Catalysis Today 178 (2011) 110–116

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Carbon formation and gasification on metals. Bulk diffusion mechanism: A reassessment

L.S. Lobo [a], J.L. Figueiredo [b,*], C.A. Bernardo [c]

[a] Universidade Nova de Lisboa, REQUIMTE/CQFB Chemistry Department, Faculty of Sciences and Technology, 2829-516 Caparica, Portugal
[b] Laboratório de Catálise e Materiais, Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[c] IPC, Institute for Polymers and Composite/I3N, School of Engineering, Minho University, 4800-058 Guimarães, Portugal

ARTICLE INFO

Article history:
Received 29 April 2011
Received in revised form 15 July 2011
Accepted 18 July 2011
Available online 26 August 2011

Keywords:
Mechanism
Filamentous carbon formation
Transition metals
Bulk diffusion
Solid state reactions
Mass transfer dynamics

ABSTRACT

The mechanism for carbon formation from hydrocarbons on transition metals, proposed 40 years ago, is reassessed, evaluating the role of surface catalysis and bulk diffusion. Under steady-state conditions, solid state reactions, which are essential to start-up the process, will be confined to carbon growth. The dynamics of carbon mass transfer is discussed, together with the thermodynamic equilibria prevailing at the metal–gas and metal–graphite interfaces. The reverse process of carbon gasification is also addressed.

1. Introduction

Carbon formation from hydrocarbons on metals was the object of several studies in the 1960s [1–5]. In the early 1970s there was increased interest in understanding this reaction on Ni and other transition metals and alloys, since it was the cause for deactivation of industrial catalysts, particularly in steam-reforming reactions, and of fouling of reactor walls and heat exchanger surfaces. In this decade, David L. Trimm supervised several PhD theses at Imperial College of Science and Technology, London, dealing with various aspects of this topic [6–11]. Most of the early studies on carbon formation focused on the morphology of the deposits, rough kinetic data being obtained by weighing the metal specimens before and after exposure to the reactants [12–14]. Further insights into the mechanism of carbon formation (and gasification) were obtained when means were devised to follow the reaction continuously. One such technique, developed at David Trimm's group, involved the use of microbalances to obtain accurate data to establish the reaction kinetics [6,9–11,15,16]; another technique, named Controlled Atmosphere Electron Microscopy (CAEM), was developed by Baker and coworkers at about the same time, allowing for the in situ observation of the phenomena involved [17,18].

It is quite remarkable that this subject has persisted for more than 50 years as a hot topic for research; however, there has been a shift in the focus. While the early studies attempted to understand the reaction mechanism, in order to prevent or minimize carbon deposition, in the 1980s and 1990s the emphasis was on promoting the reaction to produce carbon materials, namely filaments and vapor grown carbon fibers which found important technological applications in composites [19–24]. The discovery of carbon nanotubes in 1991 [25] provided an enormous boost to the topic, since the mechanisms involved in their synthesis by CVD share common features with the original mechanisms proposed for carbon formation on metals [26]. In addition, the advent of the "hydrogen energy system" led to increased attention being devoted to the catalytic decomposition of methane as a clean method to produce CO-free hydrogen for fuel cells, a subject which has been recently reviewed [27].

Carbon formation from hydrocarbons (and syngas) on metals is a complex process, involving surface catalysis coupled with solid state reactions. A multidisciplinary approach is required to understand all the phenomena involved. Despite the enormous progress achieved in the past 50 years, it is recognized today that a unified mechanism has not yet been proposed, some aspects still remaining controversial [28].

---

* Corresponding author. Tel.: +351 22 5081663; fax: +351 22 5081449.
E-mail address: jlfig@fe.up.pt (J.L. Figueiredo).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.07.030

In the present paper we reassess the general mechanism proposed in the early 1970s, highlighting some of the original ideas and findings which originated from David Trimm's group, in which the authors worked sequentially from 1969 to 1977. In order to focus on the essentials, an Occam Razor's approach, or law of parsimony, which David taught to one of us, will be adopted.

2. Kinetics, general features

The rates of carbon deposition from hydrocarbons on metal foils (Ni, Fe, Co, steel, and alloys) show an acceleratory period and usually reach a steady state rate (Figs. 1 and 2). Hydrogen influences the rate in various ways. On Ni foils, its presence is required for a fast deposition to take place [6,15,16,29].

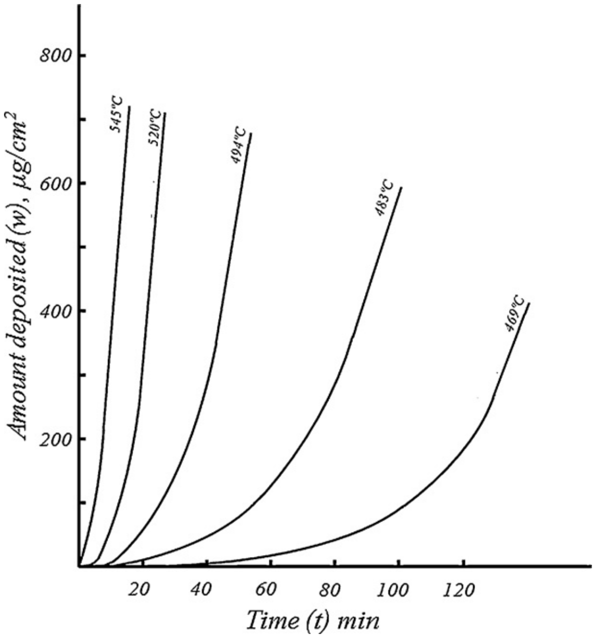

Fig. 1. Examples of transient kinetics in the deposition of carbon on Ni foils from 20 kPa of cis-2-butene. A steady-state rate of deposition is reached and sustained for a long time.

