Modeling the Channeling Action of Catalysts in Gas-Carbon Reactions

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The reactions between carbon and O_2, H_2O, CO_2, and H_2 have been the subject of many investigations. It has been well known that small amounts of impurities in carbon can have profound catalytic effects on these reactions. The effects of over forty metals, metal oxides, and salts have been studied (Walker et al., 1968; McKee, 1981). The most significant, as well as intriguing, action undertaken by the catalyst particles is channeling: the particle cuts a channel that is several graphite layers deep on the basal plane of graphite at a constant speed to gasify carbon (see Figure 1). Other important catalytic actions are: monolayer channeling, tunneling, pitting, and edge recession. Monolayer channeling and tunneling are important in relatively slow chemical reactions, such as the C-H_2 reaction (Goethel and Yang, 1988a; 1988b), whereas pitting and edge recession are important in relatively fast chemical reactions, such as the C-O_2 reaction (McKee, 1981; Baker, 1986). The best understood catalytic action is channeling by metals (both deep and monolayer) which involves the following sequential steps: dissolution of carbon into the metal at the leading edge of the metal particle, and diffusion of carbon in the metal to the top and rear surfaces of the particle where carbon is converted into gaseous products. Scattered experimental results have been reported in the literature on the particle propagation speeds, by different metals and in different gaseous environments. The most intriguing result is the dependence of the channeling speed on particle size. The dependence can be either increasing or decreasing, depending on the combination of factors such as type of metal, gaseous environement, temperature, and particle size range. The purpose of the following analysis is to develop a simple model which illustrates the interplay between diffusion and chemical (surface) reaction in determining the channeling speed. It will be shown that this simple model is capable of predicting the channeling speed as well as its dependence on particle size. The model also delineates the important role played by carbon's solubility in metal, in determining the channeling speed.

Theoretical Considerations

Channeling particles are usually faceted (Goethel and Yang, 1988a). Inasmuch as the exact shape is not known and it varies with the gas/metal system, a cubic shaped particle is considered here of side-length L, with its front face in contact with graphite, Figure 2. Moreover, two different cases are under consideration: A, where the channel depth is equal to the particle dimension, and B, where the channel depth is constant, and same for all particles. Case A occurs when channeling is initiated by particles located at the edges of the graphite crystal, whereas case B occurs when different particles initiate channels from the same ledge (or step) on the basal plane of graphite. As shown in Figure 2, the edge carbon atoms dissolve in the metal at the front face of the particle, diffuse through the bulk, and react at the gas/metal interfaces. The surface reaction is assumed to be first order with respect to surface carbon concentration. Due to the small particle size and the long channeling time (in hours), the channeling particle is assumed to be isothermal.

Analytic solution for case A is given first. Defining the dimensionless lengths as $(X, Y) = (\tilde{X}, \tilde{Y})/L$, and the dimensionless concentration as $C = \tilde{C}/C_o$ where C_o is the solubility of carbon in metal at the given temperature, the governing equations for the channeling particle are:

$$\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} = 0 \qquad (1)$$

$$\frac{\partial C}{\partial Y} = 0, \quad Y = 0 \qquad (2)$$

$$\frac{\partial C}{\partial X} = DaC, \quad X = 0 \qquad (3)$$

$$\frac{\partial C}{\partial Y} = -DaC, \quad Y = 1 \qquad (4)$$

$$\frac{\partial C}{\partial X} = \frac{L}{DC_o}\tilde{\alpha} \equiv \alpha, \quad X = 1 \tag{5}$$

where Da is the Damkohler number defined by kL/D, D is diffusivity of carbon in the metal, and k is the first-order rate constant based on the volume concentration of carbon in metal at or near the surface (and hence, with the units of cm/s).

