A CATALYTIC REACTION MODEL FOR FILAMENTOUS CARBON GASIFICATION

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1. Introduction

Filamentous coke deposition is a major fouling problem for catalysts used in synthesis gas methanation, the water-gas shift reaction and hydrocarbon steam reforming. Significant effort has been spent in studying carbon deposition rate, deposit morphology and structure, and process conditions for minimization of deposition rate. A collection of papers from a special symposium and an excellent review article which survey this work have recently appeared. (1,2) Much less study, however, has been devoted to modeling the inverse reaction or the gasification/removal of filamentous carbon deposits. Information and fundamental understanding of the kinetics of the inverse reaction are needed for improved design of catalyst regeneration schemes used in commercial catalytic fuel gas processing. Better understanding of the inverse reaction may also assist identification of improved deposit prevention methods.

The present research was undertaken to develop a model for correlating conversion rate with the extent of conversion for the gasification of filamentous carbon. In our studies of the gasification reactions of filamentous carbon, we find that traditional fluid-solid reaction models such as the "shrinking core", shrinking sphere" and progressive conversion, are not adequate for describing conversion kinetics. We suspect from our work and the results of others (3,4,5) that certain filamentous carbon gasification reactions proceed via a catalytic mechanism involving an embedded catalyst particle. We have developed a new model for this type of reaction which we have termed the "axially shrinking filament" model. The conceptual basis and formulation for this new model are presented in this paper. Refinement and experimental verification/application of this new model are in progress. An illustrative example of the model's ability for describing the conversion kinetics of the filamentous carbon-hydrogen reaction is presented from this work.

2. Axially Shrinking Filament Model

Essential features of the axially shrinking filament (ASF) model are illustrated in Figure 1. As depicted, the solid grain consists of a consumable filament-shaped particle attached to a small catalyst nodule. For a grain situated in a fluid reactant medium, the catalyst nodule serves as the site of reaction between fluid reactant and the filament particle. In reaction, fluid reactant is adsorbed by the catalyst nodule and combines with filament material in the vicinity of the nodule. The initially formed reaction product is subsequently desorbed and lost to the bulk fluid phase. Continuing reaction and loss of filament material results in axial shrinkage of the grain without change in filament cross-section. The rate of the topochemical reaction is constant throughout conversion of an individual filament and is proportional to the interfacial area between the nodule and filament. Different diameter filaments thus exhibit the same linear shrinkage rate, v, under a given set of reaction conditions. The shrinkage observed for each filament in a collection of reacting grains is given by vt, where t is the reaction time. The shrinkage rate may be a function of temperature, reactant, nodule composition and orientation, and possibly other physiochemical conditions of the reaction. Interphase heat and mass transport resistances, if significant, are assumed to be constant during reaction.

A global conversion expression may be developed for this reaction model by considering the particle collection to have a time-dependent filament length distribution. Change in filament length distribution due to reaction is related to conversion extent or in the present case, the amount of carbon gasified. A general expression for relating fractional conversion, α, to the filament length distribution is given by Equation (1). The terms l and $p_o\{l\}$ are the filament length and the fraction of the initial (t=o) population having length l. $p_o\{l\}$ is the probability density function or the length distribution function for the particle collection and may be considered a continuous function of l for large number filament populations.

$$\alpha = 1 - \frac{\int_{vt}^{\infty} l\, p_o\left\{l\right\} dl - vt \int_{vt}^{\infty} p_o\left\{l\right\} dl}{\int_{0}^{\infty} l\, p_o\left\{l\right\} dl} \qquad 1)$$

While the derivation of this expression is being presented elsewhere, the intuitive correctness of the expression may be appreciated by pointing out the essence of the integral terms. The entire ratio on the right-hand side of Equation (1) is the mass fraction of carbon remaining at time t. The denominator integral simply represents the average filament length for the particle collection before any reaction (t=0). The numerator is the difference between the average length of that portion of the initial filament population with a length equal to or greater than vt and the total shrinkage length suffered by this population segment up to time t. It is important to note that Equation (1) is a general conversion expression independent of filament geometry and is valid for any continuous probability density function. In order for the equation to be useful in practice, the distribution function must be known a priori from independent measurement or ascertained from a gasification experiment. Application of Equation (1) for describing the gasification of filamentous carbon is shown below.

