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The Roles of Ordinary and Soret Diffusion in the Metal-Catalyzed Formation of Filamentous Carbon

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The rate-determining step for the metal-catalyzed formation of filamentous carbon from hydrocarbons and carbon monoxide is commonly assumed to be diffusion of dissolved carbon through the metal particle. The driving force for the diffusion process has been proposed to be either an isothermal carbon concentration gradient or a temperature gradient, the latter leading to Soret diffusion (mass transfer due to a gradient in the chemical potential resulting from the temperature gradient) and, possibly, effects from the temperature dependence of the solubility of carbon. Metal carbides often have been postulated to play a role as intermediates. Mass transfer by these processes is examined and expressions for carbon deposition rate and activation energy are derived. Experimental results are consistent only with a mechanism in which the driving force for carbon diffusion is an isothermal carbon concentration gradient and in which metal carbides are not intermediates. The temperature gradient mechanism was found to conflict with the fact that for metals with a large negative heat of transport for carbon diffusion, such as α-Fe, temperature gradients of the type proposed (in which the gas-phase side of the particle is hotter than the carbon filament side) would lead to diffusion of carbon away from the carbon filament rather than towards it. A possible role for metal carbide intermediates is limited to Fe, Ni, and Co. However, measured activation energies for these metals are in good agreement only with those values predicted assuming metal carbides do not participate as intermediates. © 1995 Academic Press, Inc.

INTRODUCTION

In the presence of reducing and carburizing conditions, many metals catalyze the formation of filamentous carbon (1–4). The process has been studied from carbon monoxide (5–7), saturated hydrocarbons (4–6), unsaturated hydrocarbons (4, 8–13), and partially oxygenated hydrocarbons (14, 15). Carbon deposition can be catalyzed both by metal catalyst particles and reactor walls, and it can lead to yield loss, corrosion, large pressure drops, and even complete plugging of reactors. The carbon deposition process plays an important role in the steam reforming of hydrocarbons and in thermal cracking. The process has also been studied as a means for producing high modulus carbon fibers at relatively low temperatures (16–18).

Aside from its industrial importance, the catalyzed formation of filamentous carbon is of particular theoretical interest. Together with carbon gasification (19) and graphitization (20), it is one of three carbon-based reactions whose progress can be monitored visually in real time by *in situ* electron microscopy. The catalyzed formation of filamentous carbon is also noteworthy in that it is a rare example of a catalytic reaction in which the rate is believed to be controlled by a diffusion process *through the bulk catalyst*, rather than surface reactions. Finally, in one proposed mechanism (9), temperature gradients within small catalyst particles (10–1000 nm diameter) play an essential role, and if the catalytic process is indeed tied to such temperature gradients, this too would be unique for known catalytic reactions.

The commonly accepted mechanism for filamentous carbon formation is the decomposition of the carbon-containing gas on one side of a metal particle, leading to the formation of carbon atoms which then dissolve into the metal particle, diffuse through it, and precipitate on its opposite side in the form of filamentous carbon. The filaments often have a hollow core. The rate-determining step for the reaction is most often considered to be the diffusion of carbon through the metal particle at low temperature (10, 21), while surface reactions are also thought to play a role at high temperature (4, 8). The strongest quantitative evidence for the diffusion of carbon as the rate-determining step is the observation in several *in situ* electron microscopy studies that the activation energy for filament growth E from acetylene is in excellent agreement with the activation energy for diffusion of carbon through the bulk metal E_D (9–12). Results from these studies comparing E and E_D (22) are compiled in Table 1. In addition, *in situ* electron microscopy studies of filament growth indicate that the velocity of filament growth decreases with increasing particle diameter (2, 3, 10), and this too is in agreement with a bulk diffusion-controlled process.

Global kinetic studies of carbon deposition, usually carried out by gravimetric measurement of the rate of mass

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TABLE 1

Comparison of Activation Energies for Diffusion of Carbon through Metal E_D and Activation Energies for Carbon Filament Growth E

Metal	E_D (kJ/mol)[a]	E (kJ/mol)[b]	Ref.
α-Fe	78–80	67 ± 5	(11)
		76 ± 8	(13)
γ-Fe	148–154	142 ± 12	(13)
Ni	139–145	145	(10)
Co	145–162	139 ± 7	(11)
Cr	110–117	113 ± 15	(11)
V	116	115 ± 12	(12)
Mo	139–172	145 ± 17	(12)

[a] Activation energy for carbon diffusion in metal taken from the compilations of Ref. (22). Except for V, the range of activation energies reflects values reported in several studies. Most measurements of E_D were recorded at low x_C and are therefore about equal to the self-diffusion coefficient of carbon E_D^*.

[b] Activation energy for the velocity of filament growth measured by *in situ* electron microscopy.

gain, have also indicated that the activation energy for carbon deposition from acetylene, olefins, and diolefins is in close agreement with E_D at temperatures below about 550°C (Table 2). For such conditions, the deposition rate is reported to be zero-order both in the partial pressures of the hydrocarbon reactant and hydrogen by-product. At higher temperatures, a complicated temperature dependence for the carbon deposition process is often observed from these reactants, such that a regime with a negative apparent activation energy is present at moderate temperatures (4).

There are two viewpoints on the driving force for the diffusion process. Baker *et al.* (10) first postulated that the driving force is a temperature gradient resulting from the exothermic decomposition of the gaseous reactant on the leading surface of the particle. In this mechanism, the gas side of the catalyst particle is proposed to be at a higher temperature than the carbon filament side, and the temperature gradient leads to transport of carbon toward the filament. Nishiyama *et al.* (23) and Rostrup-Nielsen and Trimm (21) postulated that the driving force results from a concentration gradient produced by supersaturation of an isothermal metal particle with carbon at its leading edge.

