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In situ TEM Observation of MultiLayer Graphene Formation from CO on Cobalt Nanoparticles at Atmospheric Pressure

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Current demand for clean, renewable fuels has instigated interest in the well-known catalytic Fischer-Tropsch (FT) reaction, which produces hydrocarbons from synthesis gas (syngas, CO and H_2). One of the catalysts frequently used for this reaction is cobalt, often in the form of supported nanoparticles. Both in academia as well as in industry, efforts are being undertaken to investigate this catalytic system, in order to understand the fundamental processes involved and rationally design improved catalysts.

One of the side reactions in the FT process is the Boudouard reaction [1]:

$$2\,CO_{ads} \rightarrow CO_{2\,g} + C_s$$

This reaction leads to the deposition of carbon on the catalyst and may cause catalyst deactivation.

Using a MEMS-nanoreactor in combination with a specially designed *in situ* Transmission Electron Microscope (TEM) holder and gas supply system [2,3], we imaged the Boudouard reaction as it was taking place on a cobalt nanoparticle supported on one of the SiN windows of the nanoreactor [3]. The TEM used for the *in situ* experiments was a C_s-corrected FEI Titan^3 80-300 operated at 300 kV. Images were captured using a Digital Electronic camera (DE-12) with 6.0 μm pixel size and 4096 x 3072 pixels. To minimize beam effects on the sample, the electron intensity was kept below 500 electrons/Å^{2}s during the *in situ* experiments. An exposure time of 1 s was used for image acquisition.

Figure 1 shows a series images recorded over time during the Boudouard reaction, visualizing multiple stacked layers of graphene-like carbon being created. Fig 1a shows a fresh metallic cobalt nanoparticle. Figures 1b and 1c show that multiple layers of graphene-like carbon have been formed on the surface of the nanoparticle. The formation of consecutive carbon layers over time will be shown in detail. Due to the stress induced in the cobalt nanoparticles by the carbon layers present on their surface, their restructuring is observed (fig 1c). This will also be discussed in detail [4].

References:

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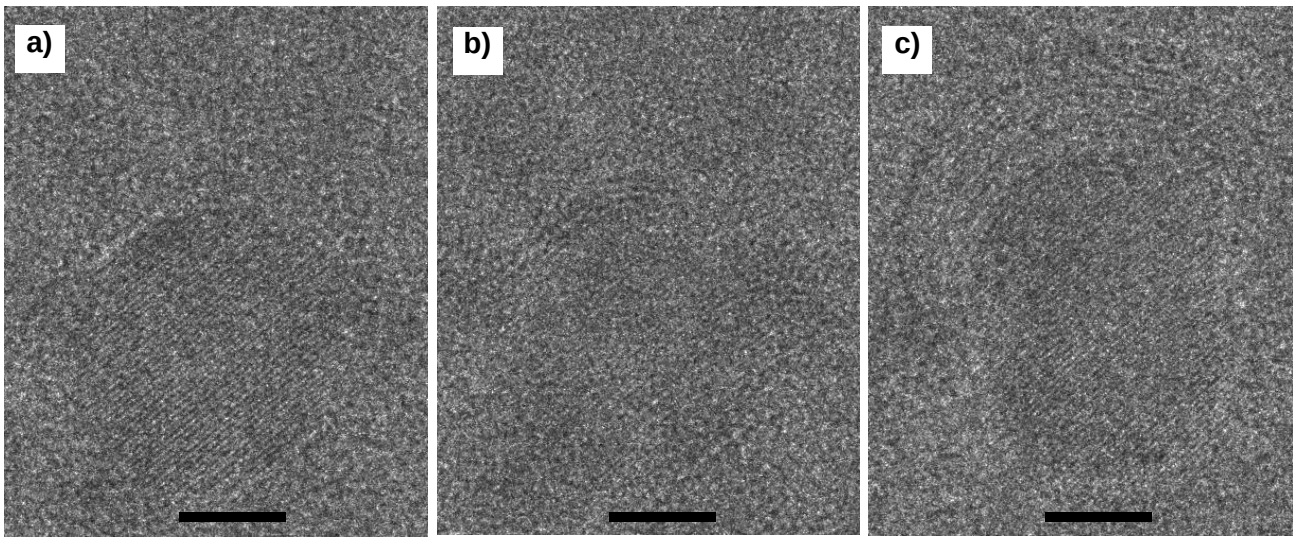

Figure 1. a) A single metallic cobalt nanoparticle, supported on an amorphous SiN window, at 1 bar CO/N_2 1:1 and 500 °C. b) The initial formation of graphene layers, followed by c) the encapsulation of the particle on one side by multiple layers of graphene. The deformation of the nanoparticle due to the stress induced by the carbon layers is also visible in this image. The scale bar is 4.0 nm.