Technical Progress Report
 "Rate Inhibition of Steam Gasification of Adsorbed Hydrogen"
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Dennis J. Miller, Principal Investigator

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This sixth quarter of the grant period has seen completion of a significant portion of the core gasification experiments set forth in the grant objectives. We have resolved all of the problems with impurities in our gas streams and all uncertainties in our mass spectroscopic analysis. Further, our initial analysis of gasified chars showed that the quantity of hydrogen adsorbed was much greater than the residue on the annealed char, so that we do not have to use deuterium (D_2) or heavy water (D_2O) as our reactant species. In addition to reducing expenses, this greatly simplifies deconvolution of our experimental results because we no longer have to struggle to separate the concentrations of deuterated methane (CD_4 , $M=20$) from heavy water (D_2O , $M=20$). Results of the gasification experiments conducted during this reporting period have been gratifying, both in terms of precision and reproducibility and in terms of information about the system under study. The extended period of time spent earlier in the grant period developing the apparatus and experimental protocol appears to be paying off in the quality of information we are now obtaining.

The remainder of the report for this period gives a review of the theory behind our work, a sample of the gasification results obtained, and interpretation of the data collected. We are now moving into the phase of the project where we will be conducting analyses of the data collected to determine the mode(s) of hydrogen inhibition taking place.

THEORY

The uninhibited gasification of carbon by steam can be described by the following two steps, where C_f is a free carbon site :

The three possible modes of hydrogen inhibition in steam gasification are as follows:

Selection of any of the possible inhibition modes gives the following basic rate expression:

$$r_{\infty} = \frac{C_A K_1 P_W}{1 + K_2 P_W + K_3 P_H^2}$$

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Dissociative adsorption gives a value of 0.5 for n , which has been found to be the case for low hydrogen pressures and subatmospheric steam pressures. Reverse oxygen exchange and associative hydrogen adsorption both give values of one for n , as reported in earlier studies.

Direct measurement of surface hydrogen concentration and inclusion of this information in Langmuir-Hinshelwood type linearized rate expressions is done to reveal the primary mode of inhibition in steam/hydrogen gasification of chars. Surface hydrogen concentration is accounted for through manipulation of the total site balance:

$$\text{Total site balance:} \quad C_t = C_f + C(O) + C(H)$$

The total number of sites available for reaction is equal to the total number of sites (C_t) minus the number blocked by hydrogen, with $C(H)$ referring to both associatively and dissociatively bound species. This quantity is then substituted into the appropriate rate expression, initial rate subtracted from continuous rate, and the expression linearized.

If dissociative hydrogen adsorption is solely responsible for inhibition, the linearized form, which includes rate constants from the elementary steps, is as follows:

$$\frac{(C(H) - C(H)_i)}{(r_{cof} - r_{co})} = \left(\frac{1}{k_1} \right) \frac{1}{P_H} + \frac{1}{k_2}$$

A plot of the left side vs. $1/P_H$ will be linear and will not be a direct function of hydrogen partial pressure. If rapid reverse oxygen exchange and dissociative hydrogen adsorption are both responsible for inhibition, the linearized form is as follows:

$$\frac{(C(H) - C(H)_i)}{r_{cof} - r_{co}} = \left(\frac{k_1}{k_1 k_2} \right) \frac{P_H}{P_H} + \frac{1}{k_2}$$

A plot of the left side vs. P_H/P_W will be linear if both reverse oxygen exchange and dissociative hydrogen adsorption are important.

If reverse oxygen exchange is solely responsible for inhibition, the original rate expression for steam gasification above is correct with a value of n equal to one and no correlation between adsorbed hydrogen and rate exists. More complicated rate expressions result from other combinations of the proposed mechanisms.

EXPERIMENTAL

Chars prepared earlier were gasified inside a quartz lined Inconel 625 differential packed bed microreactor housed inside a larger pressure vessel capable of simultaneous operation at 1273K and 6.6MPa. The entire system was designed to have absolute minimal internal volume to facilitate accurate measurement of transient species. After gasification in various proportions of argon, steam, and hydrogen at 1123K and pressures ranging from 0.3 to 3.3MPa, rapid switching to pure argon is done and transients monitored. The inherent system transient response is accounted for by using 1% krypton as a tracer in the reactant gas argon.

After gasification, chars are removed, weighed, and placed inside an alumina reactor for temperature programmed desorption to measure the quantity of adsorbed hydrogen. These chars are heated in argon at 10K/min to 1773K in a Mellen split tube furnace with a programmable temperature controller. Effluent species from both reactors are analyzed with an Ametek M100M Quadrupole Mass Spectrometer interfaced with a personal computer for data collection and deconvolution.

RESULTS

Gasification rates for several representative conditions are given in Figure 1, where it is seen that inhibition increases with increasing hydrogen partial pressure. More interesting are the trends in gasification rate with conversion: with no added hydrogen rate increases with conversion, while at 20% hydrogen in the reactant gas the rate noticeably declines with conversion. Figure 2 gives the results of surface hydrogen concentration versus extent of carbon conversion for the same experiments. The initial surface hydrogen concentration for the annealed Saran char is about 0.5 cc/g, far below the values following gasification. This fact allows us to use hydrogen instead of deuterium in our reactions, because there is essentially no hydrogen in the starting material and therefore no interference of residual hydrogen with that deposited during gasification. The results of hydrogen concentration versus conversion are surprising: the quantity adsorbed during reaction appears to be solely a function of conversion, independent of reactant gas composition or total pressure. It attains a value of about 50cc/g, which is a significant fraction of the 62cc/g desorbed during TPD of unannealed Saran char. The high temperatures (1200-1800K) at which hydrogen desorbs during TPD indicates that it is dissociatively adsorbed.

Evidence supports both reverse oxygen exchange and irreversible hydrogen adsorption as inhibitory mechanisms in steam gasification. TPD studies show that dissociative hydrogen adsorption is definitely occurring during gasification, but does not inhibit gasification rate as a function of conversion when the hydrogen concentration is low (0 or 5% in Figures 1 and 2). This suggests that reverse oxygen exchange is the important mode of inhibition at low partial pressures of hydrogen. If hydrogen adsorption did inhibit reaction, the increase in surface hydrogen would correspond to a significant decrease in the total number of active sites and would therefore significantly decrease reaction rate. This apparently does occur at 20% hydrogen partial pressure, since gasification rate does decrease with conversion at this condition. The major mode of inhibition must shift from reverse oxygen exchange to irreversible hydrogen adsorption as hydrogen partial pressure increases.

In summary, we are now conducting the core experiments on the project which are giving us important insight into the mode(s) of hydrogen inhibition in steam gasification of annealed chars. In the coming months, we will complete this first set of core experiments, then expand our efforts to other chars and to catalyzed systems to further explore the modes of hydrogen inhibition in gasification. We may also examine mixtures of H_2O/D_2 and D_2O/H_2 in an attempt to identify the source of adsorbing hydrogen on the char surface. The success of these experiments will depend largely on whether or not H-D exchange takes place on the carbon surface during reaction.

Figure 1. Annealed Saran Char H₂O/H₂ Gasification: Temp.= 850°C
Reactant Gas Comp.= Ar/H₂O/H₂ (60-x%/40%/x%)

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Figure 2. Annealed Saran Char H₂O/H₂ Gasification: Temp.= 850°C
Reactant Gas Comp.= Ar/H₂O/H₂ (60-x)%/40%/x%