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A New Model Explaining Carbon Filament Growth on Nickel, Iron, and Ni–Cu Alloy Catalysts

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Kinetic results for carbon deposition and gasification on supported nickel catalysts, in terms of rates as functions of gas composition, and a new estimate of the energy of formation of carbon filaments are presented. On the basis of these results together with results from previous studies of carbon filament growth on supported nickel, iron, and nickel–copper catalysts, as well as studies of carbon atom interactions with nickel single-crystal surfaces, a new model explaining carbon filament growth on supported transition metal catalysts is suggested. The new model is compared with the "classical" model and with a recently proposed model based on the assumption that an unstable bulk carbide governs the filament growth. In contrast to previous models, the new model explains all observations and agrees with available thermodynamic equilibrium data. It also provides in a natural way a driving force for the migration of carbon atoms through the catalyst particle. © 1988 Academic Press, Inc.

INTRODUCTION

The study of the formation of carbon on transition metals from the decomposition of hydrocarbons or carbon monoxide has a long history covering more than 50 years (*1*). In the last 15 years this phenomenon has received considerable attention, as is apparent from recent reviews (*2*).

Carbon formation on catalysts is of interest in a number of processes for several reasons. Surface carbon of the "carbidic" type is known to act as an intermediate in a number of important catalytic reactions, e.g., in the methanation reaction on nickel catalysts (*3*) and in Fischer–Tropsch synthesis on iron catalysts (*4*), while other forms of surface carbon deactivate the metal surface through blocking and possibly also through electronic effects. A particularly detrimental form of carbon is the "whiskerlike," filamentous form, which, due to the high strength of the filaments, can destroy the catalyst and block the reactor (*2*).

Dent *et al.* (*5*) concluded from their studies of the decomposition of CO and CH_4 on a nickel catalyst that both processes had smaller equilibrium constants than those based on graphite data. Kehrer and Leidheiser (*6*) examined the carbon formed during CO decomposition (Boudouard reaction) on a nickel catalyst in the electron microscope and described it as "tangled threadlike segments." Renshaw *et al.* (*7*) also observed this filament type of carbon and, in addition, flakelike material.

Rostrup-Nielsen (*8*) found deviations from graphite equilibrium for CO and CH_4 decomposition on a large number of nickel catalysts and suggested that the deviations could be explained by the extra energy required by the surface and defect structure of the filaments. Baker *et al.* (*9*) and, independently, Lobo *et al.* (*10*) suggested a model for carbon whisker growth on nickel foils. This "classical" model contains the following steps: (i) detachment of a nickel particle, (ii) production of adsorbed carbon atoms from adsorbed molecules by decomposition on the nickel particle, and (iii) subsequent diffusion of carbon atoms through the particle to a part of the surface where (iv) whisker growth takes place.

Baker *et al.* (*11*) showed that the activation energy of the rate of growth of filamentous carbon correlated for Ni, Fe, Co,

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and Cr with the activation energy of carbon diffusion in the metal and suggested that the diffusion of carbon through the metal particles is rate determining for filament growth. Moreover, they suggested that the driving force for the diffusion is a temperature difference created by the heat generated by the catalytic reaction supplying the surface carbon atoms. Rostrup-Nielsen and Trimm (*12*) pointed out that filament growth was also observed in cases where the surface reaction was endothermic. Therefore, they suggested that the driving force for the diffusion is a carbon concentration gradient due to a difference in carbon activities at the filament/metal particle interface and at that part of the metal particle surface where the decomposition takes place. This suggestion was supported by reports in the literature that the carbon activity in a metal depends on the composition of the gas phase adjacent to the metal surface.

Recent studies have revived the discussion of the mechanism of filamentous carbon growth and of the explanation for the deviation from graphite equilibrium. Manning *et al.* (*13*) made a thermogravimetric study of the rate of growth of carbon and of the equilibrium of carbon formation in a gas mixture of CO, CO_2, CH_4, H_2, and H_2O over a Ni/Al_2O_3 catalyst and over cobalt metal particles. They suggested that the observed deviation from graphite equilibrium was due to the formation of a carbide intermediate, which continuously decomposed into carbon and nickel or cobalt. They considered the model suggested by Rostrup-Nielsen and Trimm (*12*) as incomplete because it failed to explain why Manning *et al.* (*13*) rarely observed gasification at carbon activities higher than the graphite limit.

