

Carbon formation on nickel and nickel-copper alloy catalysts

Kohlenstoffbildung auf Nickel und Nickel-Kupfer-Legierungskatalysatoren

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Equilibrium, kinetic and morphological studies of carbon formation in $\text{CH}_4 + \text{H}_2$, CO , and $\text{CO} + \text{H}_2$ gases on silica supported nickel and nickel-copper catalysts are reviewed. The equilibrium deviates in all cases from graphite equilibrium and more so in $\text{CO} + \text{CO}_2$ than in $\text{CH}_4 + \text{H}_2$. A kinetic model based on information from surface science results with chemisorption of CH_4 and possibly also the first dehydrogenation step as rate controlling describes carbon formation on nickel catalyst in $\text{CH}_4 + \text{H}_2$ well. The kinetics of carbon formation in CO and $\text{CO} + \text{H}_2$ gases are in agreement with CO disproportionation as rate determining step. The presence of hydrogen influences strongly the chemisorption of CO . Carbon filaments are formed when hydrogen is present in the gas while encapsulating carbon dominates in pure CO . Small amounts of Cu alloying promotes while larger amounts ($\text{Cu} : \text{Ni} \geq 0.1$) inhibits carbon formation and changes the morphology of the filaments ("octopus" carbon formation). Adsorption induced nickel segregation changes the kinetics of the alloy catalysts at high carbon activities. Modifications suggested in some very recent papers on the basis of new results are also briefly discussed.

Es wird eine Übersicht gegeben über Gleichgewicht, kinetische und morphologische Untersuchungen der Kohlenstoffabscheidung in $\text{CH}_4 + \text{H}_2$, CO und $\text{CO} + \text{H}_2$ Gasgemischen. In allen Fällen weicht das Gleichgewicht ab von dem Gleichgewicht mit Graphit, und zwar mehr in den $\text{CO} + \text{CO}_2$ als in den $\text{CH}_4 + \text{H}_2$ Gemischen. Ein kinetisches Modell, das aus Informationen aus der Oberflächenforschung abgeleitet wurde, führt zur Chemisorption von CH_4 und wahrscheinlich auch dem ersten Dehydrierungsschritt als geschwindigkeitsbestimmenden Schritten und beschreibt die Kohlenstoffabscheidung auf Nickelkatalysatoren auf $\text{CH}_4 + \text{H}_2$ gut. Die Kinetik der Kohlenstoffbildung in und $\text{CO} + \text{H}_2$ Gasgemischen ist in Übereinstimmung mit der Annahme der CO -Disproportionierung als geschwindigkeitsbestimmenden Schritt. Die Anwesenheit von Wasserstoff beeinflusst die Chemisorption von CO sehr stark. Kohlenstoffäden werden gebildet, wenn Wasserstoff in dem Gas anwesend ist, während in reinem CO die Einkapselung durch Kohlenstoff vorwiegt. Kleine Gehalte von Cu beschleunigen die Kohlenstoffbildung, während größere Gehalte ($\text{Cu} : \text{Ni} \geq 0,1$) die Kohlenstoffabscheidung hemmen und die Morphologie der Fadenbildung ändern ("Octopus" Kohlenstoffabscheidung). Durch Adsorption induzierte Nickelsegregation verändert die Kinetik für die Legierungskatalysatoren bei hohen Kohlenstoffaktivitäten. Veränderungen der kinetischen Modelle, die in einigen vor kurzem erschienenen Veröffentlichungen vorgeschlagen wurden auf der Grundlage von neuen Resultaten, werden auch kurz diskutiert.