TABLE 2

Gravimetrically Measured Activation Energies for the Global Rate of Carbon Deposition by Nickel

Gas	Catalyst	T (°C)	E (kJ/mol)	Ref.
Acetylene	Ni	375–525	138 ± 17	(4)
Ethylene	Ni	375–525	138 ± 17	(4)
Propylene	Ni	375–525	138 ± 4	(8)
1-Butene	Ni	375–525	121	(8)
Butadiene	Ni	375–525	138 ± 17	(4)
Propylene	Ni/Al_2O_3	350–450	125	(4)
Toluene	Ni/Al_2O_3	475–600	150	(4)

The role of metal carbides in the carbon formation process has been debated. Bulk carbides (16, 24, 25) or surface carbides (26, 27) have often been suggested as the active catalyst or as an intermediate in the deposition of carbon. However, studies by Baker and co-workers (12, 28) indicate that metal carbides are inactive for carbon deposition.

As noted, experimental results indicating that $E \cong E_D$ have been cited as evidence that carbon diffusion is the rate-determining step. An important consideration in deriving the activation energy for a process is that it can depend not only on the activation energy of the rate-determining step, but also on other factors, such as contributions from the enthalpy changes of steps which occur prior to the rate-determining step (29). Below we analyze the diffusion process, considering both the case where the driving force is a concentration gradient and where it is a temperature gradient. Activation energies are derived for several limiting assumptions.

THEORY

Solid State Diffusion

While the actual three-dimensional diffusion process leading to filamentous carbon deposition is geometrically complex (Fig. 1(a)), a simple one-dimensional treatment will suffice in describing the salient aspects of mass transfer of carbon through metal (Fig. 1(b)). Fick's first law describes the diffusional flux J of a dilute concentration c of solute (carbon) in a solvent (metal) at constant temperature and pressure,

$$J = -D\left(\frac{dc}{dz}\right), \qquad [1]$$

where D is the diffusion coefficient and (dc/dz) is the concentration gradient. The velocity of individual filament growth v is related to the flux by

$$v \propto J/\rho, \qquad [2]$$

where ρ is the density of the deposited carbon. The global rate of carbon deposition r (mass per unit time) is obtained by summation of the individual rates over all of the catalyst particles in the system, and

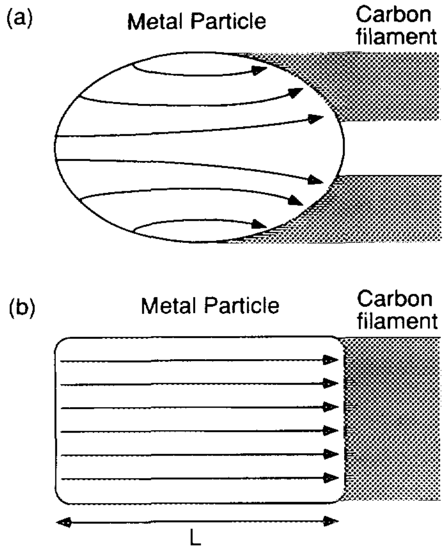

FIG. 1. (a) Schematic drawing of metal particle and hollow carbon filament showing lines of carbon diffusion, (b) idealized one-dimensional representation of the diffusion process.

$$r \propto \sum_n J_n \cdot A_n, \qquad [3]$$

where J_n and A_n are the fluxes and surface areas of the individual metal particles.

From Eqs.[1]–[3], we expect both the activation energy for the velocity of filament growth, $-R \cdot d(\ln v)/d(1/T)$, the parameter measured by *in situ* electron microscopy investigations, and the activation energy for global carbon deposition, $-R \cdot d(\ln r)/d(1/T)$, the parameter measured in gravimetric studies, to be equal to the activation energy for the diffusional flux, $-R \cdot d(\ln J)/d(1/T)$. However, this activation energy E is not necessarily equal to the activation energy for diffusion E_D. Contributions to E can also arise from the temperature dependence of (dc/dz).

Equation [1] is only valid at constant temperature and pressure. Mass transfer results from gradients in the chemical potentials of the components. For a metal–carbon binary alloy, we need only consider the chemical potential of carbon μ_C, which is defined by

$$\mu_C = \mu_C^* + R \cdot T \cdot \ln a_C, \qquad [4]$$

where μ_C^* is a function only of temperature and pressure, and a_C is the activity of carbon dissolved in the metal. We can also express a_C as

$$a_C = \gamma_C \cdot x_C, \qquad [5]$$

where γ_C and x_C are the activity coefficient and atom fraction of carbon dissolved in the metal, respectively. We define the standard state of carbon as graphite, and for dilute ideal solutions of carbon in metal, the carbon concentration c can be approximated by

$$c \cong c^{\circ} \cdot a_C \cdot \gamma_C^{\circ}/\gamma_C, \qquad [6]$$

where c° and γ_C° are the concentration and activity coefficient of carbon dissolved in the metal in equilibrium with graphite.

Since mass transfer results from a gradient in chemical potential μ_C, which is a function of temperature, pressure, and a_C, the mass transfer rate is dependent on gradients in temperature and pressure as well as carbon concentration. We consider constant pressure, but allow for the presence of temperature gradients. Then the general equation for the diffusional flux of carbon J through the metal can be expressed as

$$J = -D\left(\frac{\partial c}{\partial z}\right)_T - D^T \cdot c\left(\frac{dT}{dz}\right), \qquad [7]$$

where D is the diffusion coefficient and D^T is referred to as the thermal diffusion coefficient (30, 31). The first term on the right-hand side of the equation describes the ordinary diffusion driven by a concentration gradient. The second term describes the diffusion of carbon driven by a temperature gradient, which is referred to as Soret, or thermal, diffusion.