Equation 5 sets the rate of dissolution of carbon into the metal to a constant, $\tilde{\alpha}$, and equal to the particle channeling rate. This constant will be calculated so that the bottom corner of the particle in contact with graphite is saturated with carbon, i.e.,

$$C = 1, X = 1 \quad \text{and} \quad Y = 0 \tag{6}$$

It should be noted here that setting the carbon concentration on the same surface equal to its solubility would force the upper portion of the particle to move faster than the lower one simply in order to remain in contact with the more rapidly consumed carbon there. According to the present model, only the bottom corner of the catalytic particle is saturated with carbon. The carbon concentration in the rest of the front plane of the particle is less and is determined so that Eq. 5 is satisfied. Thus, the channeling speed of the particle is limited by the most diffusion limited position, that of the bottom-front corner. Equations 1–5 are readily solved by separation of variables, and the result is expressed in terms of the parameter α which is determined through Eq. 6. The final result is:

$$C = \sum_{n=1}^{\infty} A_n \left[\frac{\tau_n}{Da}\cosh(\tau_n X) + \sinh(\tau_n X)\right] \cos(\tau_n Y) \tag{7}$$

where the eigenvalue, τ_n, is the solution of the characteristic equation:

$$\tau_n \tan \tau_n = Da \tag{8}$$

and the coefficient, A_n, is given by

$$A_n = \frac{2 \sin \tau_n}{\tau_n + \sin \tau_n \cos \tau_n} \, \frac{Da}{\tau_n \cosh\tau_n + Da \sinh\tau_n} \tag{9}$$

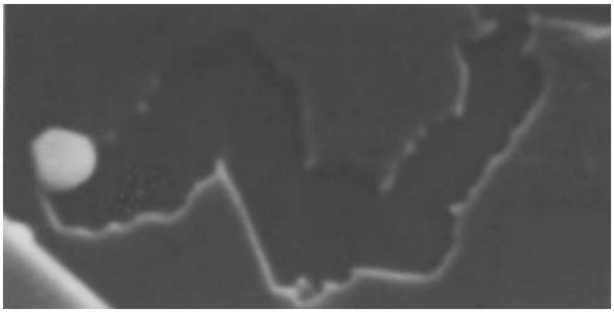

Figure 1. SEM of platinum particle channeling on graphite basal plane in 1 atm H_2 at 950°C for 3 h.
Magnified ×27,000

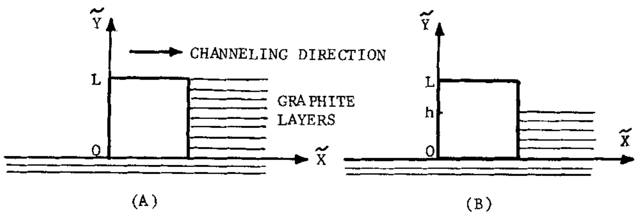

Figure 2. Cubic metal particle channeling into graphite layers at channel depth equal to particle size, case A, and at a constant depth for all particles, case B.

For the case of channeling at the same depth for all particles, case B, analytic solution is not possible. The model equations for case B are the same as Eqs. 1–6, with Eq. 5 replaced by the following:

$$\frac{\partial C}{\partial X} = \frac{L}{DC_o}\tilde{\alpha} \equiv \alpha, X = 1, 0 \leq Y \leq h/L \tag{10}$$

$$\frac{\partial C}{\partial X} = -DaC, X = 1, h/L \leq Y \leq 1 \tag{11}$$

In this model, the surface reaction on the two side surfaces has been neglected, thus it underpredicts the channeling speed; the extent of underprediction is greater for larger particles. The model equations for case B, Eqs. 1–4, 6, 10, and 11, are solved numerically by a finite difference scheme.

Results and Discussion

The overall carbon gasification rate is equal to the total carbon flux at the leading front of the particle, Figure 1. The analytic solution for case A, Eq. 7, shows that the carbon concentration is dependent only on two parameters, Da and C_o; and that it is proportional to C_o. Consequently, the flux of carbon or the velocity of the particle is proportional to C_o, and has a complex dependence on Da. The dependence of the flux on Da, expressed as channeling speed, is shown in Figure 3, under oxidation conditions. Here it is seen that the channeling speed increases with Da, but this dependence is weaker than its linear dependence on C_o.

