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Mechanisms of Carbon Formation on Nickel-Containing Catalysts

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Earlier studies of the mechanism of carbon formation on nickel are reviewed. A complex dependence of rate upon temperature is observed in many systems. Different explanations for the existence of a rate maximum and an apparent negative activation energy are discussed. The observations are shown to be best explained in terms of adsorption effects, although other effects may influence the magnitude of the observed activation energy. Another aspect of the mechanism is the method of transportation of metal particles with the surface of the growing carbon. Temperature driven dissolution-precipitation of carbon or surface migration of carbonaceous species appear less probable than a mechanism involving diffusion of carbon through nickel under a concentration gradient.

I. INTRODUCTION

1. Carbon Formation on Catalysts

Increased demands on catalyst efficiency and on catalyst life have led, in recent years, to an intensification of interest in effects such as catalyst deactivation by poisoning or by sintering. One aspect of the problem that has received attention is the formation of carbon on transition metal-based catalysts, as a result of the fact that active catalysts, such as iron, cobalt and nickel, are also efficient at catalyzing the deposition of carbon. Thus, for example, the performance of nickel-based catalysts for methanation (*1*) or steam reforming (*2, 3*) is known to be influenced by carbon formation. Deactivation may be caused by a blockage of the nickel surface (*4*) or by blockage of the pore mouths (*5*) which can also produce physical breakdown of the catalyst support.

Similar problems arise with the industrial operation of some noncatalytic processes. Reactions such as the steam cracking of hydrocarbons are carried out at high temperatures (*6*), where reactor materials must be constructed from nickel-based alloys. Carbon formation on the reactor wall can result in increased pressure drop and in frequent regenerations or early shutdown of the reactor.

The degree of interest in the problem is reflected in the published literature (*7–12*). The morphology of carbon deposits has been investigated in some detail, and identification of well-ordered graphitic deposits (*7–9*), of carbon whiskers (*9–11*), of non-oriented deposits (*8*) and of various carbides (*12, 13*) have all been reported. The kinetics of carbon deposition and of carbon gasification has received less attention, although several papers have dealt with various aspects of the problem (*5, 8, 14*).

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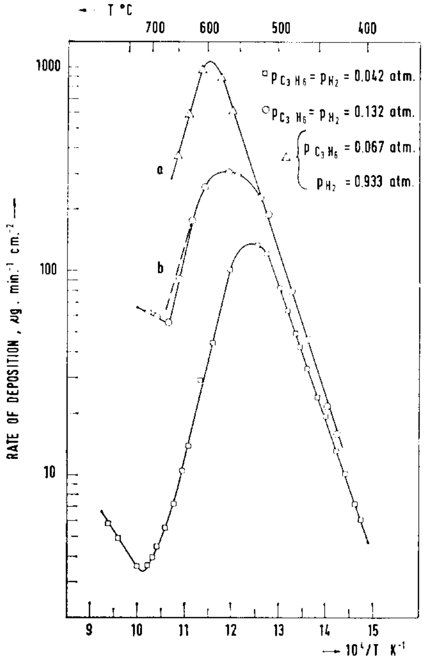

FIG. 1. Carbon deposition from propylene complex temperature dependences. (- - -) Corrected for gasification.

These studies reveal several unexpected trends, and it is the purpose of the present paper to focus attention on these results and to discuss the validity of alternative explanations that have been advanced.

2. *Basis of the Problem*

It is convenient, in this section, to use the formation of carbon during the pyrolysis of olefins over nickel foil as an example. Similar observations have been reported for other systems and these will be referred to where they are relevant.

Studies of the kinetics of carbon formation over nickel show that deposition from olefins is slow at the start of reaction (*8*, *15*). After a well-defined induction period, the rate of deposition accelerates to a constant and reproducible value, which shows a complex dependence on temperature (*15*). A typical plot of log rate of carbon deposition from propylene vs reciprocal temperature is shown in Fig. 1.

The kinetics of the reaction also change with the apparent activation energy. At temperatures less than ca. 550°C, the apparent activation energy is 32 ± 2 kcal/mol for all olefins, and the reaction is zero order. Between ca. 550 and 650°C, the apparent activation energy is ca. −44 kcal/mol and the reaction is first order both in hydrocarbon and in hydrogen. Above ca. 650°C, homogeneous carbon formation becomes significant and kinetics appropriate to the gas phase pyrolysis of individual hydrocarbons are observed.

