

## A MODEL OF NICKEL-CATALYZED GASIFICATION

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### ABSTRACT

The diffusion of carbon through a spherical nickel catalyst particle has been modeled using a finite elements approach. A steady-state model (applicable to gasification of carbons which do not lead to catalyst deactivation) is capable of explaining reported variations in reaction rate with catalyst particle size. The model uses reported values for the diffusion coefficient and solubility of carbon in nickel, and the necessary rate constants are determined from available rate data. This has the benefit of producing a model with few adjustable or empirical constants. An unsteady-state model has also been developed and can be used to explain observed deactivation with this catalyst system.

### INTRODUCTION

The gasification of carbons and coals using transition metal catalysts is well-studied experimentally, but there are several observed phenomena which are still not fully understood. With nickel catalysts for example, it has been observed that the apparent activation energy for the reaction changes as the temperature increases (1,2). Also with nickel catalysts and certain carbons there is a continuous deactivation of the catalyst as reaction proceeds (2,3,4). Recently studies have been made wherein the combined diffusion and reaction phenomena have been modeled in an attempt to explain the observed behavior of transition metal catalysts during carbon gasification (5,6). In these studies a major focus has been the explanation of the dependence of the rate of gasification upon the size of the catalyst particle. The controlled-atmosphere electron microscopy (CAEM) technique has provided a wealth of rate versus particle size data (7-9).

The present study also involves the formulation of a model which includes both diffusion and reaction phenomena occurring within and on a single catalyst particle. Previous models have used cubic (5) and cylindrical (6) particle shapes and have considered channeling along the surface of a graphite basal plane. Spherical particles tunneling inside the carbon matrix have been modeled in this study. Consequently, the results are not influenced by the channel depth. In addition to the dependence of the rate of particle movement (i. e. the rate of gasification) upon particle size, temperature effects have also been examined. This has been done in two different ways. First the shape of the rate versus particle size curve has been computed at a number of temperatures in the range of practical gasification conditions. Additionally, for a single, representative particle size the dependence of the rate of particle movement has been calculated as a function of temperature.

### METHODS

Nickel was chosen as the catalytic material to be modeled. Nickel is very active at low temperatures, and low temperature operation is desirable for thermodynamic reasons if methane is the desired product. Nickel remains

metallic under most gasification conditions, but it does deactivate (4). Additionally, the properties of carbon-nickel alloys are readily available due to the importance of these materials in steelmaking. The carbon was assumed to be isotropic and to be essentially free of impurities which would poison the catalyst.

Figure 1 depicts a spherical nickel particle as it catalyzes the gasification of carbon. The particle has one hemispherical surface which is in immediate contact with the carbon, and another which is exposed to the gas phase. As the carbon is gasified, the particle moves through the carbon creating a tunnel (or if it is on a basal plane surface of graphite it would create a channel like those which have been observed by CAEM). A spherical co-ordinate system centered on the particle center is shown in the figure. In this system  $r$  is the distance from the center of the particle and  $\theta$  is the angle measured from a line along the tunnel centerline.

It is assumed that the problem will be symmetric about the tunnel axis, and that carbon will dissolve into the particle along the leading hemisphere (from  $\theta = \pi/2$  to  $\theta = \pi$ ). The carbon is assumed to diffuse through the particle to emerge on the surface of the trailing hemisphere (from  $\theta = 0$  to  $\theta = \pi/2$ ). Finally the carbon reacts with oxygen atoms adsorbed on this surface producing the gasification products.

A material balance on the carbon within the particle at steady-state requires that

$$D \cdot \nabla^2 C = 0 \quad (1),$$

where  $D$  is the diffusion coefficient and  $C$  is the concentration of dissolved carbon in the metal. As discussed by Tsamopoulos et al. (6) the boundary condition imposed at the leading hemisphere is that the flux in the direction of tunneling is constant, and this flux is chosen such that the particle is just saturated with carbon at the leading point  $\theta = \pi$ . Additionally it is assumed that there is no flux in the  $\theta$  direction at  $\theta = 0$  and at  $\theta = \pi$ . Finally on the trailing hemisphere the flux of carbon is set equal to the rate of reaction.