Adapted from ref. [6].

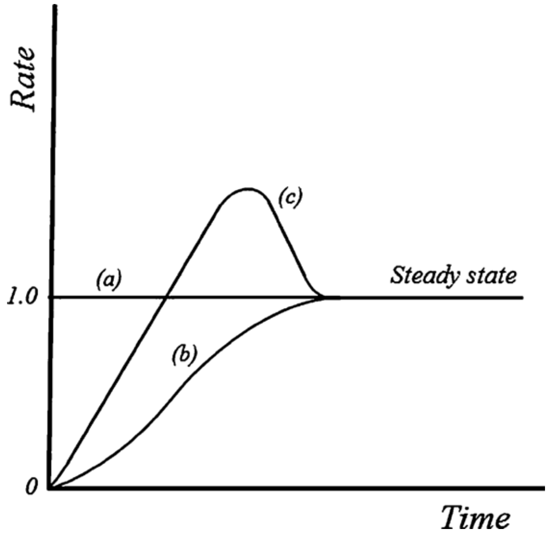

Fig. 2. Schematic representation of different transient kinetics of nucleation and acceleration. The acceleratory period may be almost instantaneous (a) or slow (b), sometimes even overshooting (c) the level of the steady-state rate (in the ordinate axis the rates are normalized by the steady-state rate). The time scale is necessarily variable; depending on the specific conditions, the transient period may last minutes or a couple of hours.

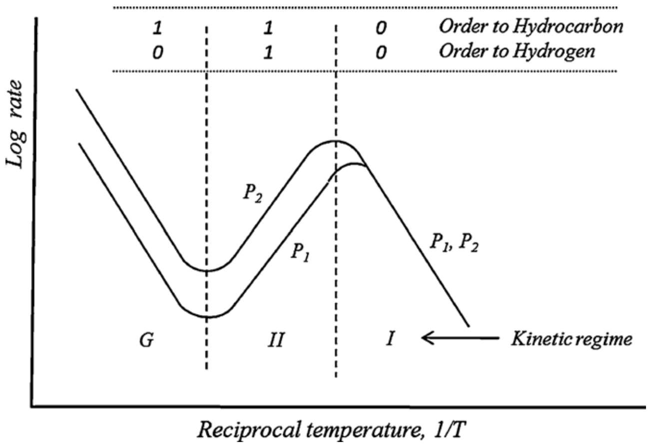

Fig. 3. Arrhenius plot of the steady-state rates of carbon deposition [6,15]. Three kinetic regimes are observed: (*I*) at lower temperatures, the rate is independent of the nature of the hydrocarbon used and of the gas pressures, showing an apparent activation energy of about 33 kcal/mol; (*II*) At intermediate temperatures, the kinetic regime shows a negative temperature dependency and 1st order with respect to H_2 and hydrocarbon; (*G*) Pyrolytic gas phase carbon formation, in fact independent of the nature of the solid surface.

Initial kinetics reflect mostly the nucleation stage. Steady state kinetics reflect the growth process when surface reaction and crystal growth conditions are stable. Understanding the mechanism of the growth process is the object of this paper.

The Arrhenius plots of the steady state rates of deposition from hydrocarbons on Ni usually show three kinetic regions, as shown in Fig. 3 [6,15,16]: region I, at lower temperatures (350–550 °C); region II, at intermediate temperatures (550–650 °C); and region *G*, at higher temperatures. The deposition in this latter region was found to be due to gas phase pyrolytic carbon, and to be independent of the substrate. Soot formed in the gas phase impinges on the metal surface and in the reactor walls as well – it is not a catalytic process. In region II surface reaction is probably controlling, in view of the orders of reaction observed. The reason for the negative activation energies observed is thought to be the effect of temperature on the surface concentration of the reactants, as mentioned in the original paper [15]. Similar kinetic regions are found in carbon formation on Co, Fe and steels [6,30,31].

The carbon deposits grown on metal foils at steady state usually consist of filaments (up to a few hundreds of nanometers in diameter) carrying a metal crystallite on top, although it is also possible to find the metal crystallites in the middle. In any case, these crystallites must be detached from the original metal foil. The same type of carbon is found in regions I and II (Fig. 3).

The same general features are observed for carbon deposition on supported Ni catalysts, but in this case there is no acceleratory period and hydrogen is not needed for a fast deposition. Moreover, the same specific rates of carbon deposition (i.e., rates per unit metal area) were determined for foils and supported catalysts [9,32].

3. Bulk diffusion mechanism: an "Occam Razor's" approach

A reassessment of the so-called bulk diffusion mechanism can be made along the following lines, using the principle of parsimony, the Occam Razor's approach.