The complex dependence of rate upon temperature is common to many such systems. Similar curves have been observed for the pyrolysis of acetylene, ethylene, propylene, butene and butadiene over nickel (*8*, *15*), with the maxima and minima occurring at approximately the same temperatures as in Fig. 1. Although the rates may be complicated by mass transfer limitations, Rostrup-Nielsen (*5*) and Figueirdo and Trimm (*16*) have also observed similar curves during the steam-reforming and pyrolysis of hydrocarbons on supported nickel catalysts. Derbyshire and Trimm (*14*) have also noted that the apparent activation energy of carbon formation changes from positive to negative with increasing temperature. These experiments, designed to investigate the pyrolysis of methane, ethane and ethylene over nickel foil, gave values of activation energy as quoted above, although the maximum in the curve was found to lie at significantly higher temperature (≥800°C) (*14*).

The amount of carbon deposited on the foil or catalyst at lower temperatures was found not to affect the rate of subsequent carbon formation, to high deposit weights (*5*, *8*). Examination of the carbon showed that nickel crystallites were being transported at the surface of the growing carbon (*8*).

Similar observations have been reported for the formation of filamentous carbon on iron, cobalt, chromium (*10*) and nickel (*17*).

A common characteristic of all filaments was a particle of metal-based material at the growing end of the filament. Transportation of metal on the growing surface of the carbon thus appears to be a common feature of this type of deposition.

In the present paper, we focus attention on the change of the apparent energy of activation from positive to negative, and on the method of transportation of metal particles with the surface of the growing carbon.

II. THE NEGATIVE APPARENT ACTIVATION ENERGY

1. Gasification of Carbon

Perhaps the most obvious explanation of the negative activation energy is that hydrogen, either produced in the reaction or added to the feed (*17*), is gasifying the deposit. As a result, detailed studies of the effect of hydrogen have been carried out (*16*). Although the gasification of carbon by hydrogen has been found to be significant only above ca. 550°C, measurement of the kinetics of gasification shows that this cannot account, *in toto*, for the observed decrease in apparent activation energy. The kinetic equation obtained for the gasification,

$$\frac{-d(c)}{dt} = k\{\text{Ni area}\}^1\{\text{carbon}\}^1\{\text{H}_2\}^2, \qquad (1)$$

was used to show that the rate of carbon deposition was in no case altered by more than 5% as a result of gasification by hydrogen (Fig. 1, curve b).

For conditions with steam present it might be argued in a similar way that steam is regasifying the carbon deposits. This has also been the basis of a model for the steam reforming process (*18*).

Experiments of Figueiredo (*19*) showed a retarding effect of steam on the rate of carbon formation, but the rate remained constant with time in the presence of steam, although the surface of carbon accessible for the gasification was increasing. Similar results were obtained for the Boudouard reaction by Tøttrup (*13*). Hydrogen and steam were found to retard the rates but not to affect the reaction order (zero with respect to time). Moreover, the addition of alkali did not change the effect of steam. These results may dispose of the said mechanism for steam reforming and they indicate that the maximum in coking rate with temperature observed by Rostrup-Nielsen (*5*) at conditions for steam reforming may hardly be ascribed to regasification of carbon.

2. Catalyst Poisoning

a. At first sight it would appear that the formation of carbon on nickel could poison the catalyst and cause the negative activation energy observed.

Poisoning effects have been reported in the literature. For the decomposition of acetylene on nickel, Baker *et al.* (*17*) observed that the growth of whisker-like carbon was preceded by formation of apparently amorphous carbon. If the excess of these deposits did not move away to form whisker-like carbon rapidly enough, the fraction of free nickel surface slowly decreased and the nickel particle lost its activity. Again, in the steam reforming of naphtha at low temperatures, as envisaged in adiabatic reformers, gradual deactivation of the nickel surface has also been reported (*4, 20, 21*), apparently as a result of the accumulation of polymer on the surface. The rate of deactivation appears to depend on the relative rates of aging and gasification (*21, 22*).