In three papers (*14–16*), Geus and collaborators reported on extensive studies of carbon filament formation from decomposition of CH_4 and CO over Ni/SiO_2 and Fe/SiO_2 catalysts by gas-phase analysis, temperature-programmed hydrogenation, thermomagnetic analysis, and electron microscopy. They concluded from results of equilibrium studies and from estimates of the surface and defect energies of carbon filaments that the energy of filament formation could not be responsible for the observed equilibria. They suggested that this conclusion together with the results of the magnetic measurements supported the idea that the deviation from graphite equilibrium is determined by an intermediate, unstable carbide (carbide equilibrium model).

In the present paper the above-mentioned results are briefly reviewed. Kinetic results, in terms of rates of carbon formation and gasification on supported nickel catalysts as functions of gas composition, and a new estimate of the energy of formation of carbon filaments are presented. A new model explaining carbon filament growth is suggested and its compatibility with known experimental results, including studies of carbon atom interactions with nickel single-crystal surfaces and the above-mentioned magnetic measurements, is discussed.

Finally, the force responsible for the migration of carbon atoms through the catalyst particles is briefly discussed.

TREATMENT AND RESULTS

Kinetics of Carbon Deposition and Gasification

As indicated above, in a thermogravimetric study of carbon deposition on Ni/Al_2O_3 and Co catalysts, Manning *et al.* (*13*) observed that there were no weight changes in a significant interval of ΔG_c near $\Delta G_c = 0$, where

$$\Delta G_c = -RT \ln\left(\frac{K_e}{K_p}\right). \quad (1)$$

K_p is the graphite equilibrium constant for the gas of the experiment and K_e is calculated in the same way as K_p but by using the actual and not the equilibrium partial pressures, e.g.,

$$K_e = \frac{P_{H_2}^2}{P_{CH_4}} \quad \text{and} \quad K_e = \frac{P_{CO_2}}{P_{CO}^2} \quad (2)$$

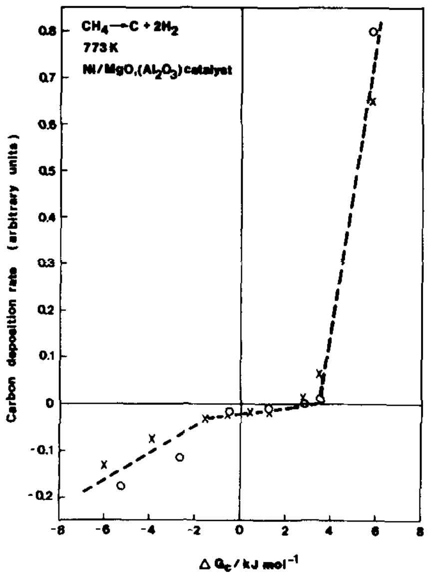

FIG. 1. Carbon deposition and gasification rates in CH_4–H_2 gas mixtures at 773 K for two different preparations of a Ni/MgO, (Al_2O_3) catalyst. From unpublished rate results by Rostrup-Nielsen used for obtaining the equilibrium ΔG_c values published in Ref. (*8*). $\Delta G_c = RT \ln(K_p P_{CH_4}/P_{H_2}^2)$, where K_p is the graphite equilibrium constant.

for CH_4 and CO decomposition, respectively. The interval in which no reaction was observed varied from about 8 kJ/mol at 750 K to about 3 kJ/mol at 900 K and carbon removal was rarely observed above the graphite equilibrium line (*13*).

The rates observed by Rostrup-Nielsen (*8*) and by Bernardo *et al.* (*17*) depend qualitatively in a similar way on ΔG_c. Outside an interval, which in some (but not all) experiments included $\Delta G_c = 0$, the rates changed rapidly; however, inside this interval the rates were not zero (except in a much smaller interval) and carbon removal was observed under conditions corresponding to graphite formation. The slope of the rate curve is much smaller inside than outside the interval. A typical plot of rate results obtained by Rostrup-Nielsen (*18*) is shown in Fig. 1. Very similar results have been obtained for other supported nickel catalysts (*19*). As mentioned in Ref. (*17*), this behavior may indicate that the mechanism or the rate-determining step changes when going from small to higher slopes. Comparison with the plots of Manning *et al.* (*13*) suggests that the apparent lack of reversibility in their experiments is due to a too low sensitivity of the balance used for the rate measurements.

