In situ dynamic observation of carbon nanotube growth on Co/SBA-15 by acetylene decomposition in an environmental TEM

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ABSTRACT

The formation of carbon nanotubes by acetylene decomposition on Co catalysts inserted in mesoporous silicas (SBA-15) has been studied in the transmission electron microscope (TEM). Two types of tubular carbon structures are observed: smaller nanotubes with internal diameters seemingly regulated by the size the Co nanoparticles formed within the SBA-15 pores and larger nanotubes. *In situ* observation of carbon nanotube growth in an environmental TEM allows both the dynamics of the formation of the nanotubes and the evolution of the morphology of the metal nanoparticles during growth to be followed under realistic conditions in order ton better understand the reaction mechanisms.

Keywords: Carbon nanotube growth, ETEM, Co/SBA-15, acetylene decomposition

1. INTRODUCTION

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[2-14] for investigation in the environmental transmission electron microscope (ETEM). Here we study the growth of carbon nanotubes 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.

2. RESULTS AND DISCUSSION

2.1 *Ex situ* study

Co/SBA-15 catalysts were prepared using several methods, including the so-called "two solvent" method, in which Co particles are preformed before catalytic reaction and located almost exclusively inside the mesopores[15]. TEM examination of the as-synthesised catalyst revealed the presence of internal Co oxide particles of similar size to the mesopore dimension, *i.e.* ~ 6 nm (Fig. 1a). After reduction of Co oxide nanoparticles in a hydrogen flow, the decomposition of acetylene takes place at 700°C, in the presence of hydrogen, to produce filaments (Fig. 1b) that are essentially multi-walled nanotubes (MWNTs). The total amount of carbon formed on the catalyst (6 wt.%) was found to be significantly lower than that produced over a catalyst prepared using a conventional impregnation method (11.9 wt.%), for which insertion of the Co nanoparticles into the mesopores of SBA-15 was less efficient[16]. This difference suggests that carbon nanotube formation takes place when particles are located or arrive at the pore mouths. The TEM images suggest that the internal diameter of the MWNTs is regulated by the Co nanoparticles formed within the pores.

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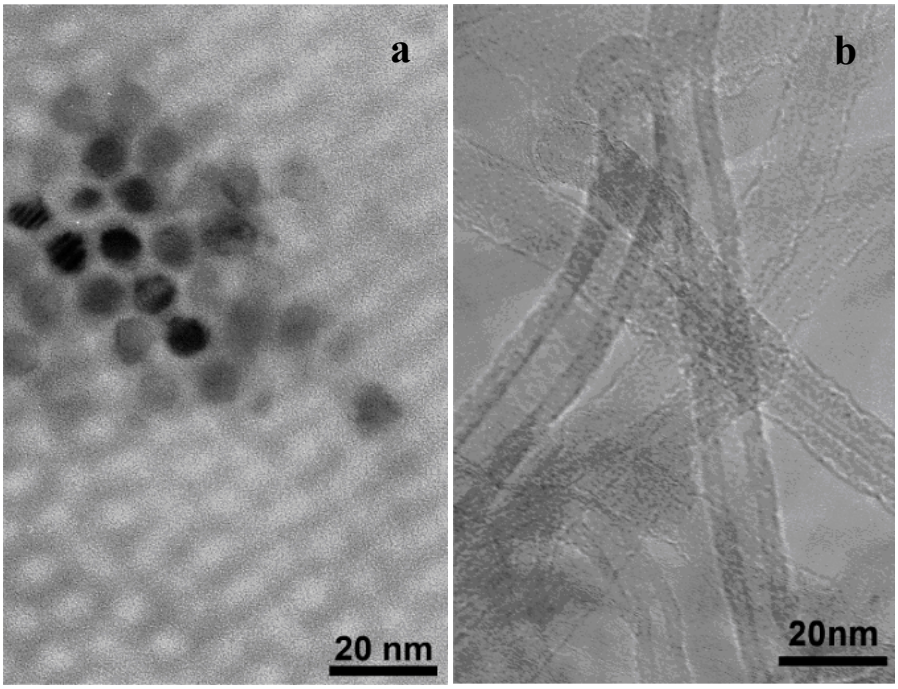

Figure 1. TEM images of (a) Co oxide nanoparticles in the mesopores of SBA-15 obtained by the "two solvent" method and (b) MWNTs obtained by the decomposition of acetylene at 700°C over the reduced catalyst.