Although the mechanism of the decomposition of hydrocarbons has not been established in detail, it is useful to discuss self-poisoning in general terms. The process must involve the adsorption of hydrocarbon at a rate r_1: the adsorbed organic material may then either gasify by further reaction

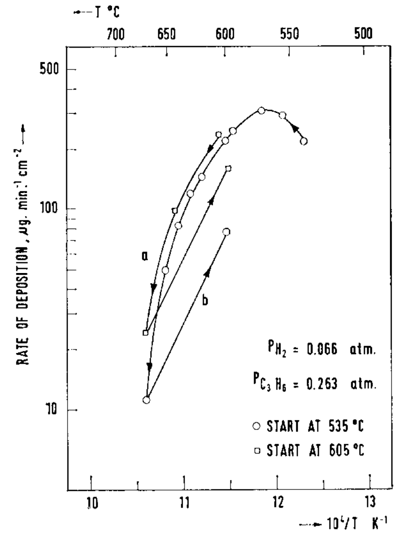

FIG. 2. Carbon deposition from propylene deactivation effects.

(r_2) or react to form nonencapsulating carbon (r_3) or encapsulating carbon (r_4). The rate of self-poisoning is then expressed by

$$r_4 = r_1 - r_2 - r_3. \tag{2}$$

The relative importance of the different reactions under different conditions of temperature and pressure would then explain the different rates of self-poisoning observed experimentally.

Thus, for example, under steam reforming conditions for which r_2 is high and r_3 is normally zero, self-poisoning will be observed when r_1 is greater than r_2. The activation energy for adsorption (around 10 kcal/mol) is less than the activation energy for hydrocracking on nickel (around 40–60 kcal/mol). As a result, r_2 should become equal to r_1 as the temperature is increased, and self-poisoning will not occur. This reflects the situation in normal tubular reformers, where stable steam reforming can be carried out even under conditions where the deposition of carbon should be favored (*3*).

In the studies of decomposition of propylene, poisoning of the catalyst could occur, as shown by the results summarized in Fig. 2 (*16*). At low inlet hydrogen pressure, the decrease in rate with increasing temperature was found to adopt a curved plot (curve a: Fig. 2): if the temperature was subsequently decreased, the plot became linear (curve b: Fig. 2). At relatively high hydrogen pressures, however, the plot was linear and reversible and paralleled line b. It would appear that, at low hydrogen pressure, at least some of the nickel crystallites at the surface were being deactivated, presumably as a result of carbon encapsulation. High hydrogen pressures prevented such encapsulation and ensured reversibility of the plot. Even under these conditions, however, the negative activation energy persisted, showing that the effect cannot be caused by poisoning by carbon.

b. A less obvious possibility is that the catalyst could be poisoned by hydrogen, and there is some evidence that this could be so. Thus, for example, during studies of the hydrogen-induced sintering of nickel, the presence of various nickel hydrides has been established at temperatures between 550 and 650°C (*23*, *24*). Assuming that the hydrides are poor catalysts for carbon production, and that their relative importance will increase with temperature (*25*), a decrease in carbon formation would be expected as the temperature is increased.

Against this, on the other hand, is the observation that carbon formation rates increase with both the pressure of hydrocarbon and of hydrogen (*8*). Increased hydrogen should lead to increased amounts of hydride and, by the arguments above, to decreased carbon formation.

In the absence of quantitative information on kinetics of hydride formation, this seems to be unlikely to account for the negative apparent activation energy.

3. Adsorption Effects

It is evident (except for zero order reactions) that the rate on a catalytic surface, which increases with temperature, is partly compensated for by a decreasing coverage of reactants. Therefore, the rate may pass through a maximum when temperature is increased, and a negative apparent activation energy is possible when the decline in surface concentration of reactants with increasing temperature is so great that this more than offsets the increasing rate of the surface reaction. This phenomenon was originally observed in studies of hydrogenation of ethylene by Zur Strassen (*26*), who suggested that a negative apparent activation energy can be expected when the heat of adsorption is greater than the true activation energy. Lobo and Trimm (*27*) proposed that a similar effect may account for the negative apparent activation energy for carbon formation.

The effect can easily be demonstrated for a reaction which is first order with respect to the adsorbed reactant, A:

$$r = ke^{-E/RT}\theta_A = \frac{kKe^{(-E+Q)/RT}p_A}{1 + Ke^{Q/RT}p_A}. \quad (3)$$

This kinetic expression can change, with respect to the partial pressure of A, from zero order at low temperatures ($Ke^{Q/RT} \gg 1$) to first order at high temperatures ($Ke^{Q/RT} \ll 1$). For a constant pressure of A ($KP_A = C$), it can be shown that the rate has a maximum as function of temperature for $Q > E$ at the temperature:

$$T_m = Q/R \log[(1/C)(Q - E)/E]. \quad (4)$$

Rate expressions and T_m equations for other situations are given in Table 1. Although a maximum is always observed, the criteria for the maximum and the equation for T_m are seen to vary with the sequence in question. This makes quantitative evaluations doubtful, if the mechanism has not been established. Moreover, it should be noted that, for all expressions, T_m increases with the partial pressure of the reactant.

