Solid-Solid Contacting in Catalyzed Gas-Char Reactions

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Introduction

Coal char samples that are used for gas-carbon reaction studies can possess a wide range of porosities depending upon preparation techniques. In general, the char may be classified as non-porous, slightly porous, or highly porous. The total particle reaction rate is a summation of the intra-particle reaction rate and the external surface reaction rate and is dependent upon the type of char under investigation, viz.

$$r_{meas} = (\eta A^{int} + A^{ext}) r_{true} \tag{1}$$

where r_{meas} is the measured total particle reaction rate, r_{true} is the true reaction rate, A^{int} and A^{ext} are the internal and external surface areas, respectively, and η is the effectiveness factor.

Further elaborations on the total particle reaction rate arise in gas-carbon reactions when reaction at specific sites warrants the inclusion of an internal and external active site density, C_t, and when r_{true} applies to a complex reaction path such as gasification, viz. char-CO_2 gasification,

$$r_{meas} = (\eta A^{int} C_t^{int} + A^{ext} C_t^{ext}) \frac{k_1(CO_2)}{1 + \frac{k_1}{k_3}(CO_2) + \frac{k_{-1}}{k_3}(CO)} \tag{2}$$

It is often difficult to determine when the effectiveness factor is approximately unity for complex reaction paths, consequently rate expressions simpler than equation (2) are often used. For example, Jalan and Rao[1] assumed a first order reaction rate with respect to CO_2 during char-CO_2 gasification. Also note that in the case of equation (2) only "apparent" activation energies can be obtained from Arrhenius plots of r_{meas} vs. 1/T since k_1, k_{-1}, and k_3 all depend on T, and even this approach is invalid if the surface areas and site densities are not constant with respect to temperature and the time duration of the experiment.

When a solid catalyst is introduced onto char, the catalyst contacting with char must be considered since it may be (a) limited to a small portion of the external char surface area, (b) contacted with the entire external char surface area, but excluded from internal pores, or (c) contacted with the entire external and internal char surface areas. The consequences of catalyst contacting on measured reaction rates and measured activation energies need to be realized when interpreting experimental data since these measurements often are taken as the main basis for speculating on catalytic mechanisms.[2-4]

Analysis

It has been proposed that certain catalysts in gas-carbon reactions act only to increase the density of active sites (i.e. C_t in equation (2)).[5] Assuming this type of catalysis prevails, Table 1 summarizes, for several initial reaction conditions and for several conditions of catalyst contacting, the changes in measured reaction rates and measured activation energies which occur when a solid catalyst is introduced onto char. As shown in Table 1, the initial uncatalyzed reaction conditions may be in the regime of kinetic control ($\eta=1$), intra-particle diffusional control ($\eta<1$), or external diffusional control (i.e. proportional to the difference in bulk and surface concentrations and film thickness). When a solid catalyst is introduced, the catalyzed reaction conditions depend on the porosity of the char and the extent of catalyst contacting (i.e. catalyst penetrates internal pores or catalyst excluded from internal pores). The interplay between initial uncatalyzed reaction conditions and extent of catalyst contacting during catalytic gasification can lead to measured activation energies increasing, decreasing, or remaining constant with catalyst application. An interesting case is where the measured activation energy increases with the introduction of a solid catalyst. In such a case a slightly porous char has an uncatalyzed total particle reaction rate initially made up of nearly equivalent external and internal (diffusion controlled) reaction rates. Introduction of a catalyst, which is excluded from internal pores but which contacts the entire external surface area, can lead to the external surface reaction rate overwhelming the intra-particle reaction rate and consequently increasing the measured activation energy.

In reviews of catalyzed gas-carbon reactions, it is often noted that the measured activation energy may decrease with introduction of a catalyst as the system becomes diffusion controlled.[6] However, similar physical reaction considerations are usually not given to the case where the measured activation energy increases with introduction of a catalyst. Measured activation energies have been reported to increase, decrease, and remain constant for catalyzed gas-carbon reactions relative to the uncatalyzed reactions.[2-5,7] It is interesting to note that catalyst contacting alone may explain these differences.

Results Using Non-porous Char

In a recent study, Baker[8] presented results on the catalyzed char-CO_2 surface exchange of oxygen. Such a system was originally studied

by Orning and Sterling.[9] The char that was used in this study was nonporous thereby eliminating the need for considerations of both intraparticle reaction rates and internal catalyst contacting. By employing a unique pulsing technique, the CO_2 molecules could be followed through a char-packed microdifferential reactor without the use of radioactive tracers which were extensively used in earlier studies.[9-12] The experimental system is depicted in Figure 1. Proper choice of pulse size, pulse residence time, and reactor temperature and pressure, permitted measurements of the char-CO_2 oxygen exchange reaction for uncatalyzed char, as well as char catalyzed with alkali and alkaline earth carbonates, viz.

$$CO_2(g) + C_f \xrightarrow{k_1} CO(g) + C_o \qquad (3)$$

where C_f is a free active exchange site which can accept oxygen from gaseous CO_2 and C_o is an oxygen occupied active exchange site. The total density of active exchange sites is given by

$$C_t = C_o + C_f \qquad (4)$$

Figure 2 presents some of the data from the study. A detailed discussion and analysis is provided by Baker[8] and by Baker and Attar.[13] By initially purging the system with CO, all the active sites were converted to free active sites. Consequently, the reaction rate at low surface oxide formation is given by

$$r_{meas} = A^{ext} C_t^{ext} k_1 (CO_2) \qquad (5)$$

which allows direct measurement of $k_1(T)$. Since negligible gasification occurred, the surface area and active site density, as given in equation (5), remained constant throughout the experiments.