1 Introduction

The first step in transforming natural gas, consisting mainly of methane, into useful chemicals in the chemical industry is usually the steam reforming reaction where methane is reacted with steam to a mixture of hydrogen, carbon monoxide and carbon dioxide by means of a nickel catalyst. Thus, the hydrogen used for ammonia synthesis and the syngas, i. e. a mixture of hydrogen and carbon monoxide, used for methanol syn-

thesis is usually produced by steam reforming of natural gas. The reaction design conditions are limited by the requirement that filamentous carbon formation must be avoided because it can destroy the catalyst particles and block the reactor. The importance of being able to predict accurately the conditions at which the formation of filamentous carbon may take place has been a strong motivation for a large number of studies of carbon formation on nickel catalysts for more than 25 years. The first model explaining the growth of filamentous carbon on silica and graphite supported nickel films exposed to C_2H_2 was suggested by Baker et al. [1] on the basis of observations in controlled atmosphere electron microscope. They suggested that carbon atoms from the decomposition of C_2H_2 on the nickel surface diffuse through the nickel particle and segregate initially to the interface between particle and support causing detachment of the particle. In the subsequent steady state carbon filament growth period, the decomposition, bulk diffusion and segregation continue but now the segregated carbon contributes to the filament growth. A simi-

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lar mechanism was suggested independently by *Lobo* et al. [2]. *Baker* et al. [1] postulated that the diffusion through the particle was rate determining and that the driving force was a temperature gradient caused by the heat liberated by the decomposition of C_2H_2 . In a subsequent paper, *Baker* et al. [3] provided supporting evidence for bulk diffusion as rate determining by measurements of the activation energies for carbon filament growth on Fe, Co, Cr and Ni exposed to C_2H_2 , which were found to be equal to the activation energies for carbon diffusion through the bulk of the metals.

In the present paper the mechanism of carbon formation is discussed mainly on the basis of the results obtained in our studies of carbon formation on silica supported nickel and nickel-copper alloy catalysts. Kinetic and equilibrium results as well as electron microscopic observations are reviewed. On this basis, supplemented with results from the literature, our present understanding and lack of understanding of the various steps of carbon formation in the steam reforming process on nickel and nickel-copper catalysts are discussed.

2 Kinetic studies

Simultaneous with the methane steam reforming reaction



also the water gas shift reaction



takes place.

Dependent on the conditions, carbon may be formed by one or more of the following reactions



2.1 Kinetics of carbon formation on Ni/SiO₂ catalysts from CH₄ + H₂ gas mixtures

Kinetic results were obtained at 723, 773, and 823 K at atmospheric pressure and with partial pressures of CH₄ and H₂ in the ranges 20–80 kPa and 5–15 kPa, respectively [4]. The results were interpreted by means of a kinetic model [4] constructed on the basis of results obtained by theoretical and experimental surface science studies of the interaction of CH₄ with Ni surfaces. Molecular beam [5, 6] and environmental gas [7–10] studies of the dissociative chemisorption of CH₄ on Ni(111), Ni(100), and Ni(110) surfaces have shown that it is a direct process resulting in the deposition of CH₃ and H on the surface. At sufficiently high temperatures, CH₃ is subsequently stepwise dehydrogenated. The chemisorption probability is strongly dependent on the crystallographic orientation of the surface, being smallest for the close packed (111) surface. At temperatures above about 625 K, the surface C atoms migrate at a measurable rate into the bulk of the nickel crystal [11]. Nucleation and segregation of carbon may take place when the solubility limit has been exceeded locally [12]. Accordingly, a kinetic model for the steady

rate growth of carbon filaments from CH₄ + H₂ gas mixtures may be based on the following steps:



where * signifies an adsorption site on the nickel surface.