2.2 *In situ* study in an environmental TEM

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[17]. 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 were consistent with cubic Co (Fig. 2).

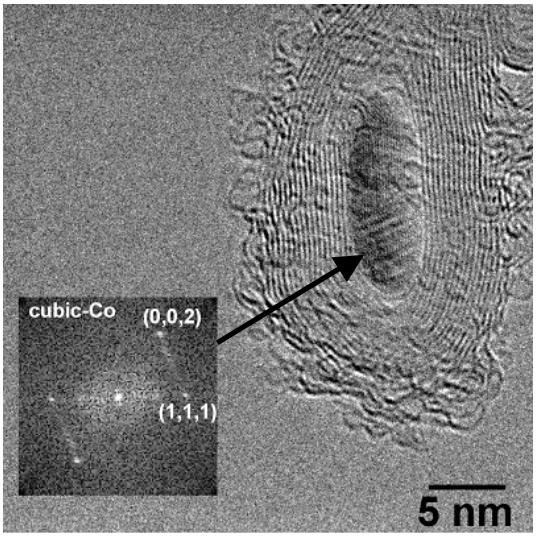

Figure 2. HRTEM image of a Co nanoparticle acquired *in situ* in an ETEM during acetylene decomposition that lead to the encapsulation of the nanoparticle by several graphitic layers. The 2D-FFT, consistent with the structure of cubic Co, is shown as an insert.

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 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 an 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 carbon nanotubes over several minutes. These conditions also reduced the coking of the nanoparticles and favoured the formation of tubular structures. Just as for the *ex situ* studies, growth occurred essentially on regions where the nanoparticles were near the pore mouths. Since the method used for synthesis yielded primarily nanoparticles that were well-inserted into the SBA-15 mesopores, growth occurred only at a few locations (Fig. 3a). Two types of carbon nanotubes following the tip-growth mechanism[18] with apparently different growth rates were observed (Fig. 3b). These were:

(i) MWNTs with diameters of 5 to 10 nm and rather uniform central channels (black arrows in Fig. 3b). These nanotubes grew primarily on small rounded nanoparticles, most of which were probably positioned at the pore mouths.

(ii) MWNTs containing voids and/or non-uniform central channels, with diameters of 15 to 20 nm (white arrows in Fig. 3b). These nanotubes grew on well-faceted nanoparticles that adopted "pyramidal shapes" during growth and were larger than the pores of SBA-15. These particles had formed on the surface of the mesoporous solid, either during impregnation or during reduction by the sintering of smaller particles.