The reactions involved are a combination of surface catalysis and solid state reactions. Again, to fully understand them, concepts from the two areas are required. The overall kinetics, however, goes together: at steady-state, all the steps proceed at the same rate, but

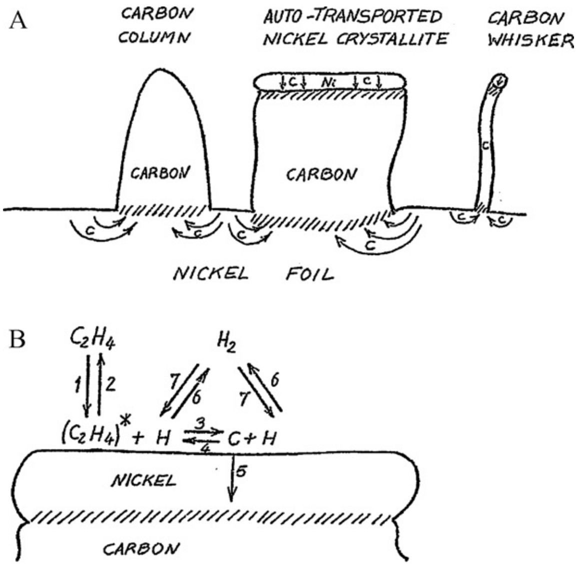

Fig. 4. Original model proposed for carbon formation on Ni [6]. A: Several modes of carbon formation observed on nickel foils; B: detail of carbon formation on a detached crystallite, showing the reaction steps of the proposed mechanism.

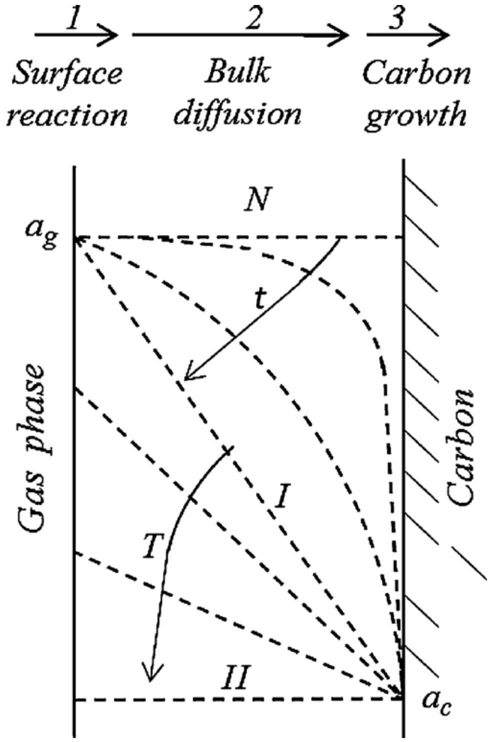

Fig. 5. The three reaction steps (at the top of the figure) and the carbon profiles in the metal at the nucleation stage (*N*) and during steady-state growth in two kinetic regimes: surface reaction control (*II*) and carbon bulk diffusion control (*I*). For simplicity, a single solid state phase in the metal catalyst is assumed. The profile transitions during nucleation (*t*) and when the temperature increases (*T*) – changing the control to the surface reaction – are shown; a_g and a_c represent the carbon activities in equilibrium with the gas phase and graphite, respectively.

the step which is farthest from equilibrium determines the rate and the observed kinetics. The steps which are not rate-determining are kinetically disguised.

A description of various forms of carbon growth is presented in Fig. 4 (taken from ref. [6], p. 179). This was in fact the original proposal of a mechanism of surface reaction followed by carbon bulk diffusion and growth.

After due nucleation of the new carbon phase, a steady state growth step occurs, often for very long periods of time. This striking feature deserves particular attention.

Carbon must be transported from the metal surface, where hydrocarbon decomposition takes place, to the regions where nucleation, in a graphitic form, has already taken place. In this way, carbon does not accumulate on the metal surface, allowing for the catalyst to remain active.

It is known that metal carbides can be formed under these conditions. Let us assume first that a single solid phase (metal or carbide) is involved in the carbon diffusion process – the stable phase under reaction conditions – and that the geometry is one-dimensional. The mechanism involves the following three steps: (1) catalytic decomposition of the hydrocarbon on the metal surface, generating chemisorbed carbon atoms; (2) diffusion of the carbon atoms through the bulk of the metal (or carbide); (3) growth of the carbon deposit. Under steady-state carbon growth, the rates of the 3 steps must be the same. The rate-controlling step will determine the kinetics and will use the maximum carbon concentration gradient possible. Fig. 5 represents carbon activity profiles across the metal in three cases: during the nucleation stage (*N*), under bulk diffusion control (I); and under surface reaction control (II).

During the nucleation stage, the solid phase will either be the metal or a carbide, whichever is the stable phase under reaction conditions. The constant carbon concentration profile will be in equilibrium with the carbon activity at the surface. As the rate increases and steady-state growth is reached, equilibrium on the graphite side will equal the carbon solubility in the metal (or carbide) in equilibrium with graphite – the growing phase. When nucleation is easy and fast, the transient profile may not actually reach the level *N*.

When drawing these profiles, we may use either the activity (a_i) or the chemical potential ($\mu^{\circ}{}_i + \mathrm{RT}\ \ln a_i$), or the Gibbs free energy. The driving force for diffusion is the difference in chemical potential of carbon in the two sides of the catalyst: in equilibrium with the gas phase on one side, and with graphite on the other side.