Soret diffusion is common in gas mixtures, and it has been recognized as being an important component of mass transfer for chemical vapor deposition (32, 33). It also occurs in liquids and solids, and in the latter it has been studied primarily in association with the diffusion of elements in alloys at high temperatures, such as might be expected to occur in power generation reactors, where appreciable temperature gradients are present (34, 35). It is common to express D^T as

$$D^T = D\left(\frac{Q^*}{R \cdot T^2}\right), \qquad [8]$$

where Q^* is known as the heat of transport. For an ideal solution, Q^* defines the energy transported per unit mass of either component relative to the center of mass of the system, while for nonideal solutions it also contains terms related to the partial molar heats of solution of the two components (36, 37). Substituting Eq. [8] into Eq. [6] yields

$$J = -D\left[\left(\frac{\partial c}{\partial z}\right)_T + \frac{Q^* \cdot c}{R \cdot T^2}\left(\frac{dT}{dz}\right)\right]. \qquad [9]$$

For nonideal solutions of carbon in metal, the diffusion coefficient D is dependent on the atom fraction of carbon (30, 38)

$$D = (D_C^* \cdot x_M + D_M^* \cdot x_C)\left(1 + \frac{d \ln \gamma_C}{d \ln x_C}\right), \qquad [10]$$

where D_C^* and D_M^* are the self diffusion coefficients of carbon and metal atoms, x_C and x_M are their atom fractions, and γ_C is the activity coefficient of carbon. We will only consider the case of dilute concentrations of carbon, such that $x_M \gg x_C$ and $D_C^* \cdot x_M \gg D_M^* \cdot x_C$. Then Eq. [10] reduces to

$$D = D_C^*\left(1 + \frac{d \ln \gamma_C}{d \ln x_C}\right). \qquad [11]$$

The term $[1 + (d \ln \gamma_C/d \ln x_C)]$ is often referred to as the thermodynamic factor (39). For carbon in γ-iron at 738°C (the lowest temperature that γ-Fe is thermodynamically stable with respect to α-Fe), the thermodynamic factor is 1.3 at the equilibrium solubility with graphite of $x_C^\circ = 0.032$ and 1.9 at $x_C = 0.09$ (40). Data on the thermodynamic factor is not available for most metal–carbon alloys.

For nonideal solutions of carbon in metal, the activation energy for diffusion of carbon is

$$E_D = E_D^* - R\frac{d}{d(1/T)}\left(1 + \frac{d \ln \gamma_C}{d \ln x_C}\right), \qquad [12]$$

where E_D^*, the activation energy for self-diffusion of carbon in the metal, is equal to the measured activation energy for dilute carbon concentrations. A negative deviation from an ideal solution, whereby $(d \ln \gamma_C/d \ln x_C) > 0$, as is commonly the case for carbon–metal solutions, leads to a small negative contribution to the activation energy from the thermodynamic factor, and it can be shown that

$$E_D = E_D^* - m \cdot R \cdot T, \qquad [13]$$

where $0 \leq m \leq 1$ (39). For dilute concentrations of carbon in the metal, which can be approximated as ideal solutions, $m = 0$ and $E_D = E_D^*$. For nonideal solutions, $m > 0$, and in the limit of highly nonideal solutions, such that increasing carbon activity leads to only small changes in dissolved carbon, $m \rightarrow 1$ and $E_D = E_D^* - R \cdot T$.

Thermodynamic Considerations

We consider the formation of filamentous carbon through three different gases: carbon monoxide (CO), methane (CH_4), and acetylene (C_2H_2). The overall reactions for the formation of crystalline graphitic carbon C(c) from these three reactions on the basis of one carbon atom are

$$2\,CO(g) \overset{K_1}{=} C(c) + CO_2(g), \qquad [14]$$

$$CH_4(g) \overset{K_2}{=} C(c) + 2\,H_2(g), \qquad [15]$$

$$\tfrac{1}{2}\,C_2H_2(g) \overset{K_3}{=} C(c) + \tfrac{1}{2}\,H_2(c), \qquad [16]$$

where K_1–K_3 are the equilibrium constants for the three reactions and ΔH_1–ΔH_3 are their heats of reaction. The standard state of carbon has already been defined as graphite, and we can define gas-phase activities for carbon deposition, $a_{C(gas)}$, for each of these reactions as

$$a_{C(gas)} = K_1 \cdot P_{CO}^2/P_{CO_2}, \qquad [17]$$

$$a_{C(gas)} = K_2 \cdot P_{CH_4}/P_{H_2}^2, \qquad [18]$$

$$a_{C(gas)} = K_3 \cdot (P_{C_2H_2}/P_{H_2})^{1/2}. \qquad [19]$$

Metal-catalyzed filamentous carbon formation does not lead to graphitic carbon, but rather to a metastable form of carbon known as filamentous carbon, C(fil),

$$C(c) \overset{K_4}{=} C(fil). \qquad [20]$$

with heat of formation $\Delta H_f[C(fil)]$, free energy of formation $\Delta G_f[C(fil)]$, and carbon activity $a_{C(fil)}$ defined by

$$a_{C(fil)} = \exp\,(\Delta G_f[C(fil)]/R \cdot T). \qquad [21]$$

Filamentous carbon formation is thermodynamically allowed when $a_{C(gas)} > a_{C(fil)}$. Rostrup-Nielsen (41) showed that when filamentous carbon is formed from carbon monoxide at 500°C, the carbon is somewhat disordered and $\Delta G_f[C(fil)] \cong 10$ kJ/mol. He estimated that $\Delta H_f[C(fil)] \cong 38$ kJ/mol for carbon formation from carbon monoxide at 450–600°C. Similar results have been reported elsewhere (6).