Energy for Formation of Carbon Filaments

Arrhenius plots of experimental equilibrium quotients K_e are shown in Figs. 2 and 3 for CH_4 and CO decomposition, respectively, together with equilibrium constants for the formation/gasification of graphite, nickel carbide, and iron carbide calculated from the thermodynamic data in Refs. (*20*, *21*).

Rostrup-Nielsen (*8*) estimated the contributions of the surface energy and of disorder to the energy of formation of carbon filaments from the observed deviation from

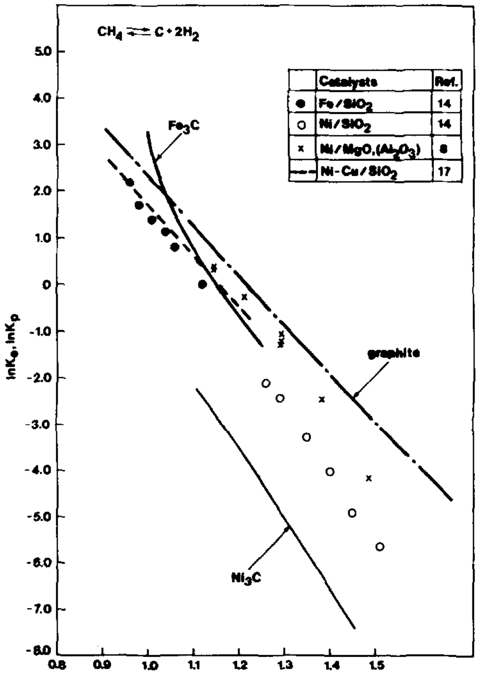

FIG. 2. Equilibria for methane decomposition on various catalysts. Graphite, Fe_3C, and Ni_3C data from Refs. (*20*, *21*).

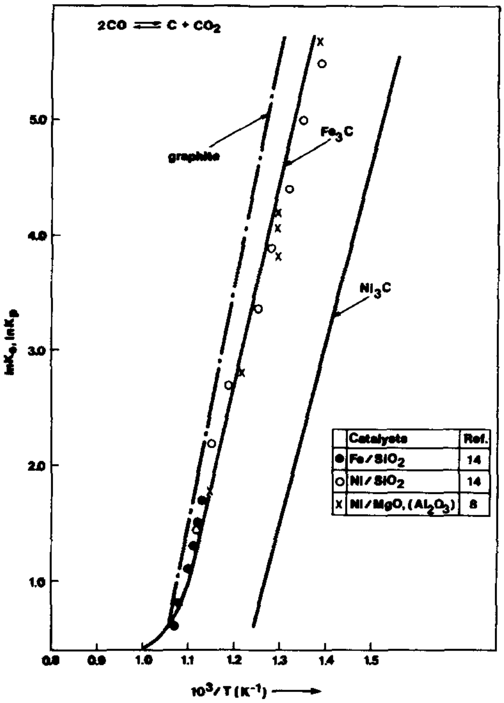

FIG. 3. Equilibria for carbon monoxide decomposition on various catalysts. Graphite, Fe_3C, and Ni_3C data from Refs. (*20, 21*).

TABLE 1

Deviations form Graphite Equilibrium: Carbon ex-CH_4, 773 K

Catalyst	D (nm)	ΔG_c (kJ/mol)		ΔH_c (kJ/mol)	$E_s + E_e$ (kJ/mol)
		Exp.	Calc.		
Fe/Al_2O_3	25	8	6.6	15	6.7
Ni/SiO_2	5.4 (11)	11	20 (11)	44	45
Ni/MgO (Al_2O_3)	250	3	2.0	—	0.6
$Ni–Cu/SiO_2$	20	7	7.3	4	8.6