To these surface reaction steps should be added steps providing transport of the carbon atoms from the surface and into the filament, i. e. corresponding to subsurface migration, diffusion through the nickel particle and segregation to the interface between the nickel particle and the carbon filament. *Grabke* [13] found that a kinetic model based on almost the same surface steps but with the addition of a molecularly adsorbed CH₄ precursor could account for the kinetics of carbon formation on iron films from CH₄ + H₂ gas mixtures, when the first dehydrogenation step was assumed to be rate determining. In the present case, all models generated by assuming that one of the steps (6)–(10) is rate determining were tested against our experimental results. The number of unknown parameters was drastically reduced by calculating the equilibrium constants of the steps using known values of the vibrational frequencies and bonding energies of the species participating in the steps. At a given temperature, the only adjustable parameters are then the forward rate constant of the rate determining step (rds), k_p , and the carbon coverage. It was argued [4] that the carbon coverage would stay close to the lower limit (ca. 0.2 monolayer) on the Ni(100) surface, and that it could be treated as a constant. With the chemisorption step (7) or the first dehydrogenation step (8) as the rds a value for the forward rate constant k_p could, for any choice of the carbon coverage, be found which gave reasonable agreement between model and experiment. Other choices of rds could be excluded. Even better agreement was obtained by assuming that both steps (7) and (8) are rate controlling, i. e. cannot be treated as being close to equilibrium. After having obtained good agreement at one temperature by adjusting the two rate constants, it was possible to obtain reasonable agreement at the other temperatures by adjusting only the rate constant for the first dehydrogenation step because the temperature dependence of the chemisorption rate is known from surface science experiments [7, 8, 10].

2.2 Kinetics of carbon formation on Ni/SiO₂ catalysts from CO

Tøttrup [14] found that his kinetic results for carbon formation on a Ni/SiO₂ catalyst in CO and in CO + CO₂ gas mixtures were well described by a model in which the dissociation of CO



is the rds. *Sakai* et al. [15] concluded, on the other hand, that a kinetic model based on disproportionation of CO



as the rds gave the best agreement with their experimental results.

Tavares et al. found [16], in agreement with Sakai et al. [15], that kinetic results for carbon formation on a Ni/SiO₂ catalyst in CO could not be described by a model with (11) as the rds but they were in good agreement with a model based on (12), i.e. the rate of carbon formation, r_c is well described by

$$r_c = k \frac{P_{\text{CO}}^2}{[1 + K_A P_{\text{CO}}]^2} \quad (13)$$

where K_A is the equilibrium constant for CO adsorption. K_A values giving best agreement between model and experimental results were in good agreement with values determined from surface science experiments [16]. A closer look at the results of Tøttrup [14] showed that only his results for carbon formation in CO + CO₂ gas mixtures were well described by a model based on (11) as rds. His results obtained in pure CO were in better agreement with (13).

2.3 Kinetics of carbon formation on Ni/SiO₂ catalysts from CO + H₂ gas mixtures

Tavares et al. [17] also studied the kinetics of carbon formation on the Ni/SiO₂ catalyst from CO + H₂ gas mixtures. In this case, a high rate of methanation was always measured independent of carbon formation. The carbon formation rate results showed that hydrogen has a far stronger influence than can be explained by simple blocking of sites on the surface. A good description was obtained by assuming, in agreement with results of coadsorption experiments [17], that adsorbed hydrogen diminishes the chemisorption bond energy of CO. The modification giving good agreement consisted of introducing a simple linear dependence on hydrogen coverage.

3 Equilibrium studies

Already in the early studies of carbon formation from CO and CH₄ by Dent et al. [18], attempts were made to characterize the thermodynamic properties of the carbon formed and it was observed that the equilibrium constants of reactions (3) and (4) were smaller than the equilibrium constants corresponding to the formation of graphite. Rostrup-Nielsen made a similar observation [19]. In addition he observed that the deviations depend on the nickel particle size and suggested that they could be explained by the extra energy required by the surface and defect structure of the carbon filaments.