Since we will be considering the diffusion of carbon dissolved in the metal, we are interested in expressions relating the carbon concentration to measurable properties. The dissolution of graphite in the metal to form a solid solution occurs through the reaction

$$C(c) = C(sol). \qquad [22]$$

The concentration of dissolved carbon in the metal in equilibrium with graphite is defined as c° and the partial molar enthalpy for the dissolution of carbon in the metal is $\Delta\overline{H}_C$. Non-equilibrium concentrations of carbon can be related to the activity of carbon dissolved in the metal, a_C, by Eq. [5]. When the carbon content in the metal is equilibrated with the gas phase, $a_C = a_{C(gas)}$, and

$$c \cong c^\circ \cdot a_{C(gas)} \cdot \gamma_C^\circ / \gamma_{C(gas)}, \qquad [23]$$

where $\gamma_{C(gas)}$ is the activity coefficient for carbon dissolved in metal in equilibrium with the gas. For dilute carbon concentrations that can be approximated as ideal solutions, $\gamma_{C(gas)} = \gamma_C^\circ$ and $c \cong c^\circ \cdot a_{C(gas)}$.

We next consider the formation of metal carbides $Me_xC(c)$,

$$C(c) + x Me(c) \overset{K_6}{=} Me_xC(c), \qquad [24]$$

and $\Delta G_f[Me_xC(c)]$ and $\Delta H_f[Me_xC(c)]$ are the free energy and heat of formation of the metal carbide, respectively. The concentration of dissolved carbon in the metal in equilibrium with the metal carbide is defined by the reaction

$$Me_xC(c) \overset{K_7}{=} C(sol) + x Me(c), \qquad [25]$$

where the activity of carbon dissolved in the metal in equilibrium with the metal carbide $a_{C(Me_xC)}$ is

$$a_{C(Me_xC)} = K_7. \qquad [26]$$

Equation [25] is linear combination of Eqs. [22] and [24], and $\Delta H_7 = \Delta\overline{H}_C - \Delta\overline{H}_f[Me_xC]$. When carbon dissolved in the metal is in equilibrium with that in the metal carbide, $a_C = a_{C(Me_xC)}$, and

$$c = c^\circ \cdot a_{C(Me_xC)} \cdot \gamma_C^\circ / \gamma_{C(Me_xC)}, \qquad [27]$$

where $\gamma_{C(Me_xC)}$ is the activity coefficient for carbon dissolved in metal in equilibrium with metal carbide.

ANALYSIS

Isothermal Diffusion of Carbon

We first consider the case of isothermal diffusion, in which the rate of carbon transfer through the metal particle is determined solely by a concentration gradient. This isothermal treatment is an extension of an earlier treatment by Lund and co-workers (26, 42). For this case, the surface of the metal particle in contact with the gas phase is supersaturated with carbon with respect to the formation of filamentous carbon. For isothermal diffusion, Eq. [9] reduces to Eq. [1]. For nonideal solutions, we must consider the concentration dependence of the diffusion coefficient (Eq. [11]).

Limit of low $a_{C(gas)}$. At temperatures below 600°C and in the limit of low $a_{C(gas)}$, the carbon atom fraction in the metal is low. We thus treat the metal–carbon alloy as an ideal solution. The equilibrium concentration of carbon dissolved in the metal at the gas surface c_1 is

$$c_1 \cong c^\circ \cdot a_{c(gas)}, \qquad [28]$$

while the equilibrium concentration of carbon dissolved in the metal at the carbon filament surface c_2 is

$$c_2 \cong c^\circ \cdot a_{C(fil)}, \qquad [29]$$

where $a_{C(fil)}$ is defined by Eq. [21]. For an ideal solution, $D = D_C^*$, and solution of Eq. [1] yields

$$J = -\frac{D_C^* \cdot c^\circ}{L}(a_{C(gas)} - a_{C(fil)}), \qquad [30]$$

where L is a characteristic diffusion length, which is proportional to the particle diameter. The reaction order in the reactant and product is readily defined through the dependence of $a_{C(gas)}$ on their partial pressures. For CO–CO_2 gas mixtures, $a_{C(gas)}$ is defined by Eq. [17], while for CH_4–H_2 gas mixtures, $a_{C(gas)}$ is defined by Eq. [18].

The activation energy for carbon filament growth for the isothermal concentration gradient mechanism at low $a_{C(gas)}$ is

$$E = E_D^* + \Delta\overline{H}_C - R\frac{d}{d(1/T)}(\ln[a_{C(gas)} - a_{C(fil)}]), \qquad [31]$$

where E_D^* is the activation energy for self-diffusion of carbon through the metal–carbon alloy and $\Delta\overline{H}_C$ is the partial molar heat of solution of carbon in the alloy. The first term in Eq. [31] accounts for the activation energy for diffusion of carbon through the particle, the second term accounts for the increased solubility of carbon in the particle with increasing temperature, and the third term accounts primarily for the changing activity of carbon on the left-hand side of the catalyst particle with temperature. From Eqs. [17] and [18], Eq. [31] can also be expressed as

$$E = E_D^* + \Delta\overline{H}_C + q \cdot \Delta H_R, \qquad [32]$$

where $0 \le q \le 1$, and ΔH_R is the heat of reaction for the formation of graphite from the gas ($\Delta H_R = \Delta H_1$ for carbon deposition from carbon monoxide and $\Delta H_R = \Delta H_2$ for carbon deposition from methane). In the limit $a_{C(gas)} \gg$

$a_{C(fil)}$, $q \cong 1$ and $E = E_D^* + \Delta\bar{H}_C + \Delta H_R$, but this approximation has limited utility since it applies only for a narrow range of conditions where $a_{C(gas)}$ is much greater than $a_{C(fil)}$, yet not so high as to invalidate the initial assumption of low $a_{C(gas)}$. This latter assumption appears to be valid only for $a_{C(gas)} < 20$ (26, 32). In the limit of low $a_{C(gas)}$, such that $a_{C(gas)} \rightarrow a_{C(fil)}$, $q \cong 0$ and $E \cong E_D + \Delta\bar{H}_C$. Such an activation energy is also obtained if the gas composition is varied with temperature, so as to keep $a_{C(gas)}$ constant.

