Carbon nanotubes growth modes and rates: Explaining negative temperature dependence and Pt, Pd role.

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The kinetic study of carbon formation from hydrocarbons over a large temperature range (vg. 300 to 800 ^{0}C) shows a region with negative activation energies: the Arrhenius plots exhibit a maximum rate at about 550 ^{0}C [1-3]. This volcano shape is not very common. Puretzky et al. observed a similar maximum in the rate in carbon formation from C_2H_2 on Ni and questioned its meaning [4].

The similar sharp maximum observed in carbon formation from olefins and hydrogen exhibiting apparent negative activation energy is most probably due to high values of the enthalpies of adsorption for reactant gases [2]. Taking the case of C formation from C_2H_4/H_2 in the T region were *a slower surface reaction step controls* followed by a fast carbon bulk diffusion step (500-550 ºC), we may write:

Gas phase: $[C_2H_4]_g$ $[H_2]_g$ $[H_2]_g$ CNTs

$\downarrow\uparrow$ $\downarrow\uparrow$ $\downarrow\uparrow$ $\uparrow$

Surface reaction: $C_2H_4 + H_2 \rightarrow 2\,C + 3\,H_2 \rightleftharpoons (C)_d + (H)_d$

Active crystal faces: (100)/(110)… (111)

Reaction rate: $r = k\,[C_2H_4]_a \times [H_2]_a = k' \exp(E_a + \Delta H_{Ac} + \Delta H_H)$

If the sum of the estimated enthalpies (ΔH) of acetylene (-70 kcal/mole) and hydrogen (-20 kcal/mole) adsorption has a net (negative) value (-90 kcal/mole) higher than the activation energy of the surface reaction (~30 kcal/mole) and so the overall temperature dependence of the reaction rate is negative (check Fig. 1) [2].

Boudart and Djéga-Mariadsu in their book on Kinetics of Heterogeneous Catalytic Reactions [6] discuss in detail the work by Engel and Ertl in 1978 on catalysis of CO oxidation in which a volcano shape was observed [7].

In two articles on carbon nanofibers growth Pd and Pt were used: Pd with Co by Atwater, Phillips and Leseman [8] and Pt with Co-Cr by Teng et al. [9]. In the first case C_2H_2 and H_2 were used as reactants, and CH_4 and H_2 in the second case. In the presence of Pt or Pd, H_2 splits easily in 2 atoms. The decomposition of the reactant gas on the catalyst surface is accelerated. The H atoms diffuse easily through metals. A Co-Cr mixture forms an alloy. H atoms can also diffuse easily

through a silica wafer [8] or a ceramic boat [9]. The role of Pt or Pd is most certainly to supply H atoms to the metal catalyst nanoparticles reaching the catalytic surface and accelerating the hydrocarbon surface reaction decomposition and C atoms formation - which diffuse through the bulk metal nanoparticle to sustain CNTs growth.

Catalytic routes	**T Range**	**Gas Phase reactions**	**Surf. catalysis**	**C bulk diffusion**	**Nucleation**
I Catalytic	Low T	None or negligible	Yes	Through catalyst nanoparticle	On catalyst surface Ex: Ni(111)
II Hybrid	Medium	Pyrolysis: carbon black	No	Through catalyst nanoparticle	On catalyst surface Ex: Ni(111)
III Pyrolitic	High T	Pyrolysis: carbon black	No	Moving over previous layer of graphene	Over previous graphite layer

Table 1 *Summary of the 3 alternative catalytic routes observed in CNTs growth.*

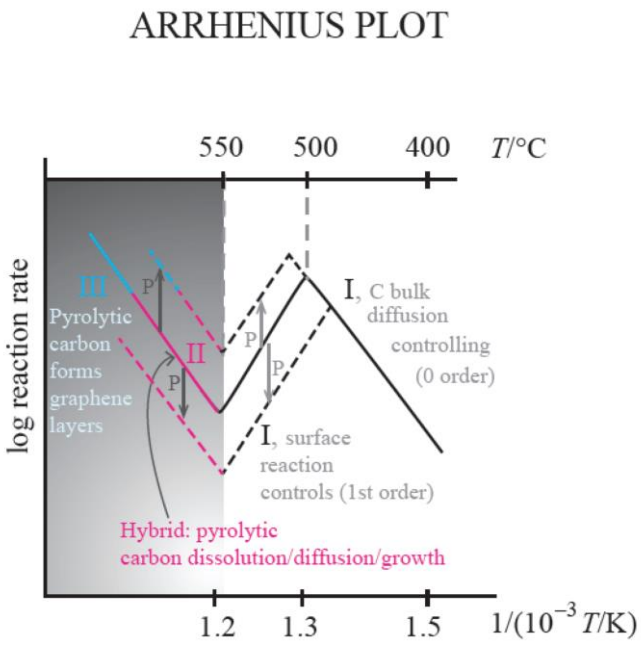

Fig. 1 *Scheme showing 3 alternative catalytic routes operating in CNT growth.*

1. Lobo LS. Carbon 114 (2017) 411-17
2. Puretzky AA et al. Carbon 79 (2014) 256-64.
3. Atwater MA, Phillips J, Leseman ZC. Carbon 49 (2011) 1058-66
4. Teng IJ, Huang CS, Hsu HL et al. Carbon 80 (2014) 808-22