It is important to realize that it is usually difficult to start carbon formation close to equilibrium conditions. A carbon activity, a_c , larger than the one corresponding to equilibrium is usually needed. In the work of Tavares et al. [16] and of Rostrup-Nielsen [19], it was observed that a significantly higher carbon activity was needed to start carbon formation on a fresh catalyst than on a used one. The determination of the carbon activity corresponding to equilibrium was made by decreasing the carbon activity of the gas in small steps until carbon formation could not be observed and

then decreasing it a little further until gasification of the carbon was measurable. The equilibrium activity was then determined by interpolation. Estimates of the surface energy and elastic energy of the carbon filaments indicate that they can explain the main part of the deviations from graphite equilibrium, at least in the case of carbon formation from CH₄ + H₂ [20]. Tavares et al. [16] found that the deviation was larger when carbon was formed in CO + CO₂ than in CH₄ + H₂.

4 The influence of copper

4.1 Kinetics

Similar kinetic studies were also performed for carbon formation on Ni_{1-x}Cu_x/SiO₂ catalysts. The method used for catalysts preparation ("dry" impregnation) resulted for $x < 0.5$ in one alloy phase with a bulk composition equal to the nominal one, while two alloy phases were observed for $x \geq 0.5$ [21]. Kinetic results were obtained for carbon formation on Ni_{0.99}Cu_{0.01}/SiO₂ and Ni_{0.9}Cu_{0.1}/SiO₂ catalysts exposed to CH₄ + H₂ [22] at the same conditions as the above mentioned results for the Ni/SiO₂ catalyst. The kinetic model based on steps (6)–(10) with calculated equilibrium constants and with the CH₄ chemisorption step (7) as rds gave, as mentioned above, a reasonable agreement with the experimental results for the Ni/SiO₂ catalyst. The agreement was further improved if also step (8) was treated as deviating from equilibrium. The models with only one rds have the advantage that they can be linearized, i.e. written as

$$y = ax + b \quad (14)$$

With step (7) as rds we obtain

$$x = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} \quad \text{and} \quad y = \frac{r_c}{P_{\text{H}_2}^2} \quad (15)$$

Using a and b as fitting parameters gave excellent fits to the results obtained for the Ni/SiO₂ catalyst [22]. Comparisons of plots of y versus x for the Ni/SiO₂ and the two alloy catalysts show that the kinetic model describes also the results for the Ni_{0.99}Cu_{0.01}/SiO₂ catalyst very well and that the presence of 1 at% Cu enhances the carbon formation rate. The results for the Ni_{0.9}Cu_{0.1}/SiO₂ catalyst can, on the other hand, only be described by the same kinetic model at low values of x , i.e. at low carbon activities, a_c , and then the rate is much smaller than the rate for the Ni/SiO₂ catalyst. At higher values of x or a_c , the rate increases drastically and approaches the values obtained for the Ni/SiO₂ catalyst.

Also carbon formation in CO [16] and in CO + H₂ [17] is promoted by the presence of 1 at% Cu to the Ni catalyst. The promotion increases strongly at higher hydrogen pressures [17]. Cu concentrations of 10 at% or higher poison the carbon formation strongly. In both cases the same type of kinetic model describes the results well for Cu concentrations in the range 0–10 at%.

4.2 Equilibrium

The studies of the equilibrium of carbon formation in CH₄ + H₂ showed that it does not depend significantly on the Cu content of the catalyst for Cu concentrations in the range 0–50

at% [21]. Equilibrium results in CO + CO₂ gas mixtures were independent of Cu concentrations in a smaller range, 0–10 at%, while higher deviations from graphite equilibrium were found at higher Cu contents [16]. The deviations from graphite equilibrium were significantly higher in CO + CO₂ than in CH₄ + H₂.

5 Electron microscopic observations

Systematic electron microscopic studies of catalysts after carbon formation at a range of different conditions have unfortunately not been made. However, a few chance observations are worthwhile mentioning.