The form of the rate expression used on this surface was derived by assuming that the gas phase composition in the vicinity of the particle is constant and that a pseudo-equilibrium is established between gas phase  $H_2O$  and  $H_2$  and surface oxygen. This gives a rate expression of the form

$$r = k \cdot \theta_C \cdot (1 - \theta_C) \quad (2),$$

where  $r$  is the reaction rate,  $k$  is a combination of rate constants, the pseudo-equilibrium constant and  $H_2O$  and  $H_2$  partial pressures, and  $\theta_C$  is the fractional surface coverage of carbon. In the present study the bulk concentration at the surface has been converted to a fractional surface coverage by simply preserving the ratio of carbon to nickel atoms. That is, no surface enrichment or bulk enrichment has been accounted for.

The Galerkin/finite elements approach was used to solve equation (1) subject to these boundary conditions. Published values of the solubility of carbon in nickel and the diffusion coefficient of carbon in nickel were used (10-12).

The value of the constant  $k$  in equation (2) was found using a particle size of 6 nm, a rate of 0.252 mmol C/(min mg<sub>Ni</sub>), and a temperature of 825 K. A second value of  $k$ , at 975 K, was similarly found using a rate of 1.70 mmol C/(min mg<sub>Ni</sub>). These values for the rate and average particle size were measured experimentally by Wigmans and Moulijn (2). To find these values of  $k$ , equation (1) was solved varying  $k$  until the predicted carbon gasification rate matched the experimental rate.

The constant  $k$  in equation (2) was then assumed to vary with temperature according to the Arrhenius expression,  $k = k_0 \cdot \exp(E_A/RT)$ . Thus from these two data points the only "missing" constants in equation (1) and its boundary conditions were found. It is then possible to use the model to predict the rate behavior for any particle size and at any temperature.

## RESULTS AND DISCUSSION

Using the procedure described in the preceding section, the activation energy for the surface rate constant was found to equal 7.18 kcal/mol. This value is very low, probably due to the assumption made in relating the bulk concentration to the fractional surface coverage. This is discussed further later in this section.

Equation (1) was then solved for a number of particle sizes and temperatures. The results are plotted in Figure 2 as a family of curves of tunneling rate versus particle size. For each temperature, the rate is plotted relative to a 10 nm particle at that same temperature. In the figure it is seen that as the temperature increases the rate becomes less dependent upon the particle diameter. This is because the rate of diffusion of carbon through the metal increases rapidly with temperature, and at the higher temperatures shown in the figure, the surface reaction has become the rate-limiting step. Indeed, in these cases the solution of equation (1) shows that the particle is essentially saturated with carbon everywhere.

In the original CAEM work reported by Baker and Sherwood (8) a very strong dependence of rate upon particle size was observed at 1150 °C. However in the present modeling study virtually no dependence upon particle size is predicted at this temperature. Subsequent work by Baker et al. (9) indicates that in fact nickel metal is active at much lower temperatures than suggested in (8). Based upon the present results, it might be possible that in the original study (8) the catalyst was nickel oxide and not the metal. If the diffusion coefficient for carbon in nickel oxide was available, equation (1) could be solved to see if a dependence of rate upon particle size would be expected; we could find no values for that diffusion coefficient. It does not seem unlikely, however, that the diffusion coefficient for carbon in nickel oxide would be several orders of magnitude smaller than that for carbon in nickel metal, and consequently a strong dependence of rate upon particle size would be expected for nickel oxide catalyst at 1150 °C.