Studies of carbon deposition rate as a function of $a_{C(gas)}$ have shown that Eq. [30] describes the rate of carbon deposition catalyzed by nickel and iron as a function of gas stream partial pressures when $a_{C(gas)} < 20$ for both CO–CO_2 (5, 32) and CH_4–H_2 (26, 42, 43) gas mixtures at temperatures of 500–760°C. These experimental results are consistent with isothermal diffusion of carbon through the metal particle as the rate determining step at low $a_{C(gas)}$. Activation energies have not been reported.

Limit of high $a_{C(gas)}$. For CO–CO_2 and CH_4–H_2 gas mixtures, it is possible to create conditions corresponding to $a_{C(gas)}$ much greater than 1000 (Eqs. [17] and [18]). Even higher values of $a_{C(gas)}$ can result for carbon deposition from other hydrocarbons, such as acetylene (Eq.[19]). At high $a_{C(gas)}$, we can no longer postulate that steps occurring on the gas-phase surface are equilibrated.

We postulate that at high $a_{C(gas)}$ the reaction occurs through an irreversible reaction involving the formation of a surface carbon intermediate. The surface becomes fully covered with the adsorbed carbon, limiting further catalytic decomposition of the hydrocarbon and preventing the decomposition reaction from becoming equilibrated. This full coverage of the surface with adsorbed carbon sets an upper limit on c_1 of

$$c_1 = c^\circ \cdot a_{C(surf)} \cdot \gamma_C^\circ / \gamma_{C(surf)}, \qquad [33]$$

where $a_{C(surf)}$ and $\gamma_{C(surf)}$ are the activity and activity coefficient of carbon dissolved in the metal in equilibrium with a surface fully covered with adsorbed carbon. Since c_1 is fixed by the limited availability of sites on the surface for adsorbed carbon rather than by the partial pressures of participating molecules and since $c_1 \gg c_2$, (dc/dz) is constant and the rate (described by Eq. [1]) is zero order in the partial pressures of both the reactant and the by-product. The results of Lund and co-workers (26, 43) suggest that the limiting value of $a_{C(surf)}$ is about 20–50 for α-Fe, γ-Fe, and Ni. Since the solubility of carbon in metals at high a_C is nonideal, the diffusion coefficient D_C is defined by Eq. [11] and its activation energy by Eq. [13]. We note that at high $a_{C(gas)}$ this diffusion process is not truly a "rate-determining step" in the classical use of the term (29), since the steps leading to the formation of adsorbed carbon are not equilibrated.

Metal Carbide Formation. Metal carbides are thermodynamically stable with respect to the gas atmosphere only for $a_{C(gas)} > a_{C(Me_xC)}$, and they are stable with respect to the formation of filamentous carbon only for $a_{C(Me_xC)} > a_{C(fil)}$. Thus, in order for carbides to play a role as intermediates in filamentous carbon growth, it is necessary that $a_{C(gas)} > a_{C(Me_xC)} > a_{C(fil)}$, and only metastable carbides can participate as intermediates. Iron, nickel, and cobalt form metastable carbide phases (including Fe_3C, Fe_7C_3, Co_3C, and Ni_3C), and these elements are among the most active for carbon deposition. A connection between carbide formation and carbon deposition has been postulated (9, 25).

We consider the case where metastable carbides on the surface act as intermediates in the deposition of filamentous carbon. Such carbides would act to limit the activity of the carbon at the surface of the metal particle to that value in equilibrium with the activity of carbon in the metal carbide. Then c_1 is defined by Eq. [27] and c_2, as before, by Eq. [29]. Solution of Eq. [1] yields

$$J = -\frac{D_C^* \cdot c^\circ}{L}(a_{C(Me_xC)} - a_{C(fil)}), \qquad [34]$$

and the carbon deposition rate is zero order in the partial pressures of the reactant and any gaseous products. The activation energy for carbon deposition is

$$E = E_D^* + \Delta\bar{H}_C - R\frac{d}{d(1/T)}(\ln(a_{C(Me_xC)} - a_{C(fil)})). \qquad [35]$$

From Eq. [26], for $a_{C(Me_xC)} \gg a_{C(fil)}$, the third term in Eq. [35] approaches $\Delta\bar{H}_C - \Delta H_f[Me_xC(c)]$, and

$$E \cong E_D^* + \Delta H_f[Me_xC(c)], \qquad [36]$$

while for $a_{C(Me_xC)} \cong a_{C(fil)}$, the third term is small and

$$E \cong E_D^* + \Delta\bar{H}_C. \qquad [37]$$

We thus expect the activation energy to fall between the limits of Eqs. [36] and [37].