It was mentioned earlier that experimental observations (*8*, *15*) revealed that

TABLE 1

Expressions for Temperature Maximum in Coking Rate

No. Adsorption	Rate of surface reaction	Max. criterion	T_m
1 Reversible	$r = k\cdot\theta_A = \frac{k'\cdot\exp\{(-E+Q_A)/RT\}\cdot p_A}{1+K\exp(Q_A/RT)\cdot p_A}$	$E<Q_A$	$\frac{Q}{R}\frac{1}{\log\{(1/Kp_A)[(Q-E)/E]\}}$
2 Irreversible[a]	$r = k\cdot\theta_A = \frac{k'\exp[(-E_3+E_2-E_1)/RT]\cdot p_A}{1+K\exp[(E_2-E_1)RT]\cdot p_A}$	$E_3<E_2-E_1$	$\frac{E_2-E_1}{R}\frac{1}{\log\{(1/Kp_A)[(E_2-E_1-E_3)/(E_2-E_3)]\}}$
3 Reversible	$r = k\cdot\theta_A{}^n = \frac{k'\exp[(-E+nQ_A)/RT]\cdot p_A{}^n}{[1+K\exp(Q_A/RT)\cdot p_A]^n}$	$E<nQ_A$	$\frac{Q}{R}\frac{1}{\log\{(1/Kp_A)[(nQ-E)/\mathrm{E}]\}}$
4 Reversible	$r = k\cdot\theta_A\cdot\theta_B = \frac{k'\exp[(-E+Q_A+Q_B)/RT]\cdot p_A\cdot p_B}{[1+K_A\exp(Q_A/RT)\cdot p_A][1+K_B\exp(Q_B/RT)\cdot p_B]}$	$E<Q_A+Q_B$	—[b]

[a] Subscripts designated in Sect. II 2a. Irreversible sequence of steps (1)–(4), $r_4 = 0$, $r_3 \ll r_2$.

[b] No analytic solution.

TABLE 2

Calculation of T_m for Pyrolysis of Propylene[a]
Data from (*29*)

$P_{C_3H_6}$ (atm)	P_{H_2} (atm)	C ($\times 10^{20}$)	T_m (K)	
			Obsd	Calc
0.042	0.042	0.3616	810	810
0.132	0.132	3.571	842	851
0.067	0.933	12.81	867	876
0.133	0.867	23.64	894	888

$$T_m = \left(\frac{-E_{\mathrm{neg}} + E_{\mathrm{pos}}}{R}\right) \times \left(\frac{1}{\log\left[(1/C) - (E_{\mathrm{neg}}/E_{\mathrm{pos}})\right]}\right).$$

$E_{\mathrm{pos}} = 32$ kcal/mol, $E_{\mathrm{neg}} = -44$ kcal/mol; $C = K \cdot p_{C_nH_m} \cdot p_{H_2} = 2.05 \times 10^{-18} \cdot p_{C_nH_m} \cdot p_{H_2}$.

the kinetics of carbon formation from pyrolysis of olefins is first order in hydrocarbon and hydrogen at high temperature and zero order at low temperature. This was also found for the pyrolysis of actylene (*27*). Empirically, this situation can be represented by the expression

$$r = \frac{k \cdot e^{(-E+Q)/RT} \cdot p_{C_nH_m} \cdot p_{H_2}}{1 + Ke^{Q/RT} p_{C_nH_m} \cdot p_{H_2}} = \frac{k' \cdot Ce^{-E_{\mathrm{neg}}/RT}}{1 + Ce^{(E_{\mathrm{pos}} - E_{\mathrm{neg}})/RT}}. \quad (5)$$

For $C = K \cdot P_{C_nH_m} \cdot P_{H_2}$, Eq. (5) is equivalent to Eq. (*3*). E_{pos} and E_{neg} are the observed positive and negative activation energies, respectively. When assuming reversible adsorption of the two gases an expression is derived as shown for case 4 in Table 1. The maximum criterion may be fulfilled, since the sum of the values of adsorption, 58 kcal/mol for ethylene on nickel, 30 kcal/mol for hydrogen (*28*), is greater than that of the "true activation energy," 32 kcal/mol, observed in the region with zero order kinetics. The predicted value of the "apparent negative energy of activation," −56 kcal/mol, is of the same order of size as the observed value for olefins, −44 kcal/mol.

