

# THE "INERT GAS EFFECT" ON CARBON REACTIVITY

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## Introduction

One factor affecting carbon reactivity that has not received much attention is the role of "inert," diluent gases. Pentz and Walker [1] appear to be the first to report this effect for the C-O<sub>2</sub> reaction. In a subsequent study involving both O<sub>2</sub> and CO<sub>2</sub> gasification of P-33 carbon black and SP-1 graphite, respectively, Walker and coworkers found that diluent gases increased the gasification rate in the order Xe > N<sub>2</sub> > Ar > He > no diluent [2]. There have also been other reports on the effects of water vapor and "inert" gases on the C-O<sub>2</sub> reaction [3], and on the effect of "inert" gases on the thermal desorption of surface oxygen complexes as CO from a porous, graphitized carbon black [4].

In the current work, the effects of "inert" gas diluents on the reactivities of three porous chars gasified in CO<sub>2</sub> are examined, and post-reaction temperature programmed desorption (TPD) is used to explore this effect.

## Experimental

The samples used in the current work were prepared from Wyodak subbituminous coal, obtained from the Argonne Premium Coal Sample Bank [5], and phenol-formaldehyde resin synthesized in our laboratory. Carbonization was performed in a tube furnace in flowing, ultra-high purity helium for 2h at 1000°C for the Wyodak coal, and 950°C for the resin. A smaller sample (~20-60 mg) from this larger char preparation was used for each run in the reaction/desorption system. The Wyodak coal char was demineralized using a method similar to that described by Morgan *et al.* [6].

All the oxidations and thermal desorptions were carried out in the same TPD-MS/TGA apparatus in a "batch" (i.e., non-flowing) mode without removing the samples and exposing them to the ambient environment.

The samples were gasified in 0.1MPa total pressure of the various CO<sub>2</sub> - diluent gas mixtures at 825°C for the natural and demineralized Wyodak chars to 20% burn-off,

and at 900°C for the resin chars to 5% burn-off. The samples were all rapidly quenched in ultra-high purity helium to room temperature following reaction. Thermal desorptions were all carried out at 50K/min to 1200°C in ultra-high purity helium flowing 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.

## Results and Discussion

The reactivities of all three chars were determined over a range of diluent gas - CO<sub>2</sub> mixture ratios. For all the runs, for all three char samples the resultant reactivities under the same conditions decreased according to the diluent gas in the order of Xe > N<sub>2</sub> > Ar > He. Figure 1 presents the reactivities for the demineralized Wyodak char for the 20% diluent gas - 80% CO<sub>2</sub> mixtures.

In Figure 2 are presented post-reaction CO TPD spectra for the four different diluent gases for the demineralized Wyodak char samples following gasification in the 20% diluent gas - 80% CO<sub>2</sub> mixture runs presented in Figure 1. As shown, the CO desorption spectra for this char are centered *ca.* 960°C. For the natural Wyodak and resin char samples the results were similar, except that the peak for the He diluent run was shifted to about 1000°C. Unlike the reactivity, which was always in the order Xe > N<sub>2</sub> > Ar > He, the peak intensities for the TPD spectra were always in the order N<sub>2</sub> > Ar > Xe > He.

One possible explanation for the effect proposed by Walker *et al.* [2] was that the diluent gas affected the lifetime of reactive nascent sites during gasification. In other words, the heavier the diluent, the lower the collision rate with highly reactive *sp*<sup>3</sup> sites, formed during gasification, and the lower the rehybridization rate to less reactive *s*<sup>2</sup>*p*<sup>2</sup> sites. In other work, Britten *et al.* [4] concluded that "inert" gases can affect the desorption step of the C-CO<sub>2</sub> reaction, and that in the presence of Ar and Kr, transport rates of surface oxides to desorption sites were

higher than in He, and that this can result in faster overall reaction rates in the presence of the heavier gases.

The CO desorbed upon TPD originates for the most part from stable oxygen surface complexes. If this population is taken to be reflective of the creation rate of highly reactive nascent sites, then the explanation put forward by Walker *et al.* [2] is consistent with the TPD data in Figure 2 for the diluent gases He, Ar and N<sub>2</sub>. That is, the total post-reaction surface oxygen population increases from He to Ar to N<sub>2</sub>, consistent with longer lifetimes for highly reactive nascent sites which are oxidized and subsequently converted to stable complexes. Xe, however, behaves anomalously in this respect.

In other work [7] involving isothermal transient desorption of oxygen surface complexes following a switch from pure CO<sub>2</sub> to an inert gas, it was observed that argon initially impeded the desorption rate of oxygen complexes more than did helium. In the current case, the transport of gases following gasification is in the reverse direction, out of the porosity. Therefore, if a particular diluent gas is more effective at causing the transport of surface complexes along with it, then a switch to helium at the end of a reactivity run may cause a slight, but rapid decrease in the surface oxygen population, dependent on the diluent gas. Therefore, the "diluent gas effect" may involve both a mechanism which affects the lifetime of nascent reactive sites, as well as one that results in variations in the transport of oxygen surface complexes within the porosity. Both could result in higher reactivities, but only the latter would tend to reduce the oxygen surface population following reaction. This hypothesis is currently being investigated further.

### Conclusions

The CO<sub>2</sub> reactivities for three different chars for the same concentration of diluent gas all decreased in the order of Xe > N<sub>2</sub> > Ar > He. The corresponding TPD spectra indicate that the total oxygen surface populations decrease in the order N<sub>2</sub> > Ar > Xe > He. A hypothesis has been proposed to account for these observations.

### Acknowledgement

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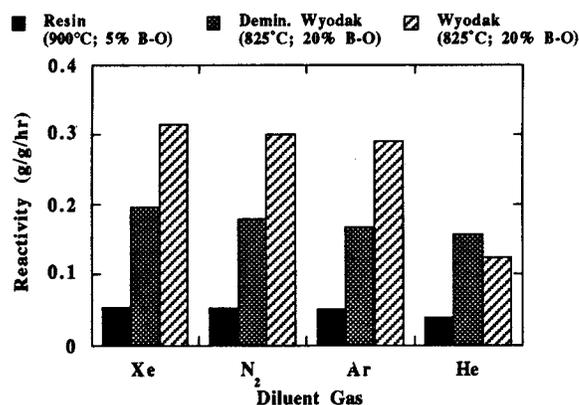


Figure 1. Comparison of the reactivities of the three char samples in 20% diluent-80% CO<sub>2</sub> gas mixtures.

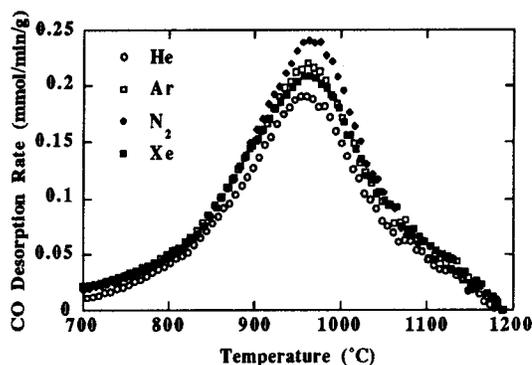


Figure 2. 50K/min CO TPD spectra for demineralized Wyodak coal char following gasification to 20% burn-off in 80% CO<sub>2</sub> - 20% diluent gas mixtures at 825°C.