Diffusion of Carbon in a Temperature Gradient

We next consider the presence of a temperature gradient, and in particular, the possibility of a temperature gradient serving as the driving force for the transport of carbon through the metal particle. In principle, a temperature gradient can lead to mass transfer through two routes: (1) Soret diffusion or (2) effects from a concentration gradient resulting from the increasing solubility of carbon with temperature. We consider each of these in turn for the case of an ideal solution.

We first consider the absence of a concentration gradient, so that carbon diffusion is driven solely by a temperature gradient. For an ideal solution in the presence of a temperature gradient, and in the absence of a concentration gradient, Eq. [9] reduces to

$$J = -\frac{D^* \cdot Q^*}{R \cdot T^2}\left(\frac{dT}{dz}\right). \qquad [38]$$

Q^* has been measured to be -100.4 ± 6.3 kJ/mol for carbon in the body-centered cubic (α-Fe) phase at 700°C and -8 kJ/mol in the face-centered cubic (γ-Fe) phase at 940°C (34). In the temperature gradient mechanism proposed by Baker *et al.* (10), exothermic decomposition reactions lead to an increase in temperature on the gas side of the particle, and carbon diffusion is proposed to occur from the hot side of the particle to the cold side, where carbon deposition occurs. However, for $Q^* < 0$, carbon diffuses preferentially in the direction of the temperature gradient; that is, to the side of the metal particle that is at higher temperature. Thus, Soret diffusion alone cannot lead to carbon deposition.

We next consider the case where a temperature gradient is present across the catalyst particle, which in turn produces a concentration gradient due to the increasing solubility of carbon in the metal particle with increasing temperature. In the absence of Soret diffusion, such a concentration gradient could lead to mass transfer of carbon from the hot side of the particle to the cold side due to ordinary diffusion. However, due to the presence of the temperature gradient, this diffusional flux from the hot side to the cold side from ordinary diffusion must exceed the diffusional flux in the opposite direction from Soret diffusion in order for the net rate of carbon diffusion from the hot side of the particle to the cold side to be positive.

An understanding of the combined effect of ordinary and Soret diffusion is best gleaned by consideration of the "stationary state," the concentration profile across the particle in the absence of mass transfer, when ordinary diffusion is balanced by Soret diffusion. We assume the presence of a linear temperature gradient (Fig. 2(a)). Setting $J = 0$ in Eq. [9] and solving yields

$$\ln\left(\frac{c_2}{c_1}\right) = -\frac{Q^* \cdot \Delta T}{R\bar{T}^2}, \qquad [39]$$

where $\bar{T} = (T_2 + T_1)/2$ is the average temperature and $\Delta T = T_2 - T_1 < 0$ for the proposed mechanism. Note that the particle size does not enter into the expression.

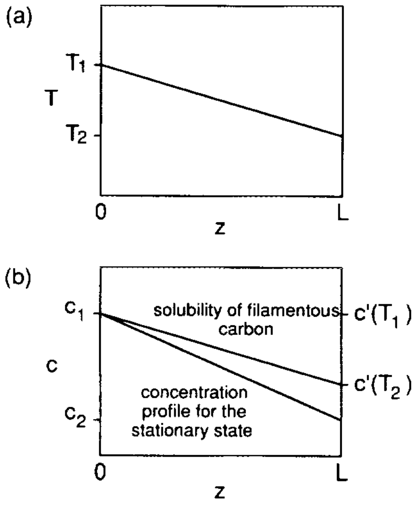

FIG. 2. (a) Linear temperature profile across an iron particle, and (b) profiles for the steady-state concentration of dissolved carbon c in the iron particle (accounting for both thermal and ordinary diffusion) and the solubility of filamentous carbon $c'(T)$. The value of c on the left-hand side of the particle has been set equal to the solubility of carbon in equilibrium with filamentous carbon at temperature T_1, $c'(T_1)$. Note that the carbon concentration on the right-hand side of the iron particle is less than the solubility of filamentous carbon in iron at T_2, $c'(T_2)$.

From Eqs. [20] and [22], the heat of solution for filamentous carbon in metal is $\Delta\bar{H}_C - \Delta H_f[C(fil)]$. The carbon concentrations in the metal in equilibrium with filamentous carbon at temperatures T_2 and T_1, $c'(T_2)$ and $c'(T_1)$, are related by

$$\ln\left(\frac{c'(T_2)}{c'(T_1)}\right) = -(\Delta\bar{H}_C - \Delta H_f[C(fil)])\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \qquad [40]$$

and for small temperature differences,

$$\ln\left(\frac{c'(T_2)}{c'(T_1)}\right) \cong \frac{(\Delta\bar{H}_C - \Delta H_f[C(fil)]) \cdot \Delta T}{R\bar{T}^2}. \qquad [41]$$

By comparison of Eqs. [39] and [41], when $(-Q^*) > \Delta\bar{H}_C - \Delta H_f[C(fil)]$, the ratio of the steady-state carbon concentrations (c_2/c_1) in the presence of a temperature gradient is greater than the ratio of their solubilities $[c'(T_2)/c'(T_1)]$, and carbon precipitation on the cold side of the particle is not possible, as illustrated in Fig. 2(b). In the event that a concentration profile corresponding to the solubility of carbon were present, the net rate of carbon diffusion would be toward the higher temperature, higher carbon concentration side of the particle. This reflects the fact that the driving force for carbon diffusion is not solely a gradient in carbon concentration, but rather in the chemical potential.

