THE EFFECT OF CHAR "AGE" AS REVEALED BY THERMAL DESORPTION SPECTRA

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Introduction

The formation and desorption of oxygen surface complexes play a critical role in carbon gasification by steam. In the current communication we explore the relationship between distributions of oxygen surface complexes, as determined by desorption techniques, and steam reactivity of chars as a function of "age."

Experimental

Two types of char samples were used in the current work: Pittsburgh #8 bituminous coal char produced from samples obtained from the Argonne Premium Coal Sample Bank [1]; and resin char produced from phenol-formaldehyde resin synthesized in our laboratory. Char samples of four different ages were prepared by pyrolyzing the char precursors at 850°C, 900°C, 950°C, and 1000°C in a tube furnace in flowing ultra-high purity helium for 2h.

The resultant char samples were gasified in a TGA fitted to generate variable ratio steam - helium mixtures ranging from 9% to 67% steam at a pressure of 0.1 MPa at temperatures between 750°C and 950°C. All the samples were burned-off to 10%. The samples were rapidly quenched in ultra-high purity helium and immediately transported to another TPD-MS/TGA system for thermal desorption. Exposure tests of the gasified samples to air at ambient conditions indicated that the desorption spectra remained quite similar with exposure time, but with slowly increasing levels of surface oxygen. A one-week exposure increased total surface oxygen by about 10%.

All the thermal desorptions were carried out at 50K/min in the TPD-MS/TGA. Improvements in this apparatus enabled extending the upper temperature limit from 1050°C, as reported in previous work [2], to 1200°C.

Results and Discussion

The behavior of the steam gasification reactivities was similar for both types of char samples. At constant steam partial pressure, reactivity increased rapidly with temperature. The global or overall activation energies for resin char and Pittsburgh #8 char were 196 kJ/mol and 225 kJ/mol, respectively. The steam reactivities of both types of chars all decreased with increasing "age" under all reaction conditions.

The CO TPD spectra of the resin char samples consisted of a broad feature centered *ca.* 970°C, while those for the Pittsburgh #8 char exhibited the same feature plus a larger one which increased steadily to the maximum desorption temperature of 1200°C. The total amount of desorbed CO decreased slightly with increasing steam partial pressure. The intensity of the total CO desorption decreased monotonically with increasing reaction temperature, and was greatest at 750°C. These results indicate that the total amount of oxygen surface coverage decreases with increasing reactivity for all the char samples of the same "age." However, for chars of the same type, although the steam reactivities decreased with "age," the total oxygen surface complex coverages increased with "age;" slightly for the resin char, and markedly for the Pittsburgh #8 char.

Figures 1 and 2 present the CO TPD spectra for the resin char samples pyrolyzed at 850°C and 1000°C, following 10% burn-off at 850°C in a 50% steam - helium mixture at a total pressure of 0.1MPa. These CO spectra were fit to the sum of first order desorption peaks in a fashion similar to that presented in our previous work [2], as shown in the figures. The results of these analyses are presented in Table I. As shown in this table, the "younger" resin char sample exhibited a higher reactivity than the "older" sample. The corresponding Peak #1 intensities increased with *decreasing* sample "age," while the Peak #2 intensities remained about the same. Peak #3 increased markedly with "age."

The same set of three peaks was also found to fit the lower temperature region of the CO TPD spectra for the Pittsburgh #8 char samples, except that the behavior of the intensities of the peaks was different. As for the resin char, the "younger" samples always exhibited greater

reactivity than the "older" samples. However, the behavior of Peak #1 was opposite to that observed for the resin char samples; it *increased* with "age." On the other hand, Peak #2 decreased considerably with "age," but Peak #3 still increased with "age" just as for the resin char samples. Unlike the resin char, Pittsburgh #8 contains significant mineral matter impurities, primarily Fe_2O_3, which have a strong effect on both the absolute and relative peak intensities.