Let us now assume that the solid phase (S_1) in equilibrium with the gas is carbide, different from the solid phase (S_2) in equilibrium with graphite (metal or another carbide). In that case the profiles of activity (and carbon concentration) will be as shown in Fig. 6.

Under reaction conditions, when graphite has not yet nucleated, the carbide will in fact extend throughout the metal, because it is the phase in equilibrium with the gas. But under steady-state growth it will recede to a slab near the catalyst–gas interface. The rate of carbon diffusion through the two solid phases of the catalyst must be the same. For that condition to be fulfilled, the slope of carbon concentration in the two phases must be inversely proportional to the respective carbon diffusivities (see Appendix A and Fig. 10). In fact, to maximize the rate (i.e., the slope), the thickness of the phase with lower carbon diffusivity must be reduced to a minimum (selvedge). It must also be understood that phase S_1 in contact with phase S_2 is probably unstable at low carbon concentrations. It must then recede to an equilibrium configuration.

A general case of carbon activity profile, with combined resistance of all steps is shown in Fig. 7. Naturally, the equilibrium carbon activities in the boundary limits (a_g, a_c) will change with temperature.

At the metal/graphite interface, surface diffusion of carbon atoms must be dominant and the process of growth is based on dislocations and crystal defects. Indeed, the energy barrier for surface diffusion has been calculated to be lower than that for bulk diffusion [33].

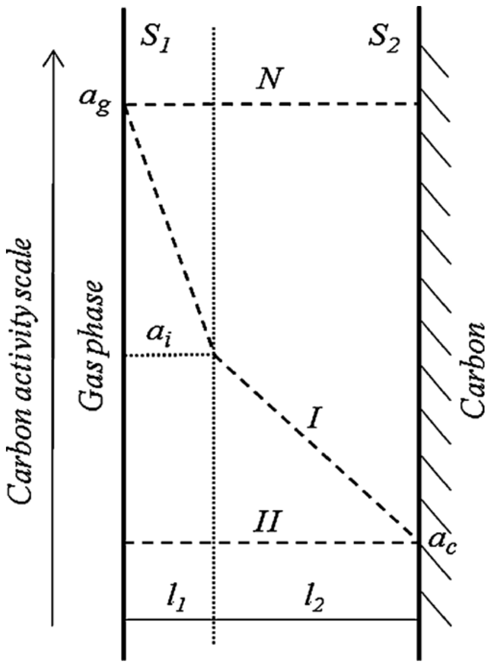

Fig. 6. The same as in Fig. 5, but considering two catalyst solid phases, S_1 and S_2. The thicknesses of the two phases, l_1 and l_2, are proportional to the respective diffusivities of carbon atoms (see note in Appendix); a_i is the carbon activity at the carbide/metal boundary; a_g, a_c, *N*, *I* and *II* as in Figs. 3 and 5.

The mechanism of bulk diffusion for catalytic carbon gasification is the reverse of the mechanism described above for carbon formation [9,34]. Direct evidence of the reversibility of these processes has been observed and recorded using CAEM [35]. As an example, Fig. 8 shows carbon activity profiles for carbon formation or gasification from CO/CO$_2$ mixtures.

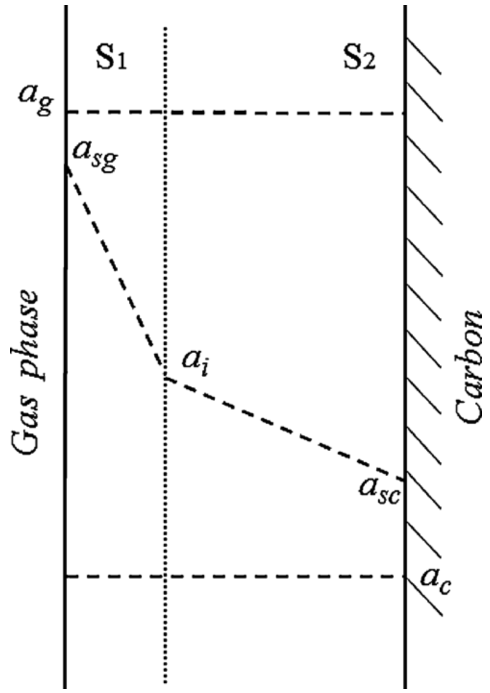

Fig. 7. General profile of the activities (or carbon concentrations) through the catalyst when all steps offer resistances of the same order – no specific step controls the overall reaction rate; a_{sg} and a_{sc} represent the carbon activities prevailing at the interfaces with the gas and graphite phases, respectively.