Difficulties arise, however, on considering the Arrhenius plots for carbon formation from, e.g., acetylene on nickel (*27*), where the slope of the plot would indicate a heat of adsorption of acetylene of the order of 200 kcal/mol, which is much too large. Recent measurements may, however, resolve this dilemma, as a result of the fact that it has been realized only recently that some deactivation of nickel may occur if the pressure of hydrogen is too low (see Fig. 2 above). Thus the Arrhenius plot reflects not only the negative energy of activation, but also the deactivation of nickel, unless the experiment is performed at relatively high hydrogen pressures. Such measurements have been completed only for propylene (*19*), and give values corresponding to an acceptable value for the heat of adsorption. Verification of the explanation must await similar measurements with a wide variety of other hydrocarbons.

It is evident that a calculation based on heats of adsorption measured at low temperatures is very doubtful. Thus, reversible adsorption of olefins and acetylene appears unlikely at the high temperatures in question and, probably, the mechanism should be described by a sequence of irreversible steps, as illustrated by case 4 in Table 1. However, a quantitative evaluation must await a better description of the mechanism, including an analysis of the function of hydrogen.

One aspect of the formulas shown in Table 1 is confirmed by the data in Fig. 1 (*29*). As predicted, the temperature maximum, T_m, moves to higher temperatures, when the partial pressures of propylene and hydrogen are increased. This effect is illustrated in Table 2. Observed values of T_m for pyrolysis of propylene are compared to values calculated from an expression derived from Eq. (5):

$$T_m = \{-E_{\mathrm{neg}} + E_{\mathrm{pos}}\} / \{R[\log(1/C)(-E_{\mathrm{neg}}/E_{\mathrm{pos}})]\}. \quad (6)$$

Using $T_m = 810$ K to calculate the constants to be used for calculation of T_m for the other measurements, a fairly good agreement is apparent.

4. Surface Nucleation and Growth

An alternative explanation of the negative activation energy has been advanced for the growth of well ordered carbon on nickel surfaces (*14*). Deposits produced under carefully controlled conditions are laminar and graphitic, often consisting of islands of thicker graphite in a matrix of thinner, equally well ordered, graphite (*14, 30*). These are suggested to be formed from two mechanisms: the thinner material originates from a dissolution–precipitation mechanism, while the islands have been suggested to result from surface nucleation and growth of carbon. It can be shown that such a theory could predict a negative activation energy.

Under these conditions, the formation of islands of graphite is related to the sequence of events:

1. Atoms collide with the surface and either adsorb or react.
2. Adatoms may be mobile on the surface.
3. Adatoms may either dissolve in the metal or may cluster to form islands.
4. Islands may grow by the addition of other adatoms.

Analysis of this type of process reveals that an overall negative activation energy for the growth of well ordered carbon could be possible for certain values of free energies of the processes above (*14*). Quantitative assessment of the model is, however, impossible, since many of these free energies are not known. In addition, the model cannot be applied to the growth of whisker-like carbon, in which metal particles are known to be transported with the growing carbon (*10, 11*). Since the latter types of carbon are much more commonly produced, the model must be regarded, at best, as being of limited applicability.

TABLE 3

Enthalpies of Reaction for Carbon-Forming Reactions[a]

Reaction	$\Delta H°$ (kcal/mol); temp (K):		
	600	800	1000
$CH_4 \rightarrow C + 2H_2$	+19.90	+20.82	+21.43
$C_2H_2 \rightarrow 2C + H_2$	−53.9	−53.6	−53.3
$C_2H_4 \rightarrow 2C + H_2$	−10.6	−9.8	−7.2
$C_3H_6 \rightarrow 3C + 3H_2$	−2	−0.7	−0.3
$C_4H_8 \rightarrow 4C + 4H_2$			
Butene-1	+3.7	+5.1	+5.95
cis-Butene-2	+5.82	+7.48	+8.45
trans-Butene-2	+6.38	+7.89	+8.73
$CO \rightarrow C + \frac{1}{2}O_2$	+26.330	+26.512	+26.768
$2CO \rightarrow C + CO_2$	−43.34	−44.85	−46.42

[a] Values based on graphite data.

