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**REACTIVITY OF YOUNG CHARS VIA ENERGETIC
DISTRIBUTION MEASUREMENTS**

**J.M. CALO (Principal Investigator), L.-H. ZHANG, W.G. RACHEL,
and W.D. LILLY**

**Division of Engineering
BROWN UNIVERSITY
Providence, Rhode Island 02912**

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SUMMARY

In this report, we present some preliminary work performed on the effect of CO₂ partial pressure on temperature programmed desorption spectra from CO₂-oxidized chars.

The following was accomplished during the reporting period:

- Temperature programmed desorption (TPD) experiments were conducted on oxidized resin and Wyodak coal char samples gasified under varying different CO₂ partial pressures.
- The following observations were made:
 - CO₂ partial pressure can be an important factor affecting TPD spectra.
 - Generally, the total amount of surface oxygen desorbed as CO and CO₂ increases with CO₂ partial pressure during gasification for both resin char and Wyodak coal char.
 - The total amount of oxygen desorbed is also a function of gasification temperature. Apparently, the higher the gasification temperature, the more CO and CO₂ are desorbed. As an example, for 0.33 atm CO₂ partial pressure, the peak CO desorption rates are 0.17 mmole/g/min and 0.13 mmole/g/min, corresponding to gasification temperature 1223K and 1173K.

Plans for the next reporting period include:

- Experiments concerning the effects of "inert," diluent gases on char reactivity in CO₂ and O₂ will be conducted.
 - Reactivity measurements, as well as corresponding TPD spectra, will be obtained in order to establish a mechanistic basis for the operative phenomena.
- The TPD reactor system will be adapted for subatmospheric/vacuum operation in order to enhance the sensitivity of the system and explore the nature of certain features in the TPD spectra which have been attributed to secondary interaction effects.

1.0. PROJECT BACKGROUND

The correlation and prediction of kinetic rates and mechanisms of the reactions of gas phase species with coal chars represent a difficulty undertaking under the best of circumstances. Solid phase heterogeneity and impurities, complex pore structure, transport limitation, and evolution of active surface represent just a few of the well known problems. Because of this complexity, this largely remains an unresolved but, nevertheless, important problem affecting many aspects of coal utilization. The only techniques available until now were empirical correlations which may be useful for a single coal, or, at best, a special subset of coals, but are by no means global because they are not *fundamental*. This severely constrains the predictive capability of such methods.

The temperature programmed desorption (TPD) has become a standard technique for investigating the physico-chemical state of adsorbed species on surfaces. The predecessor of TPD-type methods was the flash filament technique of Redhead(1962), whereby gases adsorbed on wire filaments are rapidly desorbed upon rapid heating in an ultrahigh vacuum. This technique was subsequently adapted to catalytic surfaces(e.g., see Cvetanovic and Amenomiya, 1967, 1971). Experimental method and interpretation of TPD spectra for well defined crystalline surfaces have been reviewed by King(1975).

TPD spectra usually consist of one or more peaks. The shapes of the peaks and the position of the peak maxima with respect to temperature are related in a fundamental manner to the desorption process, and, therefore, provide basic information regarding the energetics of the desorbed species.

As a result of previous work, we accomplished what amounts to a significant breakthrough in this long-standing, important problem. In short, we have developed what we believe to be the very first *a priori* prediction technique for the gasification reactivity of coal char. With this method the gasification reactivity of a coal char *as a function of temperature* can be predicted from a *single TPD experiment* following mild gasification at a *single temperature* (Calo *et al.*, 1989; Hall and Calo, 1990a). This approach has been demonstrated for CO₂ gasification of coal chars where the gasification reactivity is controlled by the thermal desorption of oxygen surface complexes formed

during gasification. This approach may be extended to other oxidant species, such as steam, and carbon-hydrogen complexes for hydrogen gasification as well.

The purpose for the current project is to investigate the effect of CO₂ partial pressures on the resultant energetic distribution of oxygen surface complex, and to obtain the TPD spectra for resin char and wyodak samples gasified in various diluent gases and O₂ or CO₂ mixture.

2.0. EXPERIMENTAL

2.1. The TPD Apparatus and Methods.

The TPD apparatus consists of three principal parts:

- (1) The gas flow/metering system which provides an inert carrier gas to convect away desorbed species from the vicinity of the char samples;
- (2) The reactor where the sample is subjected to the controlled heating program for desorption of surface species; and
- (3) The detector (quadrupole mass spectrometer) for evolved species.

The experimental details are as follows. Char oxidation/gasification was performed in a TGA apparatus in 0.1 MPa total pressure of oxidant gas at specific temperatures. Following cooling to room temperature in the TGA apparatus, the samples were transferred to the TPD reactor.