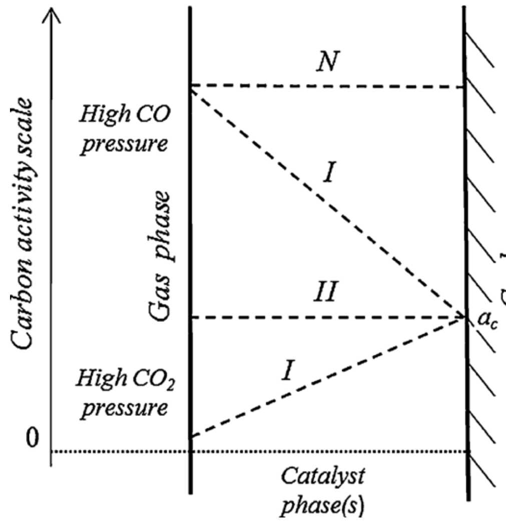

Fig. 8. Profiles of carbon activity through the catalyst (for simplicity. only one phase is shown) in carbon formation or gasification from CO/CO$_2$ mixtures, according to the relative pressures of the gases. A bulk diffusion kinetic control regime is assumed.

In real situations, the one dimensional geometry does not apply. More complex geometry simulations are required, such as that shown in Fig. 9 (taken from ref. [31]). But the principles and the mechanism remain the same.

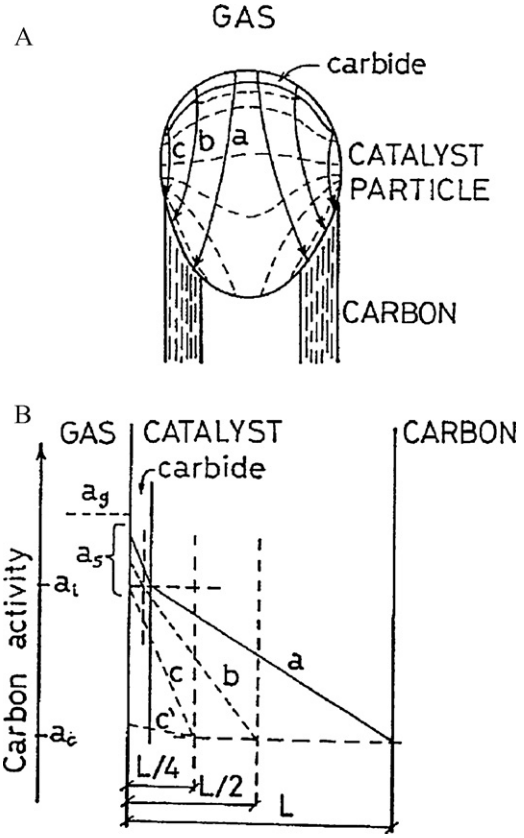

Fig. 9. Mechanism of carbon bulk diffusion in a catalyst particle during filament growth (cylindrical geometry). (A) Possible iso-concentration lines (dashed lines) and lines of flux (arrows) through the particle. (B) Carbon activity (concentration) profiles for three different diffusion paths. Taken from [31], where a more elaborate explanation can be found.

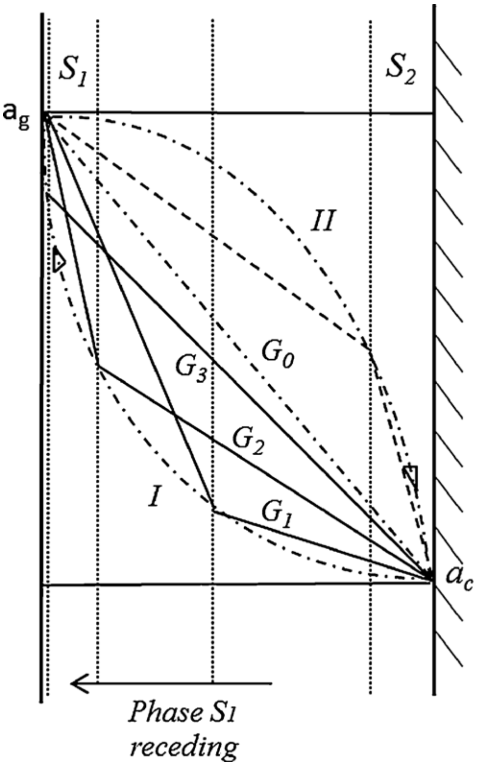

Fig. 10. Examples of activity profiles with two solid phases, S_1 and S_2, for a given ratio of the diffusion gradient ($D_2/D_1 = 10{:}1$). Phase S_1 will tend to recede to maximize the rate. The fastest carbon deposition corresponds practically to the single phase gradient G_0, with phase S_1 reduced to a thin selvedge. For the opposite case ($D_1 > D_2$), the locus of the phase and gradient transition is of type II, as shown.

4. Evidence and remarks

4.1 The kinetic studies using microbalances in the 1970s enabled a better understanding of the reactions of carbon formation and gasification on metals. Rates of nucleation, orders of reaction, and activation energies were studied over a wide range of temperatures and pressures. Comprehensive studies with various metals and alloys and various reactant gases were carried out. In addition, the role of H_2 in carbon deposition reactions was investigated. This work, coupled with post reaction SEM and TEM observations, led to the original proposal of the bulk diffusion mechanism [6].

4.2 Formal proof that bulk diffusion is involved in carbon deposition reactions has been presented in a series of experiments with a Ni single crystal foil, clean or previously covered with layers of carbon in a coating unit in one or in both faces [36]. The initial presence of carbon in one of the Ni faces inhibits nucleation and growth in the other face; that is, the pre-existence of active carbon sinks decreases its concentration in the metal, hindering conditions for nucleation even at considerable distances.