3. Experimental

Filamentous carbons used in these studies were prepared by carbon monoxide disproportionation over cobaltosic oxide. Cobaltosic oxide is an active CO disproportionation catalyst and produces filamentous carbon as the principal deposit form at temperatures below approximately 873°K. In the preparation, heated carburizing gas mixture is flowed over a sample of thinly-dispersed, fine oxide powder. Deposition is carried out until the deposit solid contains approximately 90-95 wt. percent carbon. A $CO-H_2$ mixture (85:15 mole ratio) is used for the carburizing gas and the deposition temperature is maintained at 723°K. These conditions lead to the production of filaments with diameters in the range of 50-200 nm and large apparent length-to-diameter ratios when examined by scanning and transmission electron microscopy.

Reaction of a filamentous carbon sample with hydrogen was conducted using a differential, micro-packed bed reactor system. In a typical gasification experiment, hydrogen of a constant flowrate is passed through a loosely-packed 1 gram sample of filamentous carbon and the flowrate and composition of exit gas measured as a function of time. Hydrogen and methane content of the exit gas is measured by an automatic sampling gas chromatograph. Exit flowrate is measured and recorded by a custom-designed volumetric displacement type flowmeter. The precision and accuracy of all measurements permitted carbon mass balances for test reactions of 96-102% to be routinely obtained. All reactions were conducted at near atmospheric pressure over the temperature range from 798 to 1073°K. Commercially pure bottled hydrogen and deuterium were used in all reactions. Further description of the reactor system and experimental procedures is being reported elsewhere.

4. Results and Discussion

Representative gasification curves for filamentous carbon are shown in Figure 2. For the temperature range investigated, all reactions displayed a similarly shaped conversion curve. During the initial 60-70% carbon gasification, the global rate for all reactions was virtually constant, exhibiting a zero-order dependence on carbon. Beyond approximately 70% conversion, reaction rate declined rapidly with further conversion. The zero-order rate dependence is consistent with a catalytic or topochemical reaction involving axial attack of long length filaments. The reaction span marked by an unsteady rate probably has zero-order rate dependence also, but this is masked by a diminishing percentage of reacting filaments. The zero-order dependence observation agrees with observations made in other studies (4,5) involving carbons produced from hydrocarbons and employing different deposition catalysts. The activation energy determined for the gasification reaction below 873°K is approximately 178 KJ/mole. Between approximately 873 and 1023°K an apparent maximum in reaction rate was observed. This maximum, however, was an experimental artifact due to the attainment of equilibrium and the onset of hydrogen feedrate control of the reaction.

The ability of the ASF model to quantitatively fit experimental data is illustrated in Figure 3. This correlation was made using the Gaussian normal probability function (6) for the filament length distribution term in Equation (1) and using non-linear least squares regression analysis to determine the model parameters. The integral expression used for regression is given in Equation (2). The terms $\bar{l}_o$ and σ^2 used in this equation refer to the filament length distribution parameters, mean length, and variance for the initially unreacted sample. Selection of the Gaussian function to represent the filament length distribution is a reasonable choice in the absence of any foreknowledge about the length distribution. It is intermediate between a monodisperse and uniform length distribution in its effect on the predicted shape of the gasification curve. Additionally, it requires only two parameters, a mean and variance, to fully describe the distribution.

$$\alpha = 1 - \frac{\int_{vt}^{\infty} l \exp\left\{-\tfrac{1}{2}\left(\frac{l-\bar{l}_o}{\sigma}\right)^2\right\} dl - vt\int_{vt}^{\infty} \exp\left\{-\tfrac{1}{2}\left(\frac{l-\bar{l}_o}{\sigma}\right)^2\right\} dl}{\int_{0}^{\infty} l \exp\left\{-\tfrac{1}{2}\left(\frac{l-\bar{l}_o}{\sigma}\right)^2\right\} dl} \qquad 2)$$

