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The Role of Pore Structure on Char Reactivity

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Quarterly Progress Report

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Introduction

In order to examine the role of pore structure, studies will be conducted on coal chars in the electrodynamic balance. Larger particles will also be examined using a fluidized bed to examine diffusion control reactions, and soots will also be investigated to examine the role of meso- and micro-pores without macro-pore interference. These studies will allow a full range of particles sizes and temperatures to be investigated and eventually modelled.

Progress Report

The project has examined the effect of the pore structure diffusivity changes on the generation of NO_x and N₂O from the Fluidized Bed Combustor. Furthermore, refinement of the techniques necessary to determine micropore characteristics from TEM imaging have been further refined.

The main focus of the past 3 months work has been generation of spherocarbon samples by oxidation in air at 500C. In past work^{1 2}, Spherocarbon has proven quite conducive to oxidation studies. It is virtually 100% carbon with high surface area(800 m²/g as measured by BET). Past studies have focused on relatively low oxidation levels of less than 60%. It is our intention to examine spherocarbon with the TEM at very high conversion levels(80%+). Under most characterization studies, this would be too high of a conversion level, but using new TEM techniques that have been developed here at MIT, we can now characterize the d002 spacing and lattice length of very small sample sizes

An example of the oxidation performed on the spherocarbon is given in Figure 1. Very high oxidation levels may be obtained using the TGA. However, it is interesting to examine the rate of reaction normalized by weight of the sample. If we normalize the reaction by initial weight, the rate exhibits the classic increase in reaction rate until moderate levels, where decrease in reaction rate occurs. However, if the reaction rate is normalized by remaining mass, which for the spherocarbon with very little impurities does not imply a great deal of error, one sees that the reactivity tends to increase with reaction rate. This is not the result that one would expect if the spherocarbon exhibits homogeneous shrinkage,³ where increase in lattice length would indicate that reactivity would go down.

In order to examine the more closely, examination of TEM images of the oxidized spherocarbon must be examined. After initial tests confirmed that there were no differences between samples ground in a ball mill or a mortar and pestle, the samples were ground to a powder like consistency. The powder was then ultrasonically suspended in ethanol and then dropwise deposited on lacey carbon TEM grids. An Akashi/TOPCON 002B transmission electron microscope with an LaB₆ filament operating at 200keV was then used to record high resolution images of each sample. The images were then digitized, and SEMPER6P (Synoptics Ltd., Cambridge, UK), developed specifically for use with high resolution electron microscopy was used to manipulate the stored images in order to extract data which could physically characterize the spherocarbon.

Characterization was accomplished using a Fourier Transform of the TEM images to establish periodicities. By then applying a mask to remove unwanted noise in the image, the annulus may be reverse transformed to obtain a gray filtered image. This image is then converted to a two color 'extracted structure' by establishing an intensity threshold value for the pixel intensity. This extracted structure then becomes the basis of for the statistical analysis of various properties, such as lattice length, circularity, and d_{002} carbon spacing as defined below:

The Lateral extent or length of fringes is defined as

$$La = A \cdot B \sqrt{m_{\max}}$$

where $m_{\max}$ is the maximum principal second moment. A is dependent on the shape of the object, and was determined by experiment (footnote arpad) to be 3.56 pixel units. B is a pixel to Angstrom Conversion factor, equal to 0.4336 Å/pixel for our imaging system.

The interlayer-planar spacing defined as the distance d_{002} between parallel fringes and was obtained by evaluating the center of area P_i and the long axis orientation α_i . The distance was then calculated using the following formula:

$$d_i = \frac{m_i(x_{i+1} - x_i) - (y_{i+1} - y_i)}{\sqrt{m_i^2 + 1}}$$

$$m_i = \tan\left(\frac{\alpha_i + \alpha_{i+1}}{2}\right)$$

where (x_i, y_i) represent the coordinates of P_i . This calculation was repeated several times in order to obtain statistically significant values. The interlayer spacing was then specified as a mean and standard deviation, although for spherocarbon, like other disordered carbon material, a distribution function is more meaningful.

The fractional coverage of the extracted pattern, defined as

$$C = \frac{\text{Area of Fringes}}{\text{Area of view}}$$

was also investigated. However, fractional coverage is sensitive to the area chosen, and can only be used as a distinguishing pattern for well defined situations.

The results of the Analysis are shown in Table 1. As can be seen, there is very little difference in the d002 spacing of the carbon that is measurable in our method. However, the most important factor is the fringe length, L_a . The fringe length increases 50% over the original length, which much ordering evident, as seen in Figure 3, the fractional coverage diagram. This increase in lattice length, while at the same time an increase in reaction rate is an exciting discovery. Previous studies have suggested that the increase in lattice length, and the destruction of edge carbons, results in the lower reactivity at seen at higher conversions. However, as seen by the spherocarbon results, when normalized for remaining mass, the reaction rate does not go down with increasing graphitization, but instead goes up. This is the result that will be explored further in the next few months.

Future Work

Further analysis of high oxidation level spherocarb combustion using the TEM will continue well into the next quarter in anticipation of publishing the results in the International Combustion Symposium next summer.

Table 1. Summary of Results.

Conversion Level	d_{002} spacing(Angstrom)	Coverage (%)	Lattice Length (Angstrom)
Base (0%)	3.42 ± 0.18	45 %	10.2 ± 4.6
High (95 %)	3.40 ± 0.18	42 %	15.1 ± 9.4

References

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Spherocharon Run 500 C, Air Oxidation

Figure 1. Example of oxidation of Spherocharon. The reactivity of the spherocharon is shown at the bottom.

Figure 2. Example of typical TEM image obtained of the spherocarbon.

Figure 3. Extracted structure (coverage) of spherocarbon samples, a) base spherocarbon, b) high oxidation(95% conversion).