4.3 Consensus on the existence of a concentration driven mechanism seems to have gathered wide support along the years [28,37–42]. The appreciation that a unified mechanism has not yet been proposed [28] may be misleading. The detailed mechanisms for the surface reaction step and for the carbon growth step are certainly different for different reactants and for different catalysts, but the common features of the general mechanism can be established. Then, for each particular system, it is necessary to understand each one of the 3 steps – surface reaction, bulk diffusion, carbon/graphite growth. This includes the surface chemical reactions, the nature of the solid phases present and the details of the carbon growth mechanism. Changing the temperature of the reaction may change the phases (carbides/metal) operating during reaction, which may not be stable or even metastable at room temperature. Thus, in situ TEM and X-ray studies are important to provide evidence under reaction conditions.

4.4 The role of the various crystal faces for each of the steps (front and rear of the metal particle) has been evidenced or discussed by several authors and for several systems [38,43–45].

4.5 In carbon deposition on Ni foils from butene/H_2 mixtures in batch experiments there is a delay in the speeding up of the process when H_2 is admitted first. The reducing effect of H_2 retards the nucleation. However, H_2 is required for a quick deposition to take place (fast surface reaction step). It was also found that a long annealing period speeds up the process once the gases are admitted [6].

4.6 The acceleratory period shown in Fig. 2 was never observed in the case of supported metals, in spite of the otherwise similar features of the carbon deposition process [32]. Also, hydrogen did not affect the deposition rates, at least in the kinetic regime I (cf. Fig. 3). In this case, the catalyst consists of metal crystallites dispersed on a support, while with metal foils the crystallites must be detached before carbon filaments can grow. This detachment may involve preferential nucleation of carbon at grain boundaries, during the initial stages of the process, which is known to be favoured by hydrogen [46]. Therefore, both the hydrogen effect and the acceleratory periods observed with metal foils may be related to the detachment of crystallites.

4.7 The bulk diffusion mechanism discussed above describes the growth of (filamentous) carbon deposits under steady-state, i.e., at constant rate of deposition. However, when the carbon activity in the gas phase increases (due to the increase of temperature or hydrocarbon concentration or the decrease of hydrogen concentration) the formation of a graphitic deposit may occur at the metal–gas interface, the so-called “encapsulating carbon” [18], which obviously leads to catalyst deactivation and stops filament growth.

4.8 The role of carbides was controversial in the earlier discussions of the carbon formation mechanism, but it is now widely accepted that surface carbides are involved in carbon formation from hydrocarbons on Ni [47–49]. The formation of a surface carbide was invoked to explain the observed rates of carbon formation on Ni catalysts [9,32]. de Bokx et al. [50] proposed quite a different mechanism, involving the formation and continuous decomposition of an unstable, intermediate *bulk* carbide. A more elaborated proposal considering the formation of an unstable *surface* carbide was proposed by Alstrup [38]. In fact, as discussed in this work, under steady state growth conditions the presence of a surface carbide and the bulk diffusion mechanism seem more consistent.

4.9 The rate of growth of carbon filaments was found to be inversely proportional to the square root of the diameter of the metal catalyst particles, which was taken as evidence for a diffusion controlled mechanism [51].

4.10 Baker et al. [18] proposed a modified bulk diffusion theory to explain in situ CAEM carbon deposition observations. They suggested that the driving force for carbon bulk diffusion was a temperature gradient, originating from the highly exothermic decomposition of the hydrocarbon used (acetylene). This proposal was discarded by several authors [6,9,10,37,52,53]. Calculations have shown that the high conductivity of metals does not allow any significant temperature gradient across small metal crystallites. Moreover, the temperature gradient hypothesis cannot explain carbon formation from other hydrocarbons whose decomposition is endothermic (for instance, in the case of methane).

4.11 The above proposal for a mechanism [18] was in fact inconsistent. A temperature gradient drives heat transfer, not mass transfer. The rate dependence on temperature should then be linear, not exponential. An Arrhenius law dependence, also alleged in that paper, is not in fact compatible with the modified mechanism, as we carefully calculated in many systems [6,9,10]. What is required to tune up the model when bulk diffusion controls is to check the dependence on temperature (which is approximately constant throughout the particles) of the equilibrium carbon concentration values at the boundaries, in order to correct the activation energy expected from carbon diffusivity data [6,10].

4.12 As mentioned above, no relevant temperature gradient may exist on metal particles under reaction conditions – heat transfer coefficients of metals are too high [52]. However, in growing carbon fibers, the temperature of the metal particle as a whole may be higher than the surrounding atmosphere. The particle may even melt, as observed by CAEM. This is more likely to happen when the graphite fiber grows by layers: the conductivity of graphite is much lower in the direction perpendicular to the layers. But with nanotubes, heat transfer between metal and carbon should be more efficient due to the orientation of the carbon layers, parallel to the filament axis.

4.13 A good thermodynamic discussion of the driving force across the metal particle for carbon formation or gasification has been presented by Snoeck et al. [39], but some of the activity profiles shown therein are in fact incongruent. We hope that the approach of the present paper may help to clarify certain matters of transition states and of the conditions of operation of the catalyst under carbon formation or gasification.