As indicated by Figure 2 the model appears adequately capable of describing the conversion kinetics of filamentous carbon. Appropriateness of the ASF model was further evaluated in a special series of tests. In this series, samples of carbon produced from a single deposition experiment were reacted at different temperatures and model parameters determined for each reaction. If the model is an appropriate one, only the filament shrinkage rate, v, should be observed to vary with temperature; the filament length distribution parameters should be constant within sampling and experimental error. That this is indeed the case may be seen from the results presented in Table 1. While v increases by nearly a factor of five in going from a reaction temperature of 798 to 848°K, $\bar{l}_o$ and σ remain relatively constant. Increasing the reaction temperature to 1073°K, where there is a definite change in Arrhenius activation energy, and also switching to deuterium reactant yield the same distribution parameter values. This is further evidence of the appropriateness of the model. The ASF model is a macro-physical description of the reaction and is not based on any particular, molecular rate-controlling mechanism.

Table 1. Regression fitted model parameters for various temperature reactions.

Gasification Temperature, °K	Model Parameter		
	v^a	$\bar{l}_o^{\,b}$	σ
798	.39	84	16
823	1.00	84	15
848	1.91	82	22
1073	0.80	83	20
1073	0.81^c	82^c	26^c
	Average	83	20

a Filament shrinkage rate relative to 823°K value.

b Filament distribution average length and standard deviation expressed in dimensionless length units.

c Results for deuterium - carbon gasification reaction.

5. Summary and Conclusions

A general reaction model has been proposed for describing the gasification of filamentous carbons. The model, termed the "axially shrinking filament" model, successfully correlates gasification data obtained for the hydrogen-filamentous carbon reaction where the carbon is produced from CO disproportionation over a cobalt catalyst. The model may be applicable for other filamentous carbon gasification reactions and should be useful in the design of coked catalyst regeneration schemes.

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FIGURE 1. AXIALLY SHRINKING FILAMENT MODEL.

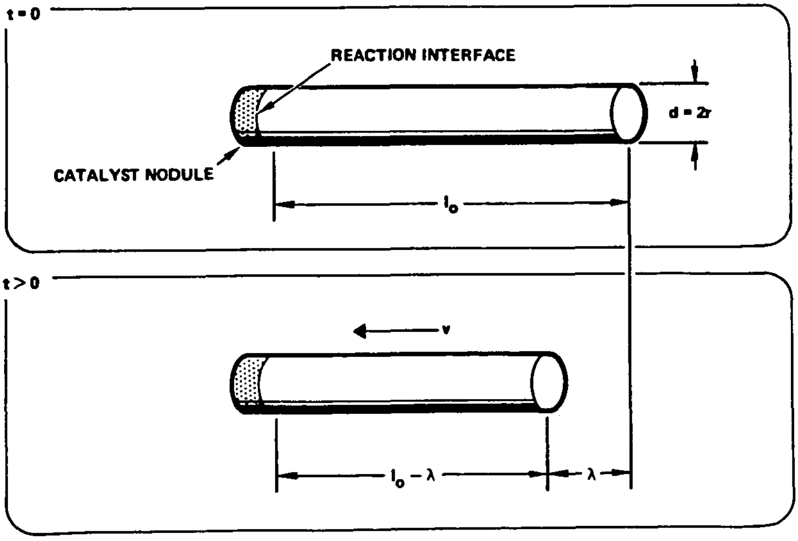

FIGURE 2. REPRESENTATIVE CONVERSION-TIME CURVES FOR FILAMENTOUS CARBON GASIFICATION.

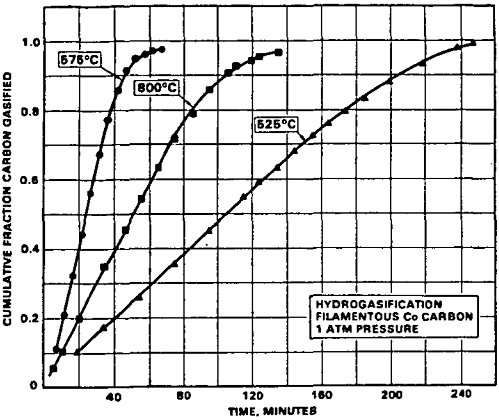

FIGURE 3. MODEL CORRELATED REACTION DATA FOR FILAMENTOUS CARBON GASIFICATION.