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Stabilities of Pd nanoparticles supported on carbon nanotubes studied by TEM

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Supported metal nanoparticles are one of the widely used catalysts in many chemical processes. Apart from metal oxides, carbon nanotubes (CNTs) have been found to be a useful support in heterogeneous catalysis. CNTs have the proper pore size, moderate high specific surface area and good mechanical and chemical stability, high thermal and electrical conductivity. However, CNTs are hydrophobic and inert in nature, and they must be functionalized to anchor metal nanoparticles. The interaction between the metal nanoparticles and CNTs becomes thus important since it determines not only the charge transfer between them, but also the stability of the metal nanoparticles at high temperature [1]. In this work, we study the stability of Pd nanoparticles on oxygen- and nitrogen-functionalized CNTs (oCNT and nCNTs) using in-situ electron microscopy and spectroscopy techniques.

Concentrated nitric acid (70%) was used to get oxygen-functionalized CNTs. Nitrogen-functionalization was carried out at 600°C by introducing NH_3 into a furnace containing oCNTs for 2 hours. Pd/oCNTs and Pd/nCNTs were prepared using palladium nitrate in diluted distilled water. The as-prepared oCNTs, nCNTs, fresh Pd/oCNTs, Pd/nCNTs are placed on TEM grids using an ethanol solution containing the samples. A FEI Tecnai G2 F20 and a Philips CM200 FEG TEM operating at 200 kV were used to conduct structural investigation. A Gatan single tilt-heating holder was used for in-situ heating experiment between 330 °Cto 600 °C. The surface properties of the samples were studied by using an ESCALAB 250 set-up with Al *K*α radiation.

XPS analysis revealed that oCNTs contain as much as 14% oxygen, and nCNTs as much as 4% nitrogen, both in form of functional groups. The as prepared Pd nanoparticles on oCNTs and nCNTs have similar size of about 1.6 nm in average. Figure 1 shows the ripening process of Pd nanoparticles on nCNTs together with the histograms of particle size distribution (PDS) at room temperature and upon heating at 330°C, and 600 °C, respectively. The image and PDS clearly show the evidence that the size of Pd nanoparticles increased significantly with increasing temperature. The distribution of Pd is uniform at room temperature and 300 °C, whereas Pd particles grow up and the distribution is no more uniform at 600 °C. This change is more clearly evidenced in STEM image of Figure 1d. The mean particle size of Pd on nCNTs heated at 600 °C is estimated to be about 6.5 nm. The similar ripening process of Pd nanoparticles is also observed on oCNTs, but the mean particles size of Pd on oCNTs when heated at 600 °C is estimated to be 3 nm. This indicates a more strong interaction between Pd and oCNTs than that between Pd and nCNTs. This difference is assigned to the different role of oxygen-functional groups and nitrogen-functional groups as the anchoring sites for the Pd nanoparticles [2].

In summary, we found that the stability of Pd nanoparticles supported on CNTs depends strongly on the surface properties of CNTs. Functionalization of CNTs with oxygen- and nitrogen-functional groups allows an uniform loading of Pd particles. However, carbon oxygen single-bonds on the CNTs surface have a stronger interaction with Pd nanoparticles than that of nitrogen-containing functional groups. The Pd nanoparticles supported on oxygen-functionalized CNTs are more stable than when they are supported on nitrogen-functionalized CNTs. Our works shows that TEM with in-situ technique is an useful tool for the study of the metal support interactions in catalysis.

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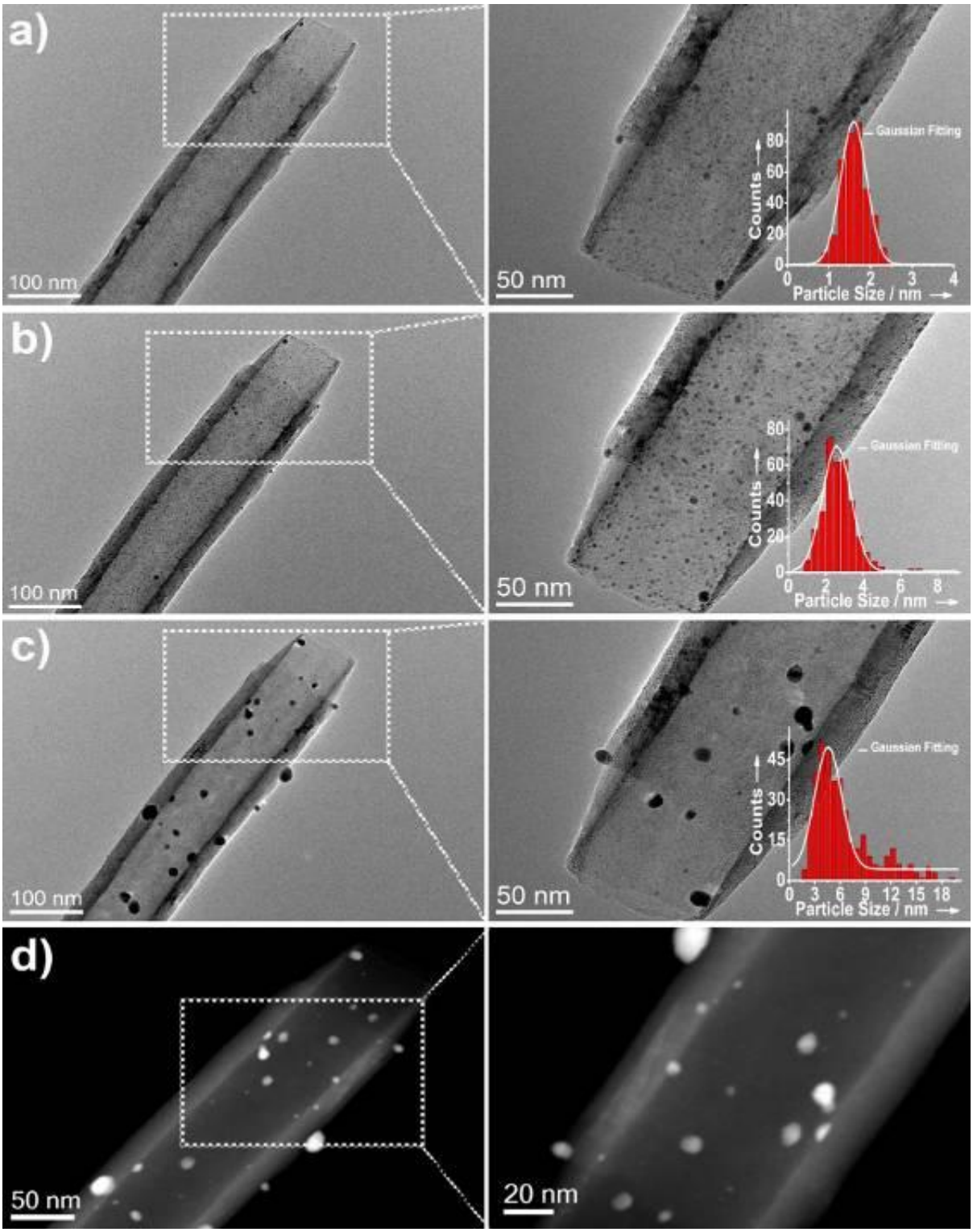

Figure 1. TEM images of Pd supported on N doped OCNT that was heated at 22 °C (a), 330 °C (b) and 600 °C (c) by heating holder in TEM, and STEM images of Pd@N-OCNT sample after heating (d). The right part is a local enlargement of the highlighted areas in the left counterpart for each illustration. The insets are the corresponding histograms of PSD.