graphite equilibrium (Figs. 2 and 3) and its particle size dependence. Surface energies of about 7.9 and 7.4 J/m^2 and disorder contributions of about 8.4 and 2.9 kJ/mol at 773 K for the $CO–CO_2$ and $CH_4–H_2$ equilibria respectively, could account for the particle size dependencies. These values for the surface energy contribution are high compared with the theoretical upper limit [5.5 J/m^2 (*22*)] for a graphite surface with the highest surface energy. De Bokx *et al.* (*14*) suggested that the estimate of the surface energy contribution of the carbon filaments based on theoretical values for the graphite surface energies should be compared with the difference in the enthalpy of formation ΔH_c instead of ΔG_c. The ΔH_c values they obtained for carbon filament formation from CH_4 dissociation on nickel catalyst (assuming negligible temperature dependence of ΔH_c and of the entropy difference ΔS_c) are about four times as large as the ΔG_c values and consequently much more difficult to explain by surface and defect energies. ΔH_c values derived from the equilibrium constants determined by de Bokx *et al.* (*14*) and Bernardo *et al.* (*17*), assuming temperature-independent ΔH_c and ΔS_c values, are shown in Tables 1 and 2 for carbon filament formation from CH_4 and CO on Ni/SiO_2 and $Ni–Cu/SiO_2$ catalysts. The ΔG_c values obtained by Rostrup-Nielsen (*8*) for a Ni/MgO, (Al_2O_3) catalyst did not depend linearly on temperature so no values are given for ΔH_c for this catalyst in Table 1 or 2.

De Bokx et al. (*14*) calculated the surface energy contribution to be 7.5 kJ/mol for a 10-nm carbon filament by using the formula suggested by Rostrup-Nielsen (*8*) and the value 6.3 J/m^2 for the surface energy. Using handbook values (*23*) for heats of oxidation of natural graphite and "amorphous" carbon they concluded that the energy contribution from disorder could not contribute

TABLE 2

Deviations form Graphite Equilibrium: Carbon ex-CO, 773 K

Catalyst	D (nm)	ΔG_c (kJ/mol)		$E_s + E_e$ (kJ/mol)
		Exp.	Calc.	
Fe/Al_2O_3	25	7	22	6.7
Ni/SiO_2	5.4	9	46	45
Ni/MgO (Al_2O_3)	250	9	—	0.6

more than 15 kJ/mol to the energy of formation of carbon filaments.

Recently, Tibbetts (*24*) suggested that the tubular filaments observed are formed by stacked, curved basal graphite planes. Tibbetts calculated the elastic energy stored in the filament and showed how the model can account for the observed relation between the inner and outer diameter of the tubular filaments. The suggestion that the filaments consist of stacked curved basal planes is in very good agreement with the results of electron microscopic studies by Boellaard *et al.* (*16*), who showed that the filaments possessed a high degree of cylindrical symmetry. An important difference between the filaments studied by Tibbetts and those studied by Boellaard *et al.* (*16*) is that the curved graphite basal planes of the former filaments form stacked cylinders with axes parallel to the axis of the filament, while the latter ones were formed by stacked cones of curved basal planes as shown by an elegant diffraction experiment (*16*). This means that the latter filaments have much higher inner and outer surface energies than the former, where the surfaces are basal planes.

The surface energy contribution E_s to the energy of a tubular filament is given by

$$E_s = \sigma\pi\,(D_o + D_i)L \qquad (3)$$

where D_o and D_i are the outer and inner diameters of the tube, respectively. For the surface energy σ, we use the upper limit estimate of 5.5 J/m^2 by Abrahamson (*22*). L is the length of 1 mol of filament and is determined from the molecular volume V_m of the filament carbon assuming a density of 2 g/cm^3.

$$L = \frac{4V_m}{\pi(D_o^2 - D_i^2)}. \qquad (4)$$

The formula derived by Tibbetts (*24*) to estimate the elastic contribution E_e to the filament energy is

$$E_e = \frac{1}{12}\pi L Y a^2 \ln\left(\frac{D_o}{D_i}\right) \qquad (5)$$

TABLE 3

Surface and Elastic Contributions to Filament Energy

D_o (nm)	E_s (kJ/mol)	E_e (kJ/mol)
5.4	27.2	17.9
20	7.3	1.3
25	5.9	0.8
250	0.6	0.01

where a is the graphite interplanar spacing (0.335 nm) and Y is Young's modulus. For Y the graphite single-crystal value 1000 GPa (*25*) is used.