In the case of the resin char, the population of the lowest temperature peak correlates well with reactivity. Consequently, it is hypothesized that these complexes are related to the oxygen surface complexes that are responsible for the char reactivity. In the case of the Pittsburgh #8 char, this is not the case. However, the complexes that desorb as Peak #1 may still be related to those responsible for reactivity, but the catalytic behavior of the mineral matter affects their population by controlling their formation and desorption rates. The effects of these mineral matter impurities is the subject of ongoing work.

Conclusions

For the two very different char samples in the current work, the steam reactivities of the "younger" chars were always found to be greater than the "older" chars. CO TPD spectra from these chars were found to exhibit significant similarities. The population of the highest temperature Peak #3 always increased with char "age." However, the lower temperature CO peaks behaved differently for the two chars. Peak #1, in particular, is believed to be directly related to the complexes responsible for char reactivity.

Acknowledgement

This work was supported by Grant Nos. DE-FG22-PC90307 and DE-FG22-91PC91305 from the UCR Program of the U.S. Department of Energy.

References

1. Vorres, K.S., *Users Handbook for the Argonne Premium Coal Samples*, ANL/PCSP-93/1, DOE, Argonne, Il, 1993.
2. Calo, J.M., Lu, W., and Zhang, L., *Proc. 21st Carbon Conf.*, p. 519, Buffalo, 1993.

Table I. Evolved CO from TPD spectra.

Resin Char	T_p (°C)	E (kJ/mol)	850°C CO (μmol/g)	%	1000°C CO (μmol/g)	%
#1	897	206	0.39	11.1	0.08	2.1
#2	967	235	2.47	69.8	2.60	67.7
#3	1057	365	0.68	19.1	1.16	30.2
Total			3.54		3.84	

Pittsburgh #8	T_p (°C)	E (kJ/mol)	850°C CO (μmol/g)	%	1000°C CO (μmol/g)	%
#1	897	206	0.14	1.8	0.44	6.9
#2	967	235	2.5	33.8	1.22	13.5
#3	1057	365	4.8	64.4	7.38	86.6
Total			7.44		9.04	

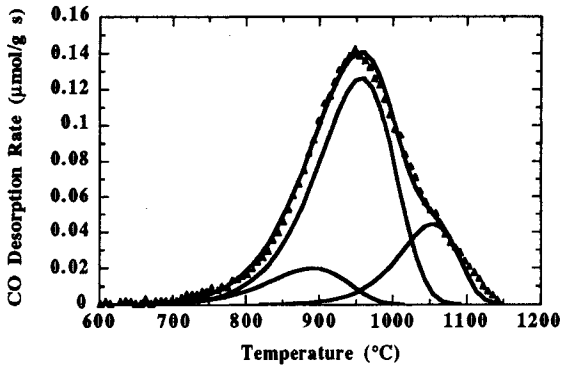

Figure 1. Deconvolution of 50K/min CO TPD spectra of 850°C resin char following reaction to 10% burn-off in a 50% steam-helium mixture at 850°C and 0.1MPa total pressure.

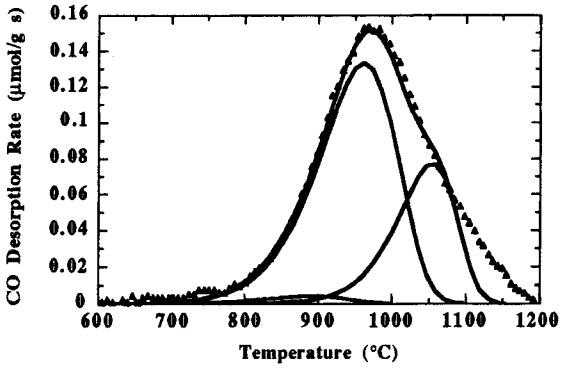

Figure 2. Deconvolution of 50K/min CO TPD spectra of 1000°C resin char following reaction to 10% burn-off in a 50% steam-helium mixture at 850°C and 0.1MPa total pressure.