Equation (1) was solved for a 6 nm particle at a number of temperatures, and the results are plotted in the form of an Arrhenius plot in Figure 3. The two triangles represent the two data points which were used to find  $E_A$  and  $k_0$  in the Arrhenius expression. This plot is remarkably similar to the experimental data reported by Wigmans and Moulijn (2) which show an Arrhenius behavior where below ca. 825 K the apparent activation energy is equal to 40.6

kcal/mol, an abrupt change is seen in the apparent activation energy at ca. 825 K, and above this temperature an apparent activation energy of 20.3 kcal/mol is measured. These authors (2) attributed the decrease in activation energy to the onset of mass transfer limitations at the higher temperatures.

When an apparent activation energy is calculated from the slope of Figure 3 in the high temperature region, a value of 16.8 kcal/mol results. A similar calculation in the low temperature region gives an apparent activation energy of 46.0 kcal/mol. These results are remarkably close to those reported by Wigmans and Moulijn. However, the present modeling study shows that in fact the gasification reaction is mass-transfer-limited in the low temperature region, and that the limiting mass transfer is that of carbon through the metal, not that of the gas phase either from the bulk gas to the carbon surface nor of the gas in the pore structure of the carbon.

This is contrary to the traditional situation in catalysis where as the temperature rises mass transfer from the flowing gas to the surface of the solid material can become rate-limiting. Indeed, the apparent activation energy in the high temperature region, 20.3 kcal/mol, is quite high to be assigned to a mass transfer coefficient. Furthermore, the high activation energy at lower temperatures nearly equals the activation energy for the diffusion coefficient of carbon in nickel.

The solution of equation (1) at the higher temperatures reveals that the particle is essentially saturated with carbon throughout its volume. Under these conditions the rate of the reaction will be determined by the rate of the surface reaction as expressed in equation (2). We have assumed that the fractional surface coverage of carbon,  $\theta_C$ , equals the carbon to nickel ratio in the bulk. At bulk carbon concentrations which are significantly less than saturation this assumption should be reasonably accurate, however, as the bulk concentration approaches saturation it will not be so. Specifically, as the bulk concentration just equals saturation, it would be expected that the fractional surface coverage would just approach 1.0 (then as the bulk concentration surpasses saturation, multi-layer carbon precipitation would ensue). Thus, in a regime where the particles are nearly saturated it would be expected that  $\theta_C$  would approach 1.0 regardless of the temperature, and this, in turn would mean that the two terms  $\theta_C$  and  $(1 - \theta_C)$  would show very little dependence upon temperature. Then all temperature dependence would be reflected in the surface rate constant,  $k$ , and the apparent activation energy would equal the activation energy of the surface reaction rate constant.

Using the assumption that the fractional surface coverage equals the bulk carbon to nickel ratio will result in a value of  $\theta_C$  which is less than unity, and further, it will result in a value of  $\theta_C$  which varies with temperature the same way that the carbon solubility does. In this case, the overall temperature dependence will be reflected in the product of the surface rate constant and the fractional surface coverage, and the apparent activation energy would nearly equal the sum of the activation energy of the solubility of carbon in nickel (9.7 kcal/mol (12)) and the activation energy of the surface rate constant.

Hence, if a more reasonable method of relating the surface coverage to the bulk concentration is employed, it is expected that the value of the activation energy for the surface reaction step will increase from the present

value of 7.18 kcal/mol to a value approximately equal to the experimentally observed high temperature value of 20.3 kcal/mol. We are presently pursuing these calculations.

Finally, Kelemen (13) has recently reported that the activation energy for the surface reaction equals 31 to 32 kcal/mol on Ni(111). The present study indicates that the maximum value expected for the activation energy is of the order of 20 kcal/mol. This perhaps suggests that the surface of the active catalyst particles does not resemble a Ni(111) surface.

#### CONCLUSIONS

The steam gasification of carbon using nickel catalysts appears to be a reaction in which the rate-limiting step changes from diffusion of carbon through the metal at low temperatures to surface reaction kinetics on the metal at high temperatures. This results in a particle size dependence of the rate of gasification which changes as the temperature changes.

