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s Aires, F. J. Cadete Santo; Epicier, T.; Wagner, Jakob Birkedal; Hansen, Thomas Willum; Aouine, M.; Dunin-Borkowski, Rafal E.; Pedrero, M. González ; Tuel, A.

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Dynamic study of carbon nanotube growth and catalyst morphology evolution during acetylene decomposition on Co/SBA-15 in an environmental TEM

FJ Cadete Santos Aires[1], T Epicier[2], JB Wagner[3], TW Hansen[3], M Aouine[1], RE Dunin-Borkowski[3,4], M González Pedrero[1], A Tuel[1]

1. Institut de Recherches sur la Catalyse et l'Environnement de Lyon.
IRCELYON (UMR 5256 CNRS/Univ. Lyon I), 2 Avenue Albert Einstein, 69626 – Villeurbanne cedex, France.
2. Laboratoire Matériaux : Ingénierie et Science – MATEIS (UMR 5510 CNRS/INSA de Lyon).
Bât. B. Pascal, 7, Avenue Jean Capelle, 69621 – Villeurbanne cedex, France.
3. Center for Electron Nanoscopy – Cen. Technical University of Denmark (DTU).
Blds 307/314, 2800 – Kongens Lyngby, Denmark.
4. Ernst Ruska-Centre (ER-C) and Peter Grünberg Institute (PGI).
Research Centre Jülich, 52425 – Jülich, Germany.

francisco.aires@ircelyon.univ-lyon1.fr
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In situ studies of micro- and nano-objects in their characteristic environment have been performed ever since the early days of electron microscopy [1]. Over several decades the *in situ* observation of the synthesis of filamentous carbon (nanotubes/nanofilaments) during hydrocarbon decomposition has been one of the most popular topics [2] for investigation in the environmental transmission electron microscope (ETEM). In this work we study the growth of carbon nanotubes (CNTs) by the decomposition of acetylene on Co nanoparticles inserted into mesoporous silicas (SBA-15) using both conventional *post mortem* TEM measurements and real-time *in situ* ETEM observations.

In situ observation of the formation of the carbon nanotubes was performed in an FEI Titan 80-300 ETEM equipped with an objective lens spherical aberration corrector [3]. Prior to acetylene decomposition, the catalyst nanoparticles were reduced *in situ* in a flow of hydrogen (1 mbar, ~500°C). Electron energy-loss spectra taken before and during reduction showed that the Co oxide nanoparticles were reduced to metallic Co. *In situ* high resolution TEM images are consistent with cubic Co. A first attempt to study carbon nanotube growth above 600°C in 0.6 mbar of acetylene in situ in the ETEM resulted in complete growth of CNTs within seconds (or faster) which was not consistent with real-time growth observation with the electron microscope. The temperature was therefore decreased to ~ 500°C and acetylene pressure in the $10^{-3}/10^{-2}$ mbar range was used to decrease the growth rate to allow real-time observation of the formation of CNTs over several minutes. These conditions also reduced the coking of the nanoparticles and favoured the formation of tubular structures. Two types of CNTs following the tip-growth mechanism with apparently different growth rates were observed : (i) CNTs with diameters of 5 to 10 nm and rather uniform central channels (black arrows in Fig. 1a). These nanotubes grew primarily on small round shaped nanoparticles and (ii) CNTs containing voids and/or non-uniform central channels, with diameters of 15 to 20 nm (white arrows in Fig. 1a). These nanotubes grew on well-faceted nanoparticles that adopted "pyramidal shapes" during growth and were larger than the pores of SBA-15. Real-time morphological changes of the catalyst were observed during growth (Fig. 1b). As reported previously in the literature [2 (fourth and eighth references therein)] the Co nanoparticle pulsated (elongated and contracted) during the growth of the nanotube. This sequential elongation, often associated with the formation of a narrow neck, is clearly responsible for the presence of small nanoparticles within the nanotubes (Fig. 2).

Furthermore it was possible to observe severe degradation of the carbon nanotube structure during exposure to the energetic electron beam (Fig. 3) revealing that during real time in situ observation of chemical processes one has to take into account the role of the energetic electron beam or devise ways to minimize its contribution.

Ultimately these *in situ* real-time studies allow measurements of the growth rates that are expected to provide new insights on the catalyst dynamics during growth including the evolution of

exposed facets and (ideally) the identification of lattice planes and/or specific sites responsible for preferential carbon expulsion essential to understand the growth mechanisms of the different CNTs.

In an more general scope it is clear that ETEM studies of catalytic processes need real-time capability not only in the range of seconds (as it is available in contemporary microscopes) but in much lower timescales (milliseconds to nanoseconds or even bellow) and in the different modes available in the ETEM (high resolution BF and HAADF imaging, diffraction, EELS, tomography…). This can of course be implemented by using the dynamic TEM approach in an ETEM even though some technological difficulties (namely for tomography) have to be overcome at the present time.