5.1 Surface planes of the active nickel particles

Because of the structure sensitivity of the chemisorption of CH₄ on nickel surfaces, it is important to know the structure of the various parts of the surface of the nickel particles responsible for the carbon formation. It turned out that it was possible to obtain this information by constructing a model of the particle in agreement with the particle contours in electron micrographs and the angles between the surface planes as determined from thickness fringes seen in weak beam, dark field images of the nickel particles [23]. The modelling showed that the surface of the nickel particle in the end of the filament consists of (111), (100), and (113) atomic planes making up 46, 23, and 31% of the total surface area, respectively. Unfortunately, no studies have been made of the interaction of CH₄ with the Ni(113) surface. It may be expected that the sticking coefficient is higher for the (113) than for the (111) surface, perhaps even higher than for the (100) surface.

5.2 Relation between the carbon filament structure and the nickel structure

HREM lattice imaging of the interface between the carbon filament and the nickel particle shows that in spite of frequent interface direction changes due to low angle faceting, the graphite planes of the filament close to the interface are always strictly parallel to the interface.

5.3 Ni particle shape as function of temperature

Comparison of the nickel particles at the end of filaments grown in CH₄ + H₂ gas at 763 and 863 K shows that the nickel particles with increasing temperature become more and more pear-shaped. The rear side of the particle develops into a cone pointing towards the filament, the lengths of the cone increasing with temperature. It may be suggested that the filament graphite planes in contact with the nickel particle during growth are acting on the nickel with a friction force drawing the metal out in a cone. At the higher temperature, the metal particle may be deformed to a higher extent. It is conceivable that if the temperature is high enough and the cohesive energy of the metal is low enough, then metal drops may be separated from the metal particle. We have observed such metal drops inside long, hollow carbon filament tubes after exposing a Cu/SiO₂ catalyst to a CH₄ + H₂ gas mixture at about 1100 K [21].

5.4 Carbon morphology

Most of our EM observations of the carbon formed have been made after growth in CH₄ + H₂ mixtures. In this case, we have always seen carbon filaments with more ordered and more disordered carbon after growth at high and low temperatures, respectively. Only one filament is connected with a pure nickel particle and the filament and particle have approximately the same size. Carbon filaments for Ni_{1-x}Cu_x alloy catalysts with small x are not different from the filaments of the pure Ni catalysts. Another type of filaments is seen for x ≥ 1.0. More than one filament (“octopus” carbon) have grown out of each almost spherical alloy particle [24]. In this case the graphite planes are perpendicular to the axis of the filament and the interfaces between the filaments and metal particle are plane facets. For higher values of x, the carbon in the octopus carbon becomes more disordered [21].

EM micrographs obtained after carbon growth in CO show yet another type of carbon, i. e. encapsulating carbon. In this case the metal particles are completely covered by a number of graphite-like layers forming a shell around the particle.

6 Discussion

6.1 Carbon formation on nickel from CH₄ + H₂

Very recently *Snoeck et al.* have published thorough discussions of the mechanism [25] and the kinetics [26] of carbon filament growth in CH₄ + H₂ gas mixtures on a commercial nickel catalyst. The kinetic studies were made at 773, 798, and 823 K with 1.5, 5.0, and 10 bar CH₄ partial pressures.

Snoeck et al. [25] advocate a model for carbon filament growth closely resembling the one suggested by *Alstrup* [20] in 1988. They agree that the “equilibrium” for carbon filament formation is determined by the thermodynamic properties of the carbon filaments and not, as suggested by some other authors [27, 28], by an intermediate, unstable carbide, although *Snoeck et al.* prefer not to call the gas composition where growth stops and gasification starts, or vice versa, for the “equilibrium” but the “coking threshold”. The surface reaction, e. g. methane decomposition or the Boudouard reaction produces, at not too high rates, adsorbed, isolated carbon atoms, which dissolve into the nickel particle, diffuse through the particle and precipitate out at the support interface. Due to the segregation behaviour of carbon in nickel, a high concentration of carbon is established in the selvedge at the surface where the carbon atoms are produced. This high concentration, which is linked to surface carbon coverage and to the bulk concentration just below the selvedge, gives the driving force for the diffusion of carbon through the particle. In the induction period, a supersaturation is established in the particle, and faceting and nucleation of graphite precipitation take place at the particle/support interface and the carbon concentration at the interface drops to the solubility limit.