The TPD reactor is constructed from a high-purity silica tube, 1-cm inside diameter, within which a close-fitting, circular silica sinter is used to support the sample. Ultrahigh purity helium carrier gas is passed over the sample in downflow. Heating is accomplished electrically via nichrome wire wrapped around the outside of the silica tube, powered by a high current variable transformer. The heating rate is controlled by a microcomputer.

Detection of desorbed species is accomplished with a quadrupole mass spectrometer (MS) which samples a small portion of the carrier flow. A simple programmer was developed which provides the DC levels required to automatically switch the mass spectrometer among four masses during the course of a TPD experiment. The MS output is fed to a microcomputer which also provides for multiple species detection via mass programming. For the current application, normally only masses $m/e=28$ and 44, corresponding to CO and CO₂, respectively, were

monitored. The electron energy in the mass spectrometer ionizer was set to ~25V in order to eliminate cracking of CO₂ to CO upon electron impact. In this manner, the two measured peak intensities reflect contributions from the parent species only.

The mass spectrometer was calibrated prior to each TPD run using 50/50 mol % CO/CO₂ mixture in order to determine relative species sensitivity. The MS signals were converted to an absolute basis *via* calibration with a series of pulse injections of calibration gas using a syringe, conducted in exactly the same fashion as the TPD experiments. The levels of the two peaks were recorded and the background at each peak was subtracted from these values. The background levels at M/e=28 and 44 were measured before and after each calibration, and were usually considerably less than the values measured with the calibration gas.

2.2. General Experimental Procedures.

The experiment procedure for a typical TPD experiment was as follows:

(1) The char sample was placed in a quartz sample bucket in the TGA apparatus. It was then thermally cleaned by heating in ultrahigh purity helium to a temperature of 1000°C, and holding at this temperature for approximately 20 min. The sample was then cooled to room temperature in ultrahigh purity helium.

(2) The sample was then heated to the desired chemisorption/gasification temperature and the oxidant gas (e.g., O₂, CO₂ or other gas mixture) was introduced. The desired temperature was then maintained until a predetermined time or burn-off achieved.

(3) A small sample of the oxidized char was then transferred to the TPD apparatus, and the helium purge gas flow was initiated.

(4) The mass spectrometer was calibrated prior to each experiment, as indicated above.

(5) The sample was then heated in ultrahigh purity helium carrier gas at the desired heating rate to an ultimate temperature (usually 1100-1150°C), and the desorption rates CO and CO₂ were measured using the MS. The temperature and the analog output from the MS were digitized and recorded in a data file on a microcomputer.

3.0. EFFECTS OF CO₂ PARTIAL PRESSURE

As a result of previous work, we established the relationship between CO₂ reactivity at one atmosphere and TPD spectra of the oxygen surface complexes responsible (Calo *et al.*, 1989). In order to extend this knowledge to the understanding of steam gasification and reactivity, the behavior of CO₂ reactivity as a function of partial pressure must first be firmly established. The TPD experiments have been performed to investigate the effects of CO₂ partial pressure on the resultant energetic distribution of oxygen surface complexes.

3.1. *Experimental.*

The chars used in the current experiments were produced from: (1) subbituminous Wyodak coal samples, obtained from the Argonne premium Coal Sample Bank; and (2) phenol-formaldehyde resin, prepared in our own laboratory (Calo *et al.*, 1989). The samples were carbonized in a tube furnace at 1000°C for 2 h. The resultant chars were sieved and those particles with sizes between -16 to +100 mesh were used for the oxidation/gasification runs. These samples were gasified in a Cahn 113 microbalance thermogravimetric analysis (TGA) system. All runs were performed at a total pressure of one atmosphere. The variation of CO₂ partial pressure was accomplished by dilution with ultrahigh purity helium. The resultant range of CO₂ partial pressure was 0.018 atm to 1 atm, and all samples were burned-off to about 5% mass loss.

A small amount of oxidized sample (~20 mg) was then transferred to the TPD apparatus. The sample was dried at 100°C for about 10 minutes to eliminate any H₂O absorbed from air prior to the TPD run. The heating rate was 100K/min to an ultimate temperature of 1423K for every sample. The temperature and the analog output from the MS were recorded. The desorption rates for CO and CO₂ were determined by means of data from calibration experiment.