As an example, we analyze the case of carbon deposition from CO on α-Fe at 550°C, an exothermic reaction with $\Delta H_1 = -172$ kJ/mol. We assume a temperature difference across the particle of $\Delta T = -20°C$. For carbon in α-Fe, $Q^* = -100.4 \pm 6.3$ kJ/mol (34) and $\Delta\overline{H}_C = 106.3$ kJ/mol (44), while $\Delta H_f[C(fil)] \cong 38$ kJ/mol for carbon formation from carbon monoxide at 450–600°C (41). Setting $T_1 = 560°C$ and $T_2 = 540°C$ leads to $[c'(T_2)/c'(T_1)] = 0.78$ while at the stationary state $(c_2/c_1) = 0.70$. Setting $c_1 = c'(T_1)$ on the hot side of the particle leads to a value of c_2 that is lower than $c'(T_2)$ on the cold side of the particle (Fig. 2(b)), and precipitation of filamentous carbon on the cold side of the particle is thermodynamically prohibited. This conclusion is independent of the magnitude of the temperature difference.

We conclude from the above analysis that temperature gradients cannot be responsible for carbon diffusion through α-Fe leading to carbon filament growth for exothermic carbon deposition reactions. But this "proof" cannot be generalized to all metals. For example, for γ-Fe, where $Q^* = -8$ kJ/mol (32) and $\Delta\overline{H}_C = 51$ kJ/mol at 1100 K (44), $(-Q^*) < \Delta\overline{H}_C - \Delta H_f[C(fil)]$, and a temperature gradient mechanism based on temperature-dependent solubilities cannot be ruled out. However, considering the high activity of α-Fe for filamentous carbon deposition (11) and assuming a commonality in the filament growth mechanism catalyzed by different metals, the analysis for α-Fe strongly suggests that the temperature gradient mechanism is uniformly invalid.

DISCUSSION

The analysis of the last section leads us to conclude that the driving force for formation of filamentous carbon must be a concentration gradient. If temperature gradients were present across the small metal catalyst particles during exothermic carbon deposition reactions, they would actually act to suppress carbon deposition. These conclusions alone, however, do not prove the absence of temperature gradients.

The postulate that a temperature gradient was the driving force for carbon diffusion was based in part on the early observation that filamentous carbon formation was not observed from methane during *in situ* electron microscopy studies (45). Since methane decomposed to carbon and hydrogen endothermically while hydrocarbons leading to copious amounts of carbon decomposed exothermically, it was postulated that exothermic decomposition reactions lead to a temperature gradient across the particle, with the gas-phase side at a higher temperature than the carbon filament side, and that this temperature gradient was responsible for the diffusion process. The more recent measurement in gravimetric studies (43) of similar rates of carbon deposition from CH_4–H_2 and CO–CO_2 gas mixtures for identical values of $a_{C(gas)}$ (Eqs. [17] and [18]) demonstrates not only that filamentous carbon formation can occur from methane, but also that it proceeds in a similar manner for both exothermic and endothermic carbon deposition reactions. This result supports our conclusion that temperature gradients do not play a role.

The only other evidence that has been reported to support a temperature-gradient driving force mechanism was the observation by Yang and co-workers that endothermic carbon deposition reactions proceeded in a different manner than exothermic carbon deposition reactions on the surfaces of nickel foil (46) and thin single crystals of MoS_2 (47). However, these studies involved the formation of patches of graphitic carbon rather than of carbon filaments, and the same authors have concluded that carbon deposition reactions proceed differently on such foils than on particles leading to filamentous carbon (48).

Theoretical calculations of maximum temperature gradients across small metal particles have indicated that temperature differences no greater than 0.1 K should be present during catalytic reactions, including filamentous carbon formation (49). Experimental measurements of metal particle temperature during exothermic chemical reactions by catalytic crystallite thermometry (50, 51) have indicated that no anomalous temperature gradients between small metal particles and their supports are present. From a philosophical viewpoint, the absence of measurable temperature gradients is reassuring. If the "particle" temperature were not equal to the "measured" temperature in the absence of interpellet and intrapellet temperature gradients for carbon deposition, the two temperatures might also be expected to differ for other catalytic reactions, and a large body of experimental data relating reaction rate to temperature would have to be reevaluated. Fortunately, this does not appear to be necessary.

The concentration gradient driving force is consistent with experimental results obtained under different conditions. The important variable is the concentration of dissolved carbon on the gas side of the particle c_1, which is only well defined for carbon deposition from methane and carbon monoxide at low to intermediate $a_{C(gas)}$ (Eqs. [17] and [18]), and for these conditions the reaction rate follows the expected dependence on reactant and by-product partial pressures predicted by Eq. [30] (5, 26, 32, 42, 43). Activation energies at low $a_{C(gas)}$ have not been reported, but they are expected to be described by Eq. [32].

At high $a_{C(gas)}$, such as for carbon deposition from acetylene, olefins and diolefins below about 550°C, experimentally observed reaction rates are zero order in the reactant gas. This reaction order is consistent with that expected for the concentration gradient driving force mechanism both when metal carbides serve as intermediates and when they are absent. As noted previously, these carbides can play a role as intermediates only when $a_{C(gas)} >$

TABLE 3

Comparison of Experimentally Measured Activation Energies for Carbon Filament Growth Rate with Calculated Values Expected at High $a_{\mathrm{C(gas)}}$ in the Absence of Metal Carbide Intermediates (Eq. [13]) and When Metal Carbides Are Intermediates (Eqs. [36] and [37]).