Also shown in Figure 3 are the experimental data for Pd particles channeling in O_2 atmosphere (Baker et al., 1976), which are the most complete data on channeling, available in the literature. However, there are some uncertainties regarding the channel depths and the temperature. The channel depths were not measurable in the experiments because the TEM technique provided only a two-dimensional view. The temperature was obtained by calibration with a thermocouple in contact with the heating ribbon (not with the graphite). This, combined with the fact that cold O_2 was used in the reaction chamber, made their reported temperatures considerably higher than the actual temperatures for the reaction, and a 40°C differential was entirely possible (Baker, private communication, 1988). The experimental data shown in Figure 3 are for a reported temperature of 575°C. In order to compare our models with the experimental data, we have measured the D and C_o values for carbon in Pd in the temperature range of 500–600°C, with the following results (Goethel, 1988):

- $D = 9.553 \text{X} 10^{-2} \exp(-13{,}744/T)$ cm^2/s
- $C_o = 0.60 \exp(-4{,}051/T)$ g/cm^3

Since no data are available on the rate constant, k, it remains as a fitting parameter. Curves a, b and c in Figure 3 are based on D

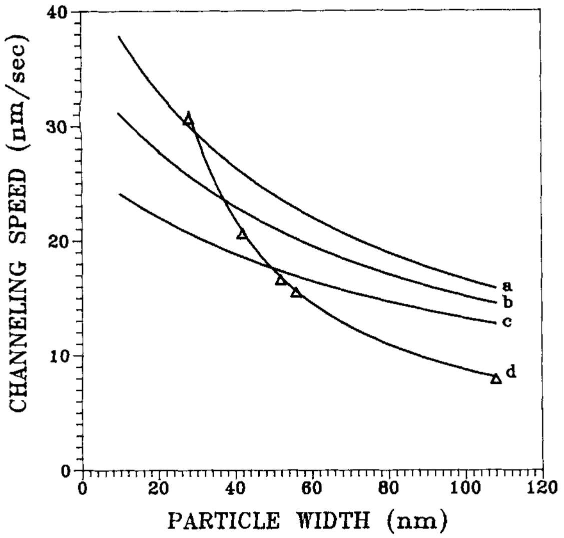

Figure 3. Channeling speed vs. catalyst particle size (Eq. 7).

Lines a–c all based on $D(8.75 \times 10^{-9}\ cm^2/s)$ and $C_o(0.005\ g/cm^3)$(for 575°C) but with varying k: a = 10^{-3}; b = 8×10^{-4}; c = 6×10^{-4} cm/s. d based on: $D = 3.53 \times 10^{-9}\ cm^2/s$, $C_o = 0.00379\ g/cm^3$ (for 530°C), and $k = 0.1$ cm/s. △ = experimental data for palladium channeling in oxygen (Baker et al., 1976).

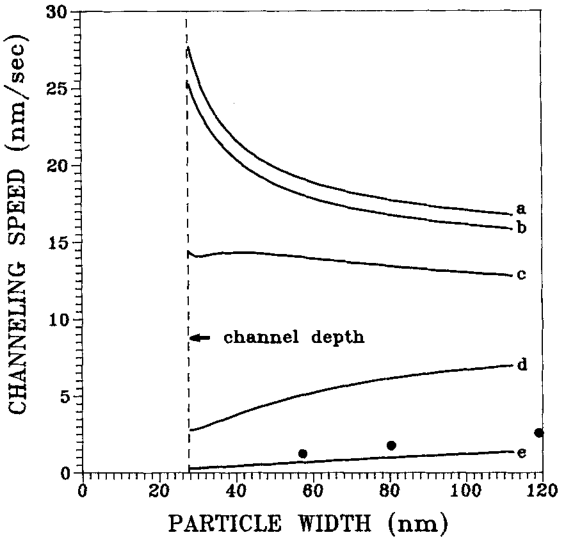

Figure 5. Prediction of channeling speed for case B at depth = 28 nm, $D = 3.17 \times 10^{-9}\ cm^2/s$, $C_o = 0.0037\ g/cm^3$, k (cm/s): a = 10^{-1}; b = 10^{-2}; c = 10^{-3}; d = 10^{-4}; e = 10^{-5}.

