the gasified samples depicted here have surface areas which are orders of magnitude higher than this (from 30 to 130 m^2/g).
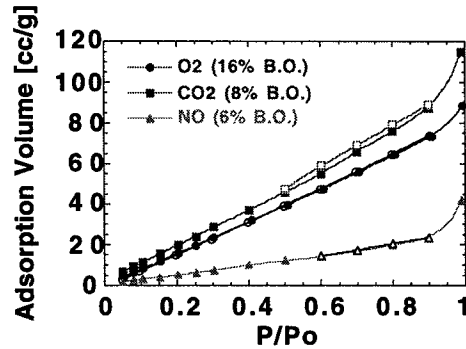

Figure 4. Adsorption isotherms for graphite gasified in three gases, under Zone I conditions.

It may be clearly seen that there is no development of microporosity in this carbon. It is well known that carbons are "imprinted" with their ability to develop microporosity during activation. In this case, the proclivity is virtually absent. It may be noted that the actual range of reactivities spanned an order of magnitude, with that in oxygen higher than that in NO. Even under these clearly Zone I conditions, micropore development is not possible in this material.

The above helps explain why the literature on the NO-carbon reaction reports that normalization of reaction rates by BET surface areas does not appear to "work" [3]. In many cases, the surface area based reactivity of graphites was higher than that of many other disordered carbons. Since it would be expected that graphites would have fewer active sites per unit surface area than disordered carbons, this result appeared to contradict the expectation. We now believe that the explanation has to do with the fact that graphite develops accessible large porosity, whereas the microporosity which dominates the surface area values of many other carbons, is of limited value in providing reaction sites.

References

1. Aarna, I. and Suuberg, E.M., 27th Symp. (Int.) on Combustion, 1998, p. 2933.
2. Barrett, E.P., Joyner, L.G., and Halenda, P.P., J. Am. Chem. Soc., 1951, 73, 373.
3. . Aarna, I. and Suuberg, E.M., Fuel, 1997, 76, 475.