The data which are plotted in Figure 2 indicate the possibility that the activation energy for k_1 at low surface oxide formation, 214 kJ/mole, is the same for catalyzed and uncatalyzed char. Mentser and Ergun determined a similar value of 222 kJ/mole for uncatalyzed carbon black.[14] At high surface oxide formation the back reaction cannot be neglected, viz.

$$CO + C_o \xrightarrow{k_{-1}} CO_2 + C_f \qquad (6)$$

and this leads to curvature in the Arrhenius data.[a] The differences in measured reaction rates for different catalysts is attributed to differences in the density of active sites, C_t^{ext}. Surface areas, A^{ext}, were essentially equivalent for all samples.

At present, the data do not allow discrimination between the degree of catalyst contacting at the char surface for the various carbonates (calcium, sodium, and potassium) and their intrinsic capability to generate active sites on the char surface. However, the data do point out some similarities between catalyzed and uncatalyzed gas-char reactions which are not accounted for in many of the proposed catalytic gasification mechanisms that are based mainly on differences in measured "apparent" activation energies.

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a Statistically meaningful data could only be obtained at conversions of >3% and the back reaction became noticeable at conversions of 10%, thus limiting the conversion range for activation energy determinations.

Conclusions

Solid-solid contacting may affect the measured reaction rate and measured activation energy during catalyzed gas-carbon reactions. The measured activation energy may increase, decrease, or remain constant with the introduction of a solid catalyst. Data for a non-porous char indicated an identical first step in catalyzed and uncatalyzed char gasification. That is, CO_2 exchanged oxygen with the char surface, apparently at active site locations. The activation energy for this reaction, 214 kJ/mole, was similar for catalyzed and uncatalyzed char, however, the reaction rates differed by orders of magnitude. The catalytic effect for the alkali and alkaline earth carbonates was attributed to differences in the density of active sites. Whether the different catalyzed rates were due to different degrees of external contacting or to true differences in catalytic properties was not resolved in this study.

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Table 1. Changes in Measured Rate (r_m) and Activation Energy (E_m) with Catalyst Application to Char

Initial Reaction Conditions		Non-Porous Char	Slightly Porous Char		Highly Porous Char	
			Catalyst Penetrates Internal Pores	Catalyst Excluded From Internal Pores	Catalyst Penetrates Internal Pores	Catalyst Excluded From Internal Pores
Kinetic Control	r_m	Increase				No Change
	E_m	No Change or Decrease				
Intraparticle Diffusional Control	r_m	NA	Increase			
	E_m		Decrease	Increase	Decrease	
External Diffusional Control	r_m	No Change				
	E_m					

NA - Not Applicable

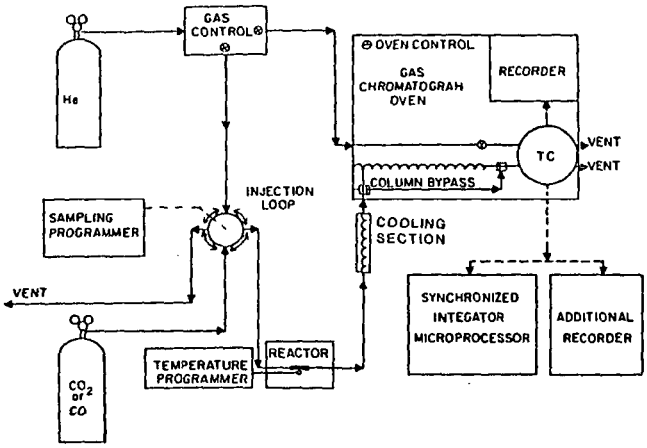

FIGURE 1

SYSTEM FOR STUDYING CHAR-CO_2 SURFACE EXCHANGE OF OXYGEN[8]

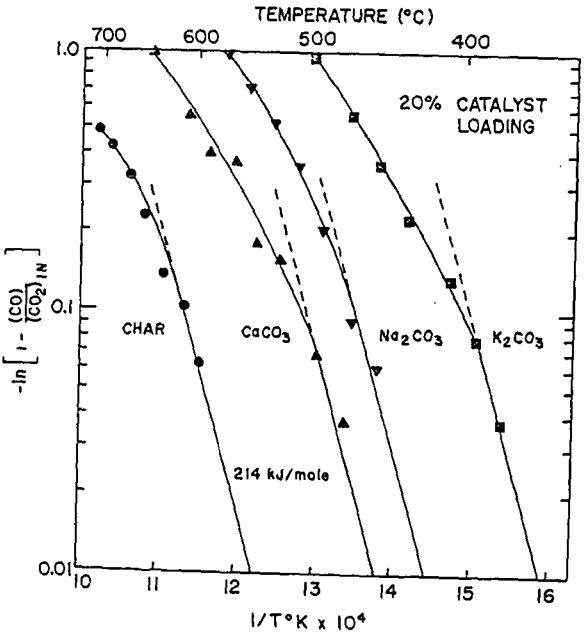

FIGURE 2

ARRHENIUS-TYPE DATA FROM CHAR-CO_2 SURFACE EXCHANGE OF OXYGEN[8]