3.2. *Results and Discussion.*

TPD spectra from the 5% gasified resin char (in 1 atm CO₂ and helium mixture, or pure CO₂ at 1173K) are presented in Figures 1 and 2. Comparison is made among three samples with CO₂

partial pressures of 0.062 atm, 0.33 atm, and 1 atm respectively. It can be seen that the CO evolution consists of a peak centered *ca.* 1250K for all three cases and that the total amount of CO desorbed is similar at 1.0 and 0.33 atm, and significantly less for the 0.062 atm case. The corresponding reactivities for these samples are presented in Figure 3. As shown, the reactivities of the the 1.0 and 0.33 atm are also quite similar, with that at 1.0 atm being slightly less. This behavior is as yet unexplained (*cf.* DE-FG22-90PC90307-2), but the TPD spectra confirm this behavior. That is, the amount of surface complex is similar for these two partial pressures, and considerably less for the low pressure sample. The peak CO desorption rate is 0.13 mmole/g/min for 0.016 atm CO₂ partial pressure, 0.17 mmole/g/min for 0.33 atm CO₂ partial pressure, and 0.19 mmole/g/min for pure CO₂. As shown in Figure 2, the CO₂ desorption rate also increases with CO₂ partial pressure, but the amount of increase is not as significant as for the CO desorbed.

Figures 3 and 4 compare the effects of varying CO₂ partial pressure on 100K/min TPD spectra for Wyodak gasified at 1 atm at 1203K; while Figures 5 and 6 are similar spectra for Wyodak gasified at 1223K. The ultimate temperature attained in these TPD runs was 1373K. As can be seen, there are certain features common to all the spectra, with three desorption peaks for CO₂ centered *ca.* 600K, 825K, and 950K, and more than one desorption peak for CO, the principal one of which is centered *ca.* 1250K, and another feature which appears to peak at a temperature higher than 1373K. CO₂ partial pressure has a similar effect on the TPD spectra for the Wyodak coal char samples as it did for the resin char samples.

These results also show that the total amount of oxygen desorbed is a function of gasification temperature. Apparently, the higher the gasification temperature, the more CO and CO₂ are desorbed. As an example, as shown in Figures 7 and 8, for 0.33 atm CO₂ partial pressure, the peak CO desorption rates are 0.17 mmole/g/min and 0.13 mmole/g/min, corresponding to gasification temperature 1223K and 1173K.

3.3. *Conclusions.*

It was found that the CO₂ partial pressure can be an important factor affecting TPD spectra. Generally, the total amount of surface oxygen desorbed as CO and CO₂ increases with CO₂ partial pressure during gasification for both resin char and Wyodak coal char.

4.0. PLANS FOR THE NEXT REPORTING PERIOD

- Experiments concerning the effects of "inert," diluent gases on char reactivity in CO₂ and O₂ will be conducted.
- Reactivity measurements, as well as corresponding TPD spectra, will be obtained in order to establish a mechanistic basis for the operative phenomena.
- The TPD reactor system will be adapted for subatmospheric/vacuum operation in order to enhance the sensitivity of the system and explore the nature of certain features in the TPD spectra which have been attributed to secondary interaction effects.
- Due to the relatively low resultant amounts of oxygen complex found on the char sample surfaces following gasification in CO₂, it is necessary to improve the sensitivity of the resultant TPD spectra. This can be achieved by either increasing the size of the oxidized sample, and/or operating the programmed desorption at lower pressures where nearly all of the desorbed gases can be sampled directly into the mass spectrometer.
- In addition, low pressure operating capability will enable the exploration of secondary interaction effects in the TPD spectra which may be related to absolute pressure during desorption.

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Figure 1. 100K/min CO TPD spectra from resin char gasified at 1173K as a function of CO₂ partial pressure at a total pressure of 0.1 MPa. Ultrahigh purity helium was used as the diluent gas.

Figure 2. 100K/min CO₂ TPD spectra from resin char gasified at 1173K as a function of CO₂ partial pressure at a total pressure of 0.1 MPa. Ultrahigh purity helium was used as the diluent gas.

Figure 3. 100K/min CO TPD spectra from Wyodak coal char gasified at 1023K as a function of CO₂ partial pressure at a total pressure of 0.1 MPa. Ultrahigh purity helium was used as the diluent gas.

Figure 4. 100K/min CO₂ TPD spectra from Wyodak coal char gasified at 1023K as a function of CO₂ partial pressure at a total pressure of 0.1 MPa. Ultrahigh purity helium was used as the diluent gas.

Figure 5. 100K/min CO TPD spectra from Wyodak coal char gasified at 1223K as a function of CO₂ partial pressure at a total pressure of 0.1 MPa. Ultrahigh purity helium was used as the diluent gas.

Figure 6. 100K/min CO₂ TPD spectra from Wyodak coal char gasified at 1223K as a function of CO₂ partial pressure at a total pressure of 0.1 MPa. Ultrahigh purity helium was used as the diluent gas.

Figure 7. 100K/min CO TPD spectra from resin char gasified to 5% burn-off in 0.33 atm of CO_2 at a total pressure of 0.1 MPa, at the two temperatures indicated. Ultrahigh purity helium was used as the diluent gas.

Figure 8. 100K/min CO₂ TPD spectra from resin char gasified to 5% burn-off in 0.33 atm of CO₂ at a total pressure of 0.1 MPa, at the two temperatures indicated. Ultrahigh purity helium was used as the diluent gas.

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