Metal	Experimentally measured E (kJ/mol)	Range of calculated values of E			
		No role for $\mathrm{Me}_x\mathrm{C}$		$\mathrm{Me}_x\mathrm{C}$ intermediate	
		E_{D}^{*} (kJ/mol)	$E_{\mathrm{D}}^{*} - R \cdot T$ (kJ/mol)	$E_{\mathrm{D}}^{*} + \Delta\bar{H}_{\mathrm{C}}$[a] (kJ/mol)	$E_{\mathrm{D}}^{*} + \Delta H_{\mathrm{f}}[\mathrm{Me}_x\mathrm{C(c)}]$[b] (kJ/mol)
α-Fe	67 (11)	79 (22)	72	185	114
γ-Fe	142 (13)	151 (22)	144	202	186
Ni	145 (13)	142 (22)	135	200	212
Co	139 (11)	153 (22)	146	232	200

[a] Experimentally measured values of $\Delta\bar{H}_{\mathrm{C}}$ are 106 kJ/mol for α-Fe (44), 51 kJ/mol for γ-Fe (44), 58 kJ/mol for Ni (52), and 79 kJ/mol for Co (52).

[b] Experimentally measured values of $\Delta H_{\mathrm{f}}[\mathrm{Me}_x\mathrm{C(c)}]$ are 35 kJ/mol for α-Fe (50), 35 kJ/mol for γ-Fe (53), 70 kJ/mol for Ni (53), and 47 kJ/mol for Co (*54*).

$a_{\mathrm{C(Me}_x\mathrm{C)}} > a_{\mathrm{C(fil)}}$. Thus, a role for carbides appears to be limited to Ni, Fe, and Co, which form the prerequisite metastable carbides, and it is for these materials where carbide intermediates have most often been postulated (16, 24–27).

In order to distinguish between these two mechanisms for Fe, Ni, and Co, we examine their expected activation energies more closely. When metal carbides serve as intermediates, the activation energy at high $a_{\mathrm{C(gas)}}$ is expected to fall in the range between $E_{\mathrm{D}}^{*} + \Delta\bar{H}_{\mathrm{C}}$ (Eq. [36]) and $E_{\mathrm{D}}^{*} + \Delta H_{\mathrm{f}}[\mathrm{Me}_x\mathrm{C}]$ (Eq. [37]), while in the absence of metal carbide formation the activation energy is expected to be in the range $E_{\mathrm{D}}^{*} - R \cdot T$ to E_{D}^{*} (Eq. [13]). Measured values of the activation energy E for the velocity of carbon filament growth catalyzed by α-Fe, γ-Fe, Ni, and Co particles are compiled in Table 3 and compared with values of $E_{\mathrm{D}}^{*} - R \cdot T$ to E_{D}^{*} and $E_{\mathrm{D}}^{*} + \Delta\bar{H}_{\mathrm{C}}$ to $E_{\mathrm{D}}^{*} + \Delta H_{\mathrm{f}}[\mathrm{Me}_x\mathrm{C}]$ calculated from experimental measurements of $\Delta\bar{H}_{\mathrm{C}}$ (44, 52), $\Delta H_{\mathrm{f}}[\mathrm{Me}_x\mathrm{C}]$ (53, 54), and E_{D}^{*} (22). The measured values of E are in good agreement only with the values expected in the absence of metal carbide intermediates, strongly suggesting that metal carbides do not play a role as intermediates.

Metal carbides, however, can play a role in the metal corrosion process leading to the initial generation of active metal catalyst particles. This process occurs in iron–chromium alloys, where carburizing atmospheres result in the formation of catalytically inactive chromium carbide particles and catalytically active metallic iron particles (55). The net result is metal dusting corrosion of the alloy and filamentous carbon formation. In a similar manner, metastable iron carbides might play a role in the generation of metallic iron particles from bulk iron surfaces, as postulated by Sacco *et al.* (56) and Stewart *et al.* (57).

The rate of carbon deposition from hydrocarbons other than methane exhibits a complicated temperature dependence above about 550°C, often exhibiting a regime of negative apparent activation energy. This phenomenon has been discussed in detail by Trimm (4), and his interpretation is consistent with an isothermal diffusion mechanism. For such conditions, the concentration of dissolved carbon on the gas side of the particle c_1 is controlled by the relative rates of carbon deposition and regasification reactions on the surface and this concentration falls below the maximum value of c_1 defined by Eq. [33]. While filamentous carbon formation still occurs through the same mechanism, several steps are not equilibrated, and no step can be considered as the rate-determining step for the overall process.

Some metals, such as copper, gold, and silver, do not catalyze filamentous carbon formation. This can be explained by their very low solubility for carbon, less than 4×10^{-8} atom fraction at 900°C (58). Due to these low solubilities, the diffusional flux of carbon through copper, gold and silver is extremely low (59), and carbon deposition, if it occurs at all, is limited to very low rates. The lack of catalytic activity of metal oxides toward the formation of filamentous carbon can similarly be explained by their very low solubilities for carbon, less than 10^{-8} atom fraction at 1000°C (60).

Finally, we note that the simple one-dimensional treatment of the diffusion process in this work lends support to a recent two-dimensional model of the carbon filament growth process based on the assumption of an isothermal catalyst particle (61). The greater sophistication of the treatment of the mass transfer process in that model provides further insight into the carbon nucleation process leading to the annular shape of the carbon filaments.

SUMMARY

An analysis of the diffusion process for the transport of carbon through metal particles, and in particular the temperature dependence of that process, leads to the conclusion that the rate of carbon deposition is controlled by isothermal diffusion of carbon through the metal particle both in the limits of low and high gas-phase carbon activity. The diffusion process is only a true rate-determining step (in the sense that other steps can be considered equilibrated) at low $a_{C(gas)}$. At high $a_{C(gas)}$, formation of adsorbed carbon on the particle surface becomes an irreversible step, while for hydrocarbons other than methane, the relative rates of hydrocarbon decomposition and carbon regasification also become important at high temperature. Bulk metal carbides can be ruled out as intermediates and Soret diffusion can be ruled out as a positive driving force for carbon diffusion.

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