

HYDROGEN INHIBITION IN STEAM GASIFICATION OF SARAN AND COAL CHAR

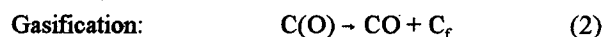
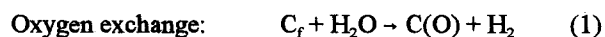
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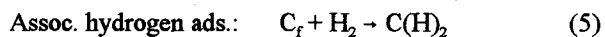
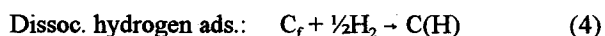
INTRODUCTION

Gasification of coal for fuels production is not currently used on a wide scale because extreme conditions are needed to achieve reasonably fast reaction rates. One reason for these extreme conditions is the inhibition of gasification by hydrogen in the reacting gas phase. For example, gasification rate decreases by an order of magnitude with the addition of only 1 ppm hydrogen to steam [1], and rate has been shown to decline significantly with conversion in hydrogen and steam/hydrogen mixtures [2,3]. Hydrogen dissociatively chemisorbed onto carbon is very stable, generally accepted as dissociative in nature, and requires temperatures approaching 1800K to completely desorb [4].

The uninhibited gasification of carbon by steam can be described by the following two steps, where C_f is a free carbon site [3]:



The three possible modes of hydrogen inhibition in steam gasification are as follows [3]:



Selection of any of the possible inhibition modes gives the following basic rate expression [3,5]:

$$r_{\infty} = \frac{C_A K_1 P_W}{1 + K_2 P_W + K_3 P_H^n} \quad (6)$$

Dissociative adsorption gives a value of 0.5 for n [3], which has been found to be the case for low hydrogen pressures [6] and subatmospheric steam pressures [7]. Reverse oxygen exchange and associative hydrogen adsorption both give values of one for n , as reported in earlier studies [5,8,9]. Associative adsorption has been found to contribute to inhibition at higher pressures, but dissociatively bound hydrogen still dominates char surfaces [10].

THEORY

In this study, 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:

$$\text{Total site balance: } C_t = C_f + C(O) + C(H) \quad (7)$$

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:

$$\frac{(C(H) - c(H)_i)}{(r_{\infty i} - r_{\infty})} = \left(\frac{1}{k_1} \right) \frac{1}{P_W} + \frac{1}{k_2} \quad (8)$$

A plot of the left side vs. $1/P_W$ 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:

$$\frac{(C(H) - C(H)_i)}{r_{CO_i} - r_{CO}} = \left(\frac{k_1}{k_1 k_2} \right) \frac{P_H}{P_W} + \frac{1}{k_2} \quad (9)$$

A plot of the left side vs. P_H/P_W will be linear. If reverse oxygen exchange is solely responsible for inhibition, Equation (6) 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 of Dow Saran Resin (MA 127) and demineralized Illinois #6 Coal (PSOC 1493) were prepared in a quartz tube reactor at 1173K in flowing nitrogen for 0.5hr., ground and sieved to -60+100 mesh, then annealed in an alumina reactor to 1773K in flowing argon for 6hr.

Chars were gasified inside a quartz lined Inconel 625 differential packed bed microreactor which was 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 was done and transients monitored. The inherent system transient response was accounted for by using 1% krypton as a tracer in the reactant gas argon.

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

RESULTS

Figure 1 clearly shows inhibition with increasing hydrogen partial pressure, as well as inhibition with increasing conversion for the case of 20% hydrogen in the reactant gas. Figure 2 shows surface hydrogen starting at a concentration of nearly zero, then increasing with conversion independently of hydrogen partial pressure. It attains a value of about 50cc/g, which is a significant fraction of 62cc/g for unannealed Saran char. The high temperatures (1200-1800K) at which hydrogen desorbs during TPD indicates that it is dissociatively adsorbed.

DISCUSSION AND CONCLUSION

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 at 5% or less. If hydrogen adsorption does inhibit reaction, the

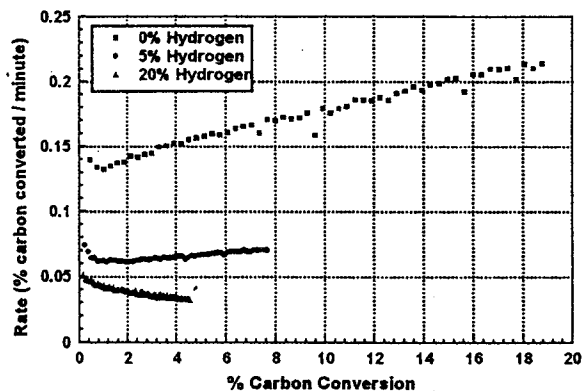


Figure 1: Annealed Saran char gasification rate at 1123K and 3.0MPa. Reactant gas composition is $(60-x)\%Ar / 40\%H_2O / x\%H_2$

increase in surface hydrogen would correspond to a significant decrease in the total number of active sites irregardless of reactant gas composition, and would therefore significantly decrease reaction rate. Since gasification rate does decrease with conversion under higher hydrogen partial pressures, the major mode of inhibition must shift from reverse oxygen exchange to irreversible hydrogen adsorption as hydrogen partial pressure increases.

ACKNOWLEDGEMENT

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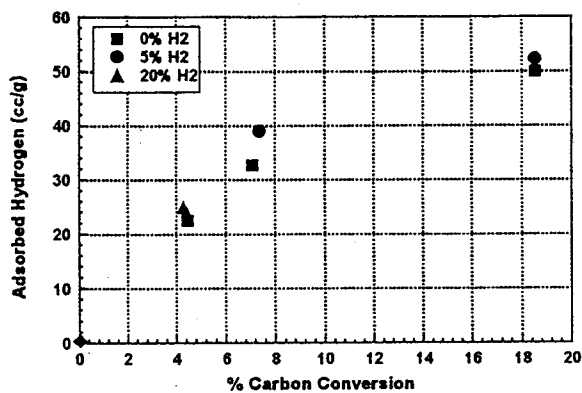


Figure 2: Adsorbed hydrogen on annealed Saran char following gasification at 1123K and 3.0MPa. Reactant gas composition is $(60-x)\%Ar / 40\%H_2O / x\%H_2$