● = experimental data for Ni channeling in graphite/H_2 at 1,025°C (Keep et al., 1980).

and C_o at 575°C, for various assumed values of k. Compared with these curves, the experimental data exhibit a stronger dependence of channeling speed on particle size, indicating that the channeling action is actually more diffusion-limited. Consequently, the surface reaction must be more rapid than those represented by the assumed values of k (6×10^{-4}–10^{-3} cm/s). The experimental data of Baker et al. (1976) on channeling speed cannot be fitted simply by increasing the k values while using the experimental values of D and C_o at 575°C. The best fit (curve d in Figure 3) can be obtained by using the D and C_o values at 530°C, and a much higher k value of 0.1 cm/s. This result indicates that 530°C was probably the actual surface temperature in Baker's experiment—considerably cooler than the reported temperature, as discussed in the foregoing. A comparison of the k value may be made with that on an active site of carbon. The active carbon atoms are the edge atoms with an unpaired sp^2 electron (Yang and Wong, 1981). The turnover frequency on a multilayer active edge atom is 0.04 s^{-1} at 530°C and 5 Torr O_2 (used in Baker's experiment) (Yang, 1984). This rate translates into a k value of 0.09 cm/s, in reasonable agreement with the value obtained from the model.

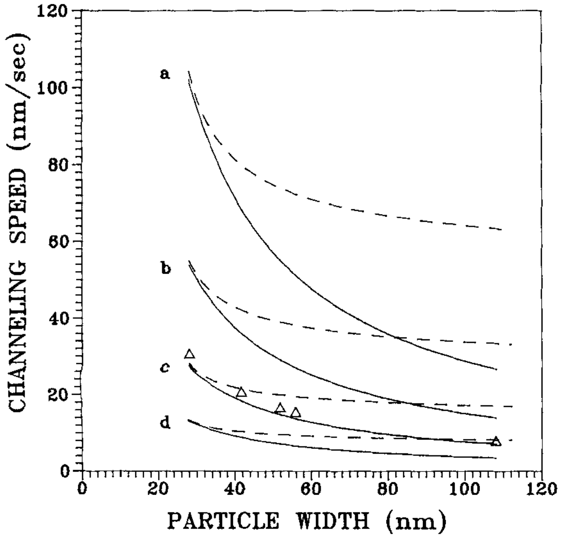

Figure 4. Channeling speed of Pd in graphite/O_2 at: a = 575°C, b = 550°C, c = 525°C, and d = 500°C; k = 0.1 cm/s.

Solid curves are predictions for case A, Eq. 7; dashed curves are numerical solution for case B at channel depth of 28 nm. △ = Baker (1976).

The model predictions for cases A and B are compared in Figure 4. The channeling speed for the same particle size is lower for case A, whereas the channeling speed-size dependence is weaker for case B.

An intriguing experimental observation about catalyst channeling has been that the channeling speed can both increase and decrease with particle size, depending on a host of experimental conditions. This phenomenon can indeed be understood through our models. Figure 5 shows the predictions of model B, for example, as the channeling action is switched from being diffusion controlled (curve a) to being surface reaction controlled (curve e). The channeling speed-particle size data of Keep et al. (1980) on the C-H_2 reaction catalyzed by Ni, can be interpreted by the model as a surface-reaction controlled case, as shown in Figure 5.

Acknowledgment

This work was partially supported by NSF Grants CBT-8703677 and MSM-8705735.

Notation

$C, \tilde{C}$ = concentration of carbon in metal, $C = \tilde{C}/C_o$
C_o = saturated solubility of carbon in metal, g/cm^3

D = diffusivity of carbon in metal, cm^2/s
Da = Damkohler number, kL/D
k = first-order rate constant based on C at the surface, cm/s
L = side length, or size of particle, cm
T = absolute temperature, K

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Manuscript received June 20, 1988, and revision received Nov. 21, 1988.