4.14 In recent years, the advent of in situ high resolution TEM techniques has allowed the direct observation of filament growth at the nanoscale. For instance, in the decomposition of methane over supported nickel nano-crystals it was found that carbon nanofibers develop through a reaction-induced reshaping of the crystals [33,54]. Detailed *ab initio* density-functional theory calculations [55] showed that the energy barrier for carbon diffusion through the bulk of the nano-crystals was significantly higher than that for surface diffusion.

4.15 Carbon deposits with filamentous morphology were designated as carbon whiskers or carbon filaments in the early literature. The issue of terminology was discussed during a summer school in 1989 [cf. ref. [23], pp. 559–562], leading eventually to proposal of the term "filamentous carbon" [56]. Nevertheless, the term "carbon nanofibers", introduced by Rodríguez [57], is more frequent in the current literature. These changes in terminology may explain why so many authors of recent publications seem to be unaware of the earlier work on carbon formation. There is also much confusion in the literature between carbon *nanofibers* and carbon *nanotubes*, a clarification that still needs to be done.

4.16 Carbon formation (or gasification) on metals involves the transport of carbon from surface reaction regions to the catalyst/graphite interface. Bulk diffusion is probably the more obvious, but certainly not the only form of mass transfer. The present work is a contribution to clarify that mechanism.

Appendix A. Note on the bulk diffusion step

When two different phases prevail under reaction conditions at the two "sides" of the catalyst, under steady-state the flux (J) of carbon atoms must be the same through each phase. Let l_1 and l_2 be the thicknesses, D_1 and D_2 be the diffusivities and Δa_1 and Δa_2 be the activity differences in the two phases. Then the flux must be:

$$J = D_1 \bullet \frac{\Delta a_1}{l_1} = D_2 \bullet \frac{\Delta a_2}{l_2} \quad (1)$$

or:

$$\frac{D_2}{D_1} = \frac{\Delta a_1 / l_1}{\Delta a_2 / l_2} \quad (2)$$

Conclusion: the slopes of the carbon activity profiles in each phase must be inversely proportional to the respective carbon diffusivities. Fig. 10 shows, for a given ratio D_1/D_2, examples of activity gradients and phase thicknesses obeying the mass transfer equilibrium condition of Eq. (2).

In addition to the above condition, the thickness of the carbide will adjust to the minimum resistance (see Fig. 10). The fastest rate for mass transfer is achieved with a thin selvedge of the phase with the lowest carbon diffusivity. So, the acceleratory period often observed before the steady state rate of carbon deposition is reached may include: carburization of the metal, nucleation of graphite (with disruption of the metal, particularly in the case of metal foils) and recess of the carbide to a thin selvedge.

References

[1] M. Escoubes, J. Quinson, J.C. Eyraud, Bull. Soc. Chim. France 163 (1967) 2435.
[2] Y. Tamai, Y. Nishiyama, M. Takahashi, Carbon 6 (1968) 593–602.
[3] Y. Tamai, Y. Nishiyama, M. Takahashi, Carbon 7 (1969) 209–212.
[4] A.E.B. Presland, P.L. Walker Jr., Carbon 7 (1969) 1–8.
[5] S.D. Robertson, Nature 221 (1969) 1044–1046.
[6] L.S. Lobo, Ph.D. Thesis, Univ. London, 1971.
[7] F.J. Derbyshire, Ph.D. Thesis, Univ. London, 1974.
[8] M. Moayeri, Ph.D. Thesis, Univ. London, 1974.
[9] J.L. Figueiredo, Ph.D. Thesis, Univ. London, 1975.
[10] C.A. Bernardo, Ph.D. Thesis, Univ. London, 1977.
[11] A.I. La Cava, Ph.D. Thesis, Univ. London, 1977.
[12] S.D. Robertson, Carbon 8 (1970) 365–374.
[13] P.A. Tesner, E.Y. Robinovich, I.S. Rafalkes, E.F. Arefieva, Carbon 8 (1970) 435–442.
[14] T. Baird, J.R. Fryer, B. Grant, Carbon 12 (1974) 591–602.
[15] L.S. Lobo, D.L. Trimm, Nature Phys. Sci. 234 (1971) 15–16.
[16] L.S. Lobo, D.L. Trimm, J.L. Figueiredo, Kinetics and mechanism of carbon formation from hydrocarbons on metals, in: J.W. Hightower (Ed.), Proceedings of 5th International Congress of Catalysis, Miami Beach, Florida, 1972, 2, North Holland, Amsterdam, 1973, pp. 1125–1135.
[17] R.T.K. Baker, P.S. Harris, J. Phys. E: Sci. Instrum. 5 (1972) 793–797.
[18] R.T.K. Baker, M.A. Barber, P.S. Harris, F.S. Feates, R.J. Waite, J. Catal. 26 (1972) 51–62.
[19] G.G. Tibbetts, Appl. Phys. Lett. 42 (1983) 666–668.
[20] M. Endo, Chemtech 18 (1988) 568–576.
[21] F. Benissad, P. Gadelle, M. Coulon, L. Bonnetain, Carbon 26 (1988) 61–69.
[22] P. Serp, J.L. Figueiredo, Carbon 34 (1996) 1452–1454.
[23] J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Hüttinger (Eds.), Carbon Fibers, Filaments, Composites, Kluwer Academic Publishers, Dordrecht, 1990.
[24] O.S. Carneiro, J.A. Covas, C.A. Bernardo, C.A.F.W.J. Van Hattum, J.M. Ting, R.L. Alig, M.L. Lake, Composites Sci. Technol. 58 (1998) 401–407.
[25] S. Iijima, Nature 354 (1991) 56–58.
[26] L.P. Biró, C.A. Bernardo, G.G. Tibbetts, Ph. Lambin (Eds.), Carbon Filaments and Nanotubes: Common Origins, Differing Applications?, Kluwer Academic Publishers, Dordrecht, 2001.
[27] Y. Li, D. Li, G. Wang, Catal. Today 162 (2011) 1–48.
[28] P. Serp, Carbon nanotubes and nanofibers in catalysis, in: P. Serp, J.L. Figueiredo (Eds.), Carbon Materials for Catalysis, John Wiley & Sons, Hoboken, NJ, 2009, pp. 309–372.
[29] L.S. Lobo, D.L. Trimm, J. Catal. 29 (1973) 15–19.
[30] C.A. Bernardo, L.S. Lobo, The kinetics of carbon formation from acetylene and 1-butene on cobalt, in: B. Delmon, G.F. Froment (Eds.), Catalyst Deactivation, Studies in Surface Science and Catalysis, Elsevier, 1980, pp. 409–420.
[31] L.S. Lobo, M.D. Franco, Catal. Today 7 (1990) 247–256.
[32] J.L. Figueiredo, D.L. Trimm, J. Appl. Chem. Biotechnol. 28 (1978) 611–616.
[33] S. Helveg, C. López-Cartes, J. Sehested, P.L. Hansen, B.S. Clausen, J.R. Rostrup-Nielsen, F. Abild-Pedersen, J.K. Nørskov, Nature 427 (2004) 426–429.
[34] J.L. Figueiredo, D.L. Trimm, J. Catal. 40 (1975) 154–159.
[35] J.L. Figueiredo, C.A. Bernardo, J.J. Chludzinski Jr., R.T.K. Baker, J. Catal. 110 (1988) 127–138.
[36] C. Bernardo, L.S. Lobo, Carbon 14 (1976) 287–288.
[37] J.R. Rostrup-Nielsen, D.L. Trimm, J. Catal. 48 (1977) 155–165.
[38] I. Alstrup, J. Catal. 109 (1988) 241–251.