As a result of these considerations, the most plausible explanation of the negative activation energy would seem to be based on adsorption effects coupled with the minor influence of gasification and self-poisoning. It is now convenient to consider how this finding is affected by the possibility of transportation of metal by the growing carbon.

III. THE TRANSPORTATION OF NICKEL

The movement of catalyst particles with growing carbon is a well-known phenomenon (*8, 17*). Two possible mechanisms have been proposed for the movement of a metal or a metal carbide, and these may be discussed in turn.

1. Surface Diffusion

One well-established mechanism of diffusion is the surface migration of adsorbed species, and it has been suggested that carbon fibers may grow behind a nickel crystallite by a similar mechanism (*31*). Thus, adsorption of a hydrocarbon on a clean metal surface may lead to the diffusion of these species across the surface to the carbon–metal interface, where decomposition occurs to give growth of the filament (*32*). Some support for this model may be obtained from studies of the Boudouard reaction by Grenga and Lawless (*32*), who observed that nucleation of carbon occurred on specific steps and kinks of the nickel surface. The role of specific surface sites was also suggested in studies of the interaction of ethylene with nickel (*33*).

Alternatively, adsorption may be followed by decomposition and by diffusion of carbon to the growing fiber.

It has been shown, however, by Massaro and Petersen (*34*) that the surface diffusion of carbon on nickel foil is negligibly small in the temperature range 350–700°C so it is fairly certain that the carbon transport does not take place through the surface diffusion of carbon atoms (*35*).

It is much more difficult to reject the possibility of surface migration of hydrocarbon species, because kinetic data for such migrations are very sparse. Energies of activation have been measured for the hydrogenation of propylene over metal/carbon molecular sieve catalysts, a reaction which is believed to be controlled by the surface diffusion of propylene on metal (*36*), and the values observed (ca. 10 kcal/mol) are much lower than values for carbon formation. In the absence of values for other hydrocarbons, no conclusions can be drawn as to the relative importance of the surface diffusion concept.

2. Temperature Driven Dissolution–Precipitation

A mechanism for the transportation of catalyst particles at the surface of the growing carbon has been postulated (*8, 10, 17*) which depends on diffusion of carbon through the metal particle from the hotter leading face, on which hydrocarbon decomposition occurs, to the cooler trailing faces, at which carbon is deposited. There is considerable experimental evidence to support this mechanism. Thus, for example, the rate of carbon deposition, by decomposition of olefins on nickel, is zero order at low temperature, and is associated with an activation energy of 32 ± 2 kcal/mol (*8*), a value in close agreement with the activation energy (20 ± 2 kcal/mol) for diffusion of carbon through nickel in the temperature range 350–700°C (*34*) plus the enthalpy of solution of carbon in nickel (~10 kcal/mol) (*37*).

Semiquantitative assessment of the temperature gradient across the metal particle has been reported for fiber growth from acetylene on nickel (*27*) and for the deposition of heavier deposits of carbon on nickel (*8*). These calculations take, as their basis, the heat of reaction which can be liberated on decomposition of the hydrocarbon on the leading face of the particle. This heat is postulated to set up the temperature difference that drives carbon diffusion.

The basic difficulty with this approach emerges on consideration of other systems. Transportation of metal at the surface of the growing carbon has been observed with pyrolysis of many gases. If we examine the heat liberated from these compounds, interesting values emerge, as are summarized in Table 3.

From Table 3 it is seen that the decomposition of several gases is, in fact, endothermic. Since these gases produce carbon deposits with nickel crystallites at the surface, diffusion of carbon through nickel driven by a temperature gradient cannot be accepted.

It was suggested by Robertson (*38*) that the whisker growth in the endothermic methane decomposition should be ascribed to the exothermic decomposition of impurities of higher hydrocarbons. Similar statements have been presented by Evans *et al.* (*39*). The methane used by Robertson contained 0.6 vol% C_2 and 0.05 vol %C_3. In the experiments reported by Rostrup-Nielsen (*11*) it was not possible to detect higher hydrocarbons in the methane, which means contents less than 0.01 vol%. With a flow of 0.3 liter (STP) CH_4/hr, rates were measured of about 1 mg C/min, corresponding to a conversion of approximately 30%. On this basis the influence of impurities on the growth mechanism was excluded.