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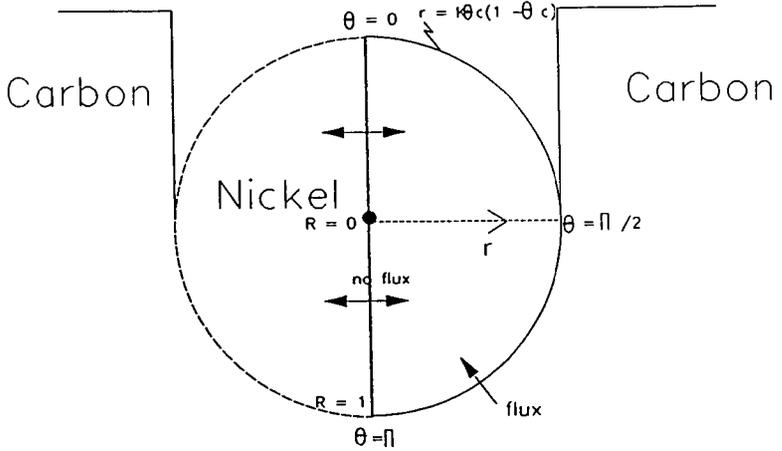


Figure 1. A schematic representation of the catalyst particle during gasification.

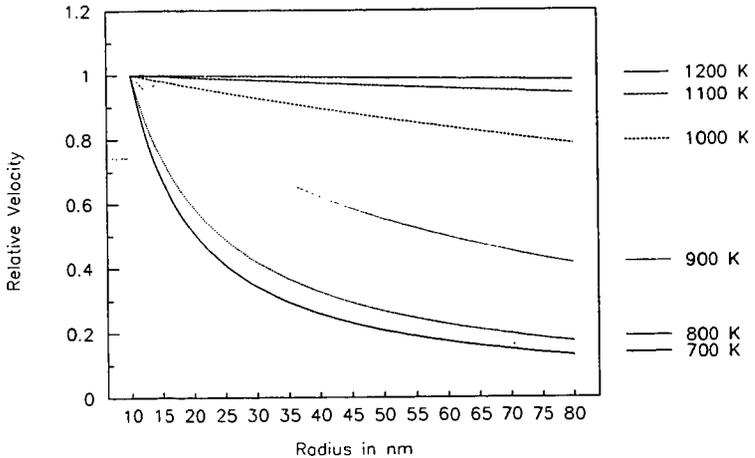


Figure 2. The dependence of the rate of gasification upon the particle size as a function of reaction temperature. At each temperature the rates are normalized to the rate of a 10 nm particle at that temperature.

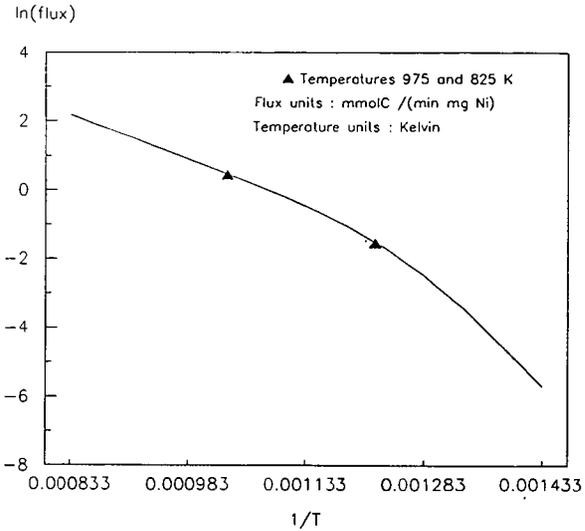


Figure 3. An Arrhenius plot of the rate of gasification computed using the model. The two points represent the experimental data used to find the surface reaction rate constant as described in the text.