Equation (5) was derived for the bending of basal planes into nested cylinders (*24*). Thus, it is not strictly valid for nested cones, which correspond to more complicated deformations of basal planes. The "effective" Young modulus may be somewhat lower in this case, and the calculated values are to be considered as upper limits. The inner diameter D_i is estimated from micrographs of de Bokx et al. (*14*) to be about one-tenth the outer diameter D_o in the present cases.

The E_s and E_e results for outer diameters corresponding to the particle diameters in Table 1 are shown in Table 3 and the sums $E_s + E_e$ are shown in the last column of Tables 1 and 2. It is seen that these estimates are in reasonable agreement with the ΔH_c values for the nickel catalyst, whereas there is less agreement with the values for the iron catalyst. It should be borne in mind that the determination of ΔH_c, E_s, and E_e values is very uncertain. The estimates indicate, however, that it is quite probable that the main part of the deviation from graphite equilibrium can be accounted for by the surface and elastic energy contributions to the filament energy together with a possible contribution from structural disorder. Assuming that the main part of the latter contribution comes from dislocations resulting from diffusion length differences in accordance with the model suggested by

Boellaard *et al.* (*16*), it is conceivable that it amounts to a significant fraction of the surface energy contribution.

New Model for Carbon Filament Growth

In constructing a model explaining the growth of carbon filaments all the abovementioned results should be taken into account. However, in addition it is also very important to use the information provided by surface spectroscopic studies of the interaction of methane with single-crystal surfaces of nickel and the segregation of carbon atoms thereon. Schouten *et al.* (*26, 27*) studied the interaction of methane with (110), (100), and (111) nickel surfaces and the diffusion of carbon into the bulk of the nickel crystal using low-energy electron diffraction and Auger electron spectroscopy. Methane was not chemisorbed and no carbon was deposited on the (111) nickel surface. On the (110) and (100) surfaces, deposition competed with diffusion of carbon into the bulk. In both cases the diffusion could be described quantitatively by assuming a constant planar source below the surface maintained by a much faster diffusion through the crystal selvedge in which the carbon concentration strongly exceeds the equilibrium solubility of carbon in bulk nickel. The authors refer to the selvedge with high carbon concentration as "surface carbide." The carbon content of the (110) selvedge can be reduced to a negligible concentration by diffusion into the bulk, while a carbon concentration corresponding to about one carbon atom for every four surface nickel atoms remains on the (100) surface even after a long time at high temperature. Thus, two surface carbides can be identified on this surface, one stable at temperatures below 600 K and the other stable below 1000 K. At the highest surface carbon concentrations a (4 × 5) structure was observed on the (110) surface and a *p*4*g* structure on the (100) surface. Eizenberg and Blakely (*28*) studied the equilibrium segregation of carbon to a number of nickel single-crystal surfaces viz., (111), (311), (110), (210) and (100), and surfaces vicinal to the (111) surface. At all these surfaces, with the exception of (100) and (210), a graphitelike monolayer is formed by a first-order transition when the temperature is lowered below a "segregation temperature," which is about 12% higher than the carbon precipitation temperature. For surfaces vicinal to the (111) surface the monolayer condensation is accompanied by reconstruction forming extended (111) and (110) facets. Qualitatively different behavior was observed with the (100) and (210) surfaces for which the changes in carbon concentration on the surfaces were gradual; however, these authors observed the formation of monolayer graphite also on the (100) surface, in contradiction to Schouten *et al.* (*27*), who stressed that they never observed the formation of graphite on the (100) surface.