[39] J.-W. Snoeck, G.F. Froment, M. Fowles, J. Catal. 169 (1997) 240–249.
[40] K.P. de Jong, J.W. Geus, Catal. Rev.: Sci. Eng. 42 (2000) 481–510.
[41] V.V. Chesnokov, R.A. Buyanov, Russ. Chem. Rev. 69 (2000) 675–692.
[42] R. Philippe, A. Morançais, M. Corrias, B. Caussat, Y. Kihn, P. Calck, D. Plee, P. Gaillard, D. Bernard, P. Serp, Chem. Vap. Dep. 13 (2007) 447–457.
[43] C. Bernardo, D.L. Trimm, Carbon 14 (1976) 225–228.
[44] F.C. Schouten, O.L.J. Gijzeman, G.A. Bootsma, Surf. Sci. 87 (1979) 1–12.
[45] R.T. Young, J.P. Chen, J. Catal. 115 (1989) 52–64.
[46] Y. Nishiyama, Y. Tamai, J. Catal. 33 (1974) 98–107.
[47] C. Klink, I. Stensgaard, F. Besenbacher, E. Lægsgaard, Surf. Sci. 342 (1995) 250–260.
[48] H. Nakano, J. Ogawa, J. Nakamura, Surf. Sci. 514 (2002) 256–260.
[49] J. Lahiri, T. Miller, L. Adamska, I.I. Oleynik, M. Batzill, Nano Lett. 11 (2011) 518–522.
[50] P.K. de Bokx, A.J.H.M. Kock, E. Boellaard, W. Klop, J.W. Geus, J. Catal. 96 (1985) 454–467.
[51] R.T.K. Baker, Electron microscopy studies of the catalytic growth of carbon filaments, in: J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Hüttinger (Eds.), Carbon Fibers, Filaments and Composites, Kluwer Academic Publishers, Dordrecht, 1990, pp. 405–439.
[52] W.L. Holstein, M. Boudart, Latin Am. J. Chem. Eng. Appl. Chem. 13 (1983) 107–119.
[53] G.G. Tibbetts, Physical modeling of carbon filament growth, in: J.L. Figueiredo, C.A. Bernardo, R.T.K. Baker, K.J. Hüttinger (Eds.), Carbon Fibers, Filaments and Composites, Kluwer Academic Publishers, Dordrecht, 1990, pp. 525–540.
[54] S. Helveg, P.L. Hansen, Catal. Today 111 (2006) 68–73.
[55] F. Abild-Pedersen, J.K. Nørskov, J.R. Rostrup-Nielsen, J. Sehested, S. Helveg, Phys. Rev. B: Condens. Matter 73 (2006) 115419.
[56] E. Fitzer, K.-H. Köchling, H.P. Boehm, H. Marsh, Pure Appl. Chem. 67 (1995) 473–506.
[57] N.M. Rodríguez, J. Mater. Res. 8 (1993) 3233–3250.