Snoeck et al. [26] made a careful analysis of all the possible kinetic models for carbon formation from CH₄ decomposition based on one rate controlling step and the same sequence of surface steps as assumed in our model with one exception: They found it necessary to add molecularly adsorbed CH₄ because the rate is significantly suppressed when the CH₄ pressure is increased from 5 to 10 bar. The main problems in the modelling are the quantitative description of the steps transporting the carbon from the surface through the bulk and

into the filament. In our model we got rid of them by assuming that surface carbon coverage can be treated as a constant. This is of course not strictly true but the good agreement obtained indicates that it may be a reasonable approximation. *Snoeck et al.* [26] have solved this problem more elegantly by assuming that the diffusion is so rapid that it is reasonable to assume that the concentration gradient is negligible in the particle so that the bulk concentration to a good approximation is equal to the solubility throughout the particle. The carbon coverage is assumed to be linked to the bulk concentration close to the surface by a segregation equilibrium constant. The end result is that *Snoeck et al.* [26] obtained a rate equation with the same partial pressure dependencies in the numerator as we did [4] when we assumed one rate controlling step. The denominator of their rate expression has an extra term accounting for the blocking action of the molecularly adsorbed CH_4 . They assume that molecularly adsorbed CH_4 is the precursor for the dissociation of CH_4 . This is not necessarily the case, as the direct dissociative chemisorption observed by molecular beam experiments may still be dominating.

6.2 Encapsulating carbon

When carbon formation takes place in $\text{CH}_4 + \text{H}_2$ or $\text{CO} + \text{H}_2$ gas mixtures the most common type formed is filamentous carbon. However, when the carbon formation takes place in pure CO , another type, encapsulating carbon, is dominating as mentioned above. *Nolan et al.* [29–31] have studied the influence of hydrogen on the morphology of carbon grown in CO . They concluded that the presence of hydrogen is necessary for the growth of filaments. The role of hydrogen is to satisfy the free valencies of the open end of the filament.

6.3 Challenges

The studies reviewed above show that very detailed information about the surface steps of the carbon formation mechanism is obtainable from independent experiments and calculations. In the near future it may even be possible to follow the steps in situ at the atomic level using high pressure, elevated temperature STM technique. The next challenges will then be to perform similar detailed studies of the subsurface events, i. e. determining the structure and concentration in the subsurface layers, the nucleation of and incorporation of carbon atoms into filaments, and the formation of encapsulating carbon.

7 Conclusions

The kinetics of carbon filament formation in $\text{CH}_4 + \text{H}_2$ on nickel catalysts is well described by a model consisting of

1. Dissociation of CH_4 , either directly from gas phase or from adsorbed CH_4 molecules. The dissociation is the rate determining step.
2. Stepwise dehydrogenation.
3. Segregation-dissolution equilibrium linking carbon surface coverage and the bulk carbon concentration close to front surface.
4. Diffusion through particle.
5. Precipitation into the filament at the rear interface.

The carbon filaments become tubes with more perfect carbon structure at higher growth temperatures.

The deformation of the nickel particle with cone formation increases with temperature.

Carbon formation in pure CO results mainly in encapsulating carbon. The rate determining step is CO disproportionation.

Carbon formation in $\text{CO} + \text{H}_2$ gives filaments. The rate determining step is CO disproportionation. Adsorbed hydrogen has a strong poisoning effect on CO chemisorption.

Cu alloying:

Small amounts of Cu (Cu : Ni = 1 : 99) promotes carbon formation.

Larger amount of Cu (Cu : Ni \geq 10 : 90) poisons carbon formation. The poisoning becomes smaller at higher C activities because of Ni surface segregation.

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