The crystallographic specificity of the surface decomposition, the segregation, and the reconstruction demonstrated in these studies provide the key elements to an understanding of the various steps in the carbon filament growth mechanism. In accordance with the observations of Schouten *et al.* (*27*) it is to be expected that when the carbon-free nickel particle is exposed to methane at about 600 K, the molecules are decomposed on (100) and (110) surface facets and probably also on surface steps and kinks [but not on perfect (111) facets]. The carbon atoms are immediately entering the selvedge, creating a "surface carbide" which forms the source for carbon diffusion into the particle. During the induction period the particle becomes supersaturated with carbon and when this supersaturation reaches (111) facets not adjacent to the surface carbide, it triggers a considerable reconstruction, strongly extending the (111) facets; at the same time graphite layers start to segregate out, forming in the subsequent steady-state period the carbon filament. The extensive reconstruction of the metal particle manifests as a change from approximately spherical shape to the

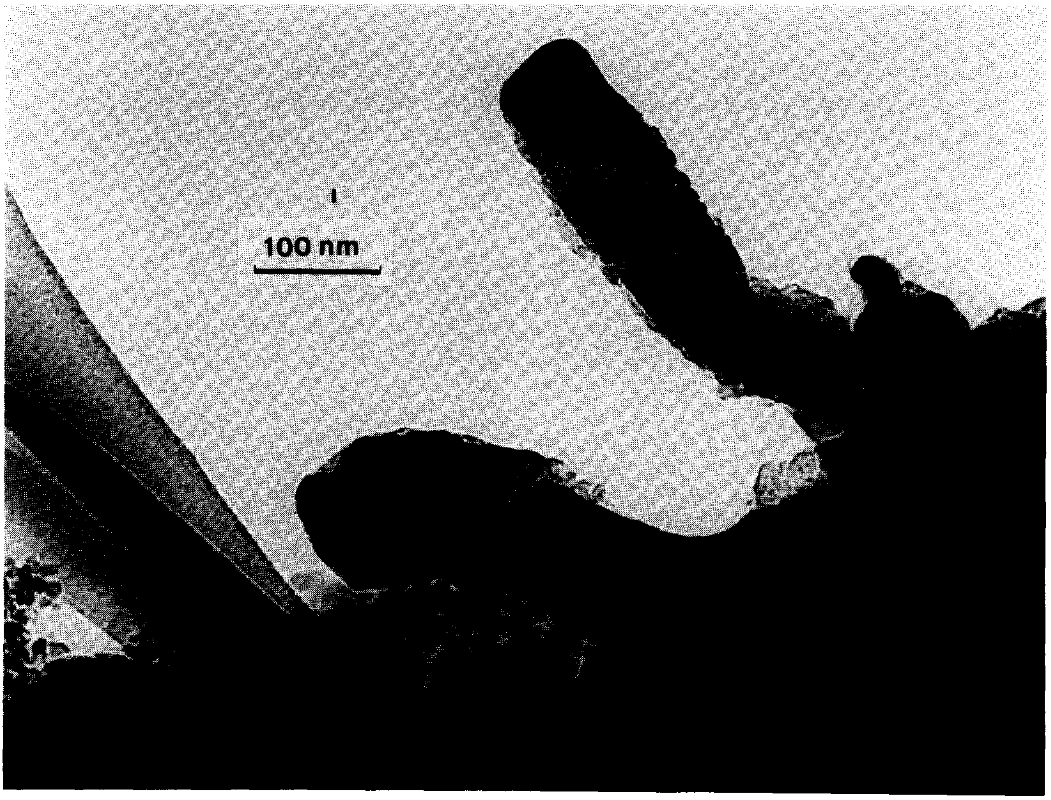

FIG. 4. Transmission electron micrograph displaying reconstructed nickel particles in the ends of carbon filaments grown by decomposition of methane on a 20 wt.% Ni/SiO_2 catalyst.

"pear" shape seen in micrographs in many publications, e.g., Refs. (*8, 9, 16, 17*). A typical example of a pearshaped nickel particle at the end of a carbon filament is seen in Fig. 4.

The new model is similar to the "classical" one with respect to the description of the steady-state growth period. An essential difference, however, is that in the new model the selvedge of the surface on which the decomposition of molecules takes place forms a surface carbide. This provides the driving force for the migration of carbon atoms through the nickel particle by maintaining a high carbon concentration in the bulk adjacent to the surface carbide; however, if the transport of heat, necessary to maintain isothermal conditions, is limited, the driving force may be modified by the presence of temperature gradients in the particle.

In the case of iron catalysts it must be taken into account that Fe_3C (cementite) is stable under the usual reaction conditions. In this case the unstable carbide (possibly and ε-carbide) formed in the induction period decomposes into carbon and a cementite particle (with a selvedge with a higher carbon concentration at the front end). This suggestion is in agreement with observations of cementite particles in front of carbon filaments (*29*).