3. Concentration Driven Dissolution–Precipitation

With the negation of diffusion of carbon through metal driven by temperature, the only remaining driving force is concentration. At first sight this appears unlikely, since it involves a concentration gradient across a particle in contact with carbon bearing gases on one side and with a graphitic whisker on the other (Fig. 3a). Close examination, however, reveals that this model could be tenable.

Considering, first, the metal–gas interface, Wada *et al.* (*37*) have shown that the activity of carbon in a mixed gas can be far higher than unity and, as a consequence, the solubility of carbon in nickel measured in a nickel–gas system can be much higher than that observed in a nickel–graphite system (*40*).

Secondly, experimental observations have established that, in general, crystals can grow quite satisfactorily from solutions of quite low supersaturation, as a result of growth initiated at a screw dislocation (*41*). As a result, if screw dislocation growth is important, supersaturation of the metal by carbon need not occur. One characteristic of screw dislocation growth is the production of spiral growth patterns in the crystal formed (*42*). Such growth patterns have been observed by Baird *et al.* (*9*), by Robertson (*38*) and by Baker *et al.* (*10*).

Thus it would seem that concentration-driven diffusion of carbon through metal is a possible mechanism for whisker growth. In practice, the metal particle has been found to have a pear-shaped appearance (*10, 11, 43*) and the growth of whiskers should be considered in terms of Fig. 3b. Carbon growth should then involve a fast gas phase reaction leading to carbon atoms on the surface: these dissolve in the metal and precipitate out at a dislocation at the rear of the particle to form a graphite whisker. This model would predict that the rate of carbon formation should pass through an induction period and then increase linearly with time, following kinetics typical of carbon diffusion through metal. Experimental confirmation of these predictions has been reported (*8, 11, 17, 44*).

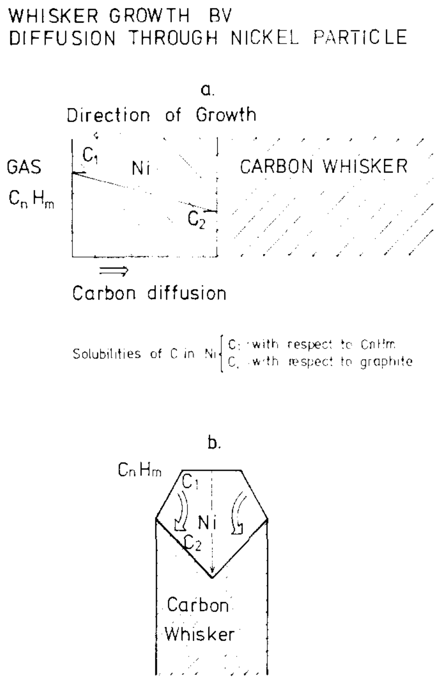

FIG. 3. Model of carbon transportation.

It is possible to carry out some quantitative testing of the model, on the basis of the experimental observation that the linear filament growth rate for 30 nm particles of nickel at 600°C was about 75 nm/sec (*17*). For a graphite density of 2.2 g/cm^3, this corresponds to a growth rate of 16.5 μg/sec/cm^2.

Taking the concentration change ΔC through the nickel particle to be the difference between the solubilities of carbon as determined by Lander *et al.* (*40*) and by

Wada *et al.* (*37*), $\Delta C = 0.042$ g/cm^3 at 600°C. If the diffusion of carbon is taken to be rate determining [diffusivity constant $D = 3.4 \times 10^{-10}$ cm^2/sec at 600°C (*44*)], the effective diffusion length, L, can be calculated from the expression

$$r = D\frac{\Delta C}{L}.$$

This gives $L \sim 9$ nm, in reasonable agreement with 30 nm particles producing filaments consisting of a dense wall with a hollow channel along the axis [(*17*), Fig. 3b].

CONCLUSIONS

1. The apparent negative activation energy observed during the deposition of carbon on nickel is probably due, in the main, to effects caused by the relative magnitude of the energy of activation of reaction and the heats of adsorption of reactants. Under certain circumstances, gasification of carbon or encapsulation of nickel by carbon may influence the value observed to a small extent.

2. Transportation of nickel at the surface of the growing carbon cannot be completely explained in terms of temperature driven dissolution–precipitation. It seems unlikely that it results from surface migration of carbonaceous species. The most probable explanation would seem to involve diffusion of carbon through the nickel under a concentration gradient, precipitation occurring at a dislocation.

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