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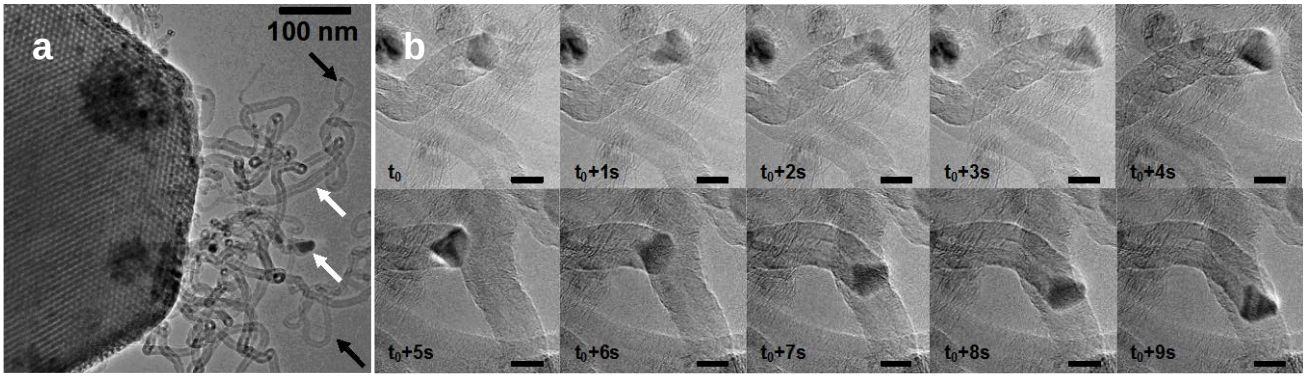

Figure 1. *(a) CNTs grown on Co/SBA-15 in the ETEM; (b) Sequence of bright-field TEM images showing the pulsation of a Co nanoparticle during carbon nanotube growth (scale bar: 10 nm).*

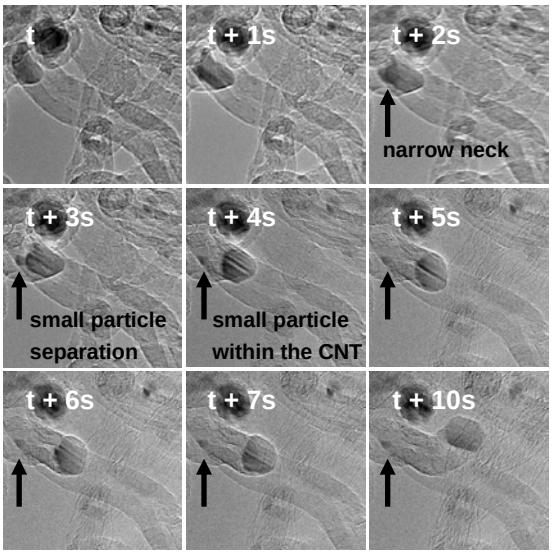

Figure 2. *Sequence of bright-field TEM images showing the formation of a nanoparticle within the CNT due to the pulsation of the catalyst during growth.*

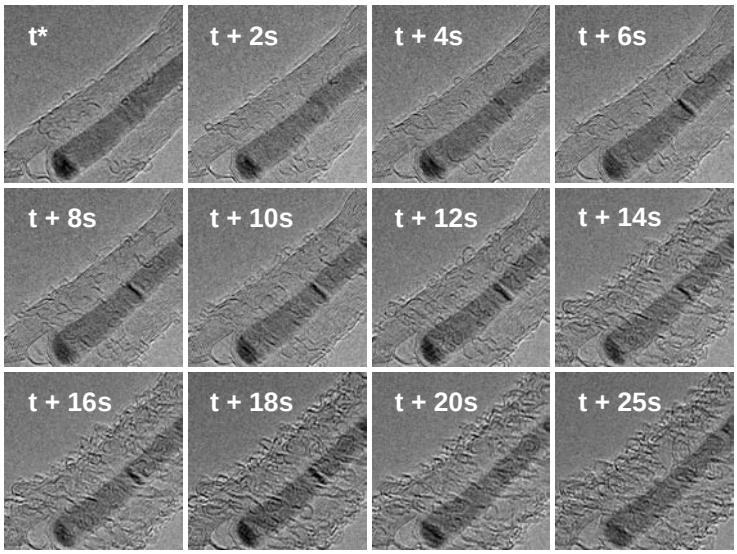

Figure 3. *Sequence of bright-field TEM images showing the degradation of the CNT structure during exposure to the electron beam.*the first micrograph was taken after several seconds (n.d.) of exposure to the electron beam.*