DISCUSSION

Kock *et al.* (*15*) interpreted their magnetic measurements on nickel catalysts during carburization to support the suggestion that an unstable bulk carbide is present during carbon filament growth. A closer examination, however, shows that the results indicate that a surface carbide but not a bulk carbide is present during steady-state growth of carbon filaments. Kock *et al.* (*15*) measured the magnetic moment of a Ni/SiO_2 catalyst during carburization in CH_4 at about 600 K. The results show that the magnetization goes through a minimum corresponding to about 25% of the initial value after which it increases again to typically 70% of the initial value. The mean Ni particle diameter of the catalysts was about 5 nm. By assuming that a nickel atom either keeps its magnetic moment unchanged or loses it completely during carbon formation, and that the nickel particles are in the form of cubooctahedral or icosahedral clusters, the initial loss of magnetization and its steady-state value during filament formation can be translated into a number of nickel surface layers magnetically passivated by the chemisorption and absorption of carbon atoms. A 5-nm cluster consists of 11 atomic shells (*30*). The loss of about 75% of the magnetic moment of the particle corresponds to the quenching of the moments of the outer four shells, while the steady-state loss of about 30% can almost be accounted for by quenching the moments of the outer surface atoms, which constitute 26% of all the atoms of the particle. Taking into account the deformation of the nickel particle during the induction period, the ratio of surface to bulk atoms should be even larger than this estimate.

Thus, the magnetic measurements can be interpreted to indicate that in the case of the nickel catalyst (*14*) no bulk carbide is present during steady-state carbon filament growth. This is in agreement with electron diffraction results.

It can be argued that the 70% regeneration of initial magnetic moment was observed 65 ks after start of carburization, which corresponds to an incredibly long induction period; however, no measurements are reported between 15 and 65 ks, and the points at about 12 and 15 ks of the 596 K experiment indicate magnetization increasing with time (*15*). Moreover, the magnetic studies are all made near the temperature at which nickel carbide becomes stable, while studies of carbon filament growth are made at higher temperatures where nickel carbide is highly unstable.

In the case of carbon formation on iron in CO–CO_2 gas mixtures, Audier *et al.* (*29*) showed that outside a very small range of temperatures and gas compositions there is potential for the formation of either cementite (Fe_3C) or magnetite (Fe_3O_4). In accordance with these results, Kock *et al.* (*15*) showed by thermomagnetic measurements that cementite was formed in considerable quantities during carbon formation on the iron catalysts, while appreciable amounts of other ferromagnetic carbides could be excluded. De Bokx *et al.* (*14*) stated that "no filamentous growth was observed under conditions where carbide formation is thermodynamically impossible." Audier *et al.* (*29*), however, showed that it is possible to increase the range of temperatures and gas compositions in which no potential for stable carbide formation exists by decreasing the iron activity through alloying. They subsequently studied the kinetics of formation of filamentous carbon on FeCo alloys in CO–CO_2 mixtures corresponding to carbide-free conditions (*29*). It was found that the rate of carbon growth near equilibrium depended linearly on the carbon activity of the gas phase. X-ray diffraction showed that the metallic structure of the alloys was not changed during the carbon deposition.

Studies of carbon filament formation on Ni–Cu/SiO_2 catalysts reported by Bernardo *et al.* (*17*) show that the equilibrium is not changed by alloying. At small copper concentrations the appearance of the filaments is the same as that of pure nickel; i.e., the filament has a deformed (pear-shaped) metal particle at the end and the filament and the particle have the same diameter. At higher copper contents, more than 10 at.%, a new type of filament, "octopus carbon," is seen with several thinner filaments emerging from one almost spherical metal particle (*31*). A similar type of filament is seen when the carbon filaments are grown on nickel catalysts on which sulfur has been chemisorbed (*32*). These observations are readily understood by taking into account the reconstruction in the induction period. The interaction of the alloy with the gas molecules creates nickel patches on the surface, making possible the operation of the same surface carbide, bulk diffusion mechanism as without alloying, but the copper content or sulfur coverage suppresses the reconstruction of the particle and the creation of extended (111) nickel facets, forcing the segregation to take place on several smaller (111) facets.

