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Pt Carbide Formation During Graphitic Carbon Growth Studied Using *in situ* TEM

H C Nerl[1] and M Plodinec[2]

[1.] Humboldt University of Berlin, Berlin, Germany.
[2.] ScopeM, ETH-Zürich, Zürich, Switzerland.
* Corresponding authors: hcnerl@physik.hu-berlin.de, mplodinec@ethz.ch

Improved understanding of structure-activity correlations are crucial to increase our knowledge of the fundamental workings of catalysts. However, despite extensive research efforts, the graphitization process of carbon is not understood in-depth yet. One hindrance is the difficulty to experimentally assess intermediary steps of the reaction due to a lack of temporal, analytical and spatial resolution. The second hindrance is that most conclusions on dynamical catalytic processes are drawn from static observations. This does not allow insights into the underlying, often unstable intermediary steps leading to the final structures. An important piece of the puzzle to understand graphitization is the role of the dissolution of carbon into the catalyst structure to form carbides. Whereas many growth studies are based on iron and nickel catalyst nanoparticles, platinum (Pt) is a standard catalyst in industrial reactions where catalyst coking is a major cause for deactivation. Iron carbide and nickel carbide has been observed experimentally. However, Pt carbide formation has been observed experimentally at very high pressure/temperatures[1] or under ethane treatment of confined Pt nanoclusters[2] only.

TEM studies of catalysts have frequently been done not in relevant conditions (mostly in vacuum, low pressure and room temperature).[3] However, using *in situ* transmission electron microscopy techniques allows to study dynamical processes live as they happen and at high spatial resolution.[4-7] In the present work, we studied Pt particles catalysing the growth of graphitic carbon structures using *in situ* TEM in a gas cell. Imaging (as shown in **Figure 1)** and fast Fourier transformation (FFT) analysis (**Figure 2**) were combined to detect and track the formation of Pt carbide. This was complemented with computational multivariant image analysis to detect how many layers deep the Pt carbide formed.

Using this approach we were able to gain experimental proof in the form of *in situ* electron microscopy FFTs and imaging, for the formation of Pt carbide in the growth process of carbon nanotubes (CNTs). Furthermore changes of the contours of particles during the growth were observed (see **Figure 1: t=0s to t=450s**). High index facets were found to produce more growth than the flat facets. Both, changing contours with high index facets producing the growth lead to the stop-and-start rhythm of the growth rather than a continuous process. It was found that the catalyst underwent morphological changes in the form of reshaping and structural changes in the form of Pt carbide formation.

Using *in situ* TEM techniques we were able to gain important insights into the mechanisms of the graphitic carbon growth processes. Understanding this process is crucial to prevent catalyst deactivation by prevention of coking and improve catalytic carbon growth processes.

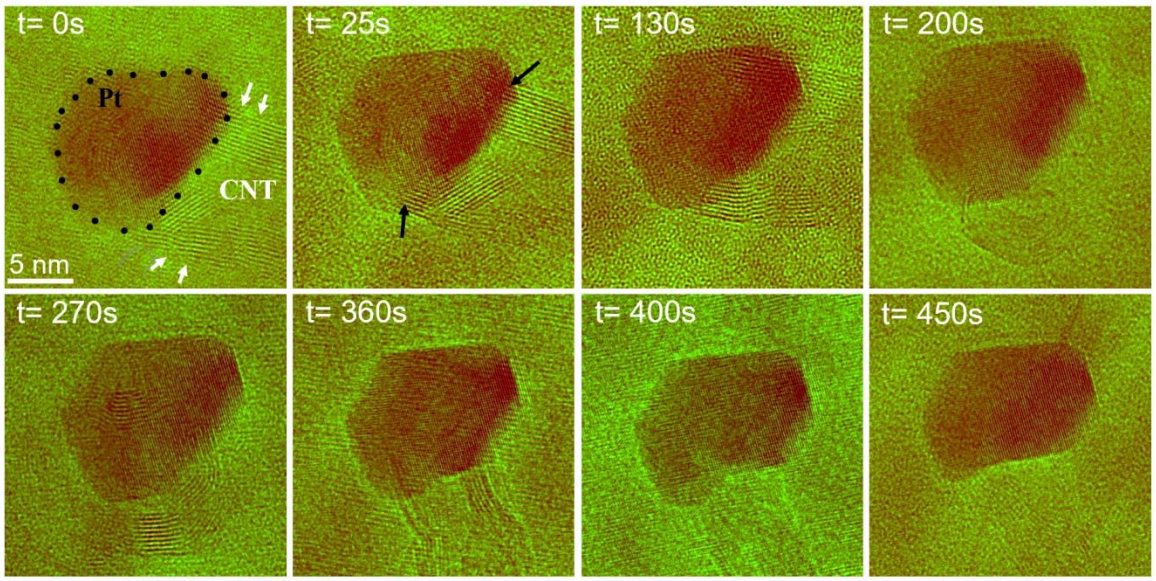

Figure 1. *In situ* investigation of carbon nanotube (CNT) growth in methane with Pt nanoparticles. *In situ* TEM imaging showed the formation of CNTs (white arrows) over time. Changes of the particle contours were also observed: see t=0s, t= 360s and t=450s.

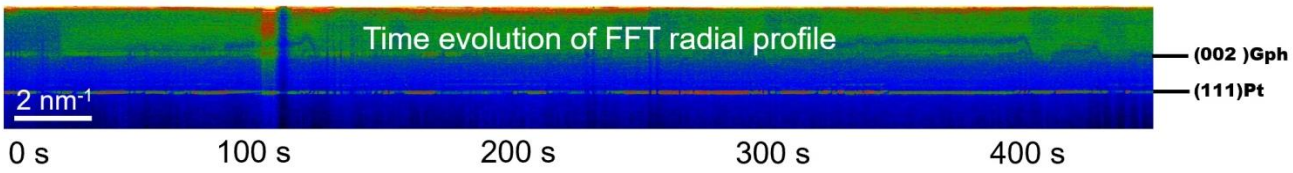

Figure 2. Time evolution of radial profiles of the fast Fourier transforms (FFT) of the images recorded *in situ* were used to track presence peaks specific to graphitic carbon, Pt and PtC formation.

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