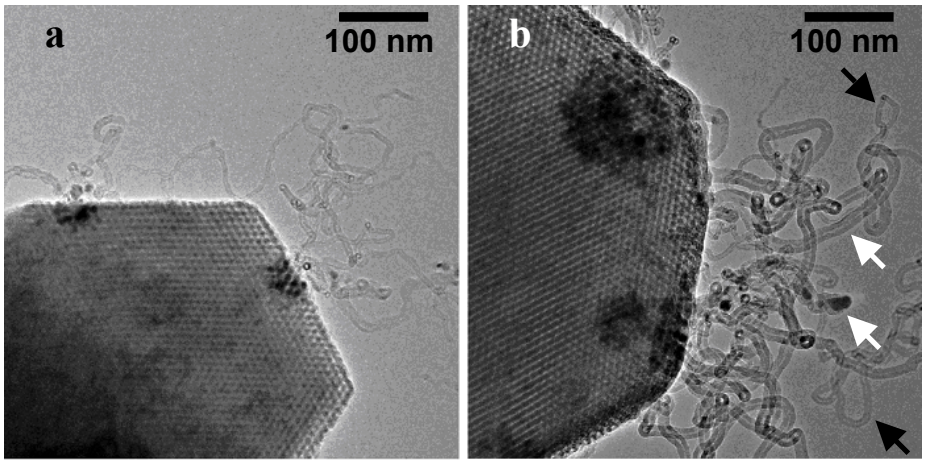

Figure 3. Bright-field images acquired *in situ* in an environmental TEM showing (a) that the carbon nanotube growth occurs primarily where nanoparticles are near the surface of the 15; (b) two types of carbon nanotubes indicated by black and white arrows (see text for further information).

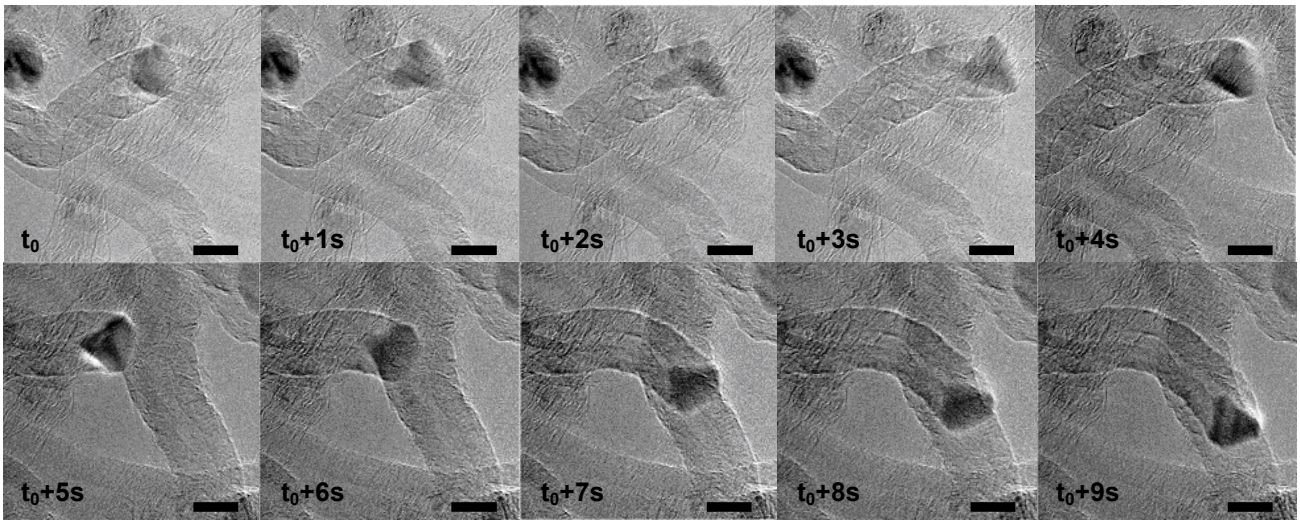

Figure 4. Sequence of bright-field TEM images showing the pulsing (elongation-contraction) of a faceted Co nanoparticle during MWNT growth. (Scale bar: 10 nm).

For the latter type of carbon nanotubes, real-time morphological changes of the catalyst were observed during growth (Fig. 4). As reported previously in the literature[8,14], the Co nanoparticle pulsated (elongated and contracted) during growth of the nanotube. This sequential elongation, which is often associated with the formation of a narrow neck, is thought to be responsible for the presence of small nanoparticles found within the nanotubes after growth.

3. CONCLUSION

In situ observations of the growth of carbon nanotubes by acetelyne decomposition on Co/SBA-15 were performed in an environmental TEM. Two different types of carbon nanotubes with different apparent growth rates and real-time dynamic changes of catalyst morphology during nanotube growth were observed. Measurements of the growth rates of the two different types of carbon nanotubes are expected to provide new insight on the catalyst dynamics during growth including the evolution of exposed facets and the identification of lattice planes and/or specific sites responsible for preferential carbon expulsion essential to understand the growth mechanisms of the different carbon nanotubes.

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