From the equilibrium results obtained by Rostrup-Nielsen (*8*) for a large number of supported nickel catalysts, the following expression for the particle size dependence of the deviation ΔG_c of the equilibrium Gibbs free energy from that of the graphite value can be derived:

$$\Delta G_c = 2.6 + 93/D \text{ kJ/mol.} \qquad (6)$$

D (in nm) is the diameter of the largest metal particles catalyzing the filament growth, because the larger particles contribute more to the observed rate than the smaller ones. ΔG_c values calculated using (6) are shown in Table 1. The agreement is very good except for the Ni/SiO_2 catalyst; however, in this case the particle diameter is a mean value. If particles with $D = 11$ nm are dominating the observed rates then agreement is also obtained for this catalyst. This particle size dependence is readily explained by the "classical" model and the new model, but not by the model based on the assumption that a bulk carbide determines the equilibrium.

Recently, Audier and Coulon (*33*) showed in an elegant experiment that CO–CO_2 and CH_4–H_2 gas mixtures give the same rate of carbon deposition (filament growth) for a FeNi catalyst with predeposited carbon if the thermodynamic activity a_c of carbon is the same for the two gas mixtures. Near equilibrium the rate depended linearly on a_c. This indicated that local equilibria were established at gas–metal and metal–filament interfaces in good agreement with the new model but unlikely according to the carbide equilibrium model. Moreover, these results show that under the conditions of the experiment it does not make any difference whether the surface decomposition is endothermic or exothermic, in contradiction to the temperature-driven migration mechanism suggested by Baker *et al.* (*9*). Thus, there is no doubt that in these experiments the driving force for the migration of carbon atoms through the metal particle was a concentration gradient as described above.

Yang and Yang (*34*) recently arrived at the opposite conclusion. By transmission and scanning electron microscopy they examined nickel films that had been exposed at 673 K to methane, *n*-hexane, benzene, and toluene, respectively. Exposure to the two gases with endothermic decomposition (methane and *n*-hexane) resulted in graphite islands only on the surface exposed to the gas, while the other two gases (exothermic decomposition) gave graphite islands on the nonexposed surface only. Thus, there is an apparent conflict between the results in Refs. (*33*) and (*34*) and it is difficult to see how it can be resolved on the basis of the information in the papers. It can tentatively be suggested that if the metal particle is in good thermal contact with the environment during the deposition experiment then the concentration gradient will be the dominating driving force for the migration of carbon atoms through the metal particle, giving the same carbon whisker results for endo- as for exothermic processes as observed in several studies, e.g., Refs. (*8, 14, 33*). Holstein and Boudart (*35*) showed by calculation that the temperature difference that can be generated between the metal particle and the support when an exothermic surface reaction takes place on the metal particle of a supported catalyst is negligible (less than 0.1 K). In the calculation it was assumed that the metal particle diameter is equal to (or less than) 100 nm. Thus, it can be concluded that for most catalysts used in practice, the metal particle is in good thermal contact with the environment. If the thermal contact is less than good, as can be the case for larger metal samples, the driving force may be modified by the heat liberated or consumed by the decomposition reaction at the gas–metal interface. In the extreme case where thermal contact with the environment is very poor, the migration may even be prevented if the surface reaction is endothermic.

CONCLUSION

A new model for carbon filament growth on supported Ni, Fe, and Ni–Cu catalysts is suggested. According to this model an unstable carbide, causing a reconstruction of the particle, is formed in the induction period. Subsequently, the carbide is decomposed into filamentous carbon and metal (or stable cementite in the case of iron catalyst). A surface carbide, however, is present after the decomposition. In the steady-state growth period the carbon atoms produced by the surface reaction diffuse rapidly through the surface carbide, maintaining a constant carbon concentration just below the selvedge. A gradient is thereby maintained, causing migration of carbon atoms to the rear end of the particle where they segregate on the interface between filament and particle.

In the case of Ni–Cu alloy catalysts with more than 10 at.% Cu, no major reconstruction, but only minor facetting, of the particle is seen and more than one carbon filament grows out of one particle. This indicates that a bulk carbide cannot be formed.

In contrast to previous models, the new model is not in conflict with known facts.

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