Catalyst nanomaterials studied by in situ heating and identical location transmission electron microscopy

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Research on catalyst nanomaterials is of high importance for chemical engineering processes, especially for finding novel approaches in the generation and implementation of renewable energy sources, since current sources of energies like fossil fuels are limited, but more critical because of the environmental harming problems they cause to earth [1]. It is therefore of great interest among the developing sustainable energies like solar and wind energies, the hydrogen based energies, where the energy conversion electrocatalyst used in fuel cells and electrolyzers still need to be optimized to fulfill the requirements and demands of the daily modern life. In the present work, we explore the application of two transmission electron microscopy (TEM) techniques to study catalyst nanomaterials [2, 3]. Firstly by employing in situ annealing STEM and observing the formation process of such catalyst we provide insight and feedback into the annealing part of the synthesis. One of the studies was performed on electrocatalyst nanoparticles PtCu3 supported on high surface area carbons (HSAC). The composite is obtained from a partial galvanic displacement of copper on carbon support with a platinum precursor salt, and subsequent annealed in order to obtain PtCu3 nanoparticles. Another study is presented where electrospun polyacrylonitrile (PAN) polymer nanofibers with Pt precursor is first stabilized at 250 °C in air and then carbonized at 750 °C and 1100 °C in a vacuum. By using in situ annealing STEM is possible to observe how the formation of 5 nm Pt particles occur at the surface of the carbon fibers. In the second part, we performed identical location STEM to study ex situ how catalysts evolve after being activated or electrochemically cycled. This technique allows to track the same location of the catalyst being investigated after different electrochemical stages, hence giving fruitful information on the changes in morphology and composition occurring on the same region during the cycling periods. This aims to provide a better understanding on the catalytic activity and stability of the catalyst. Our main study will be presented on 20-30 nm PtCu3 nanoparticles observed before and after being submitted to an activation protocol. Several distinct phenomenon were identified and analyzed: nanoparticle shrinking, faceting, facet dependent dealloying, porosity formation, and surface platinum-skin-layer effect. Of special interest is the observation of preferential facet etching favouring dealloying of facets in the following order {110}, {100} and then {111}. Since the catalytic properties of metal nanoparticles depend on size, crystal structure and shape, importantly on exposed surfaces, this approach addresses a direct view of how the material can be improved to obtain an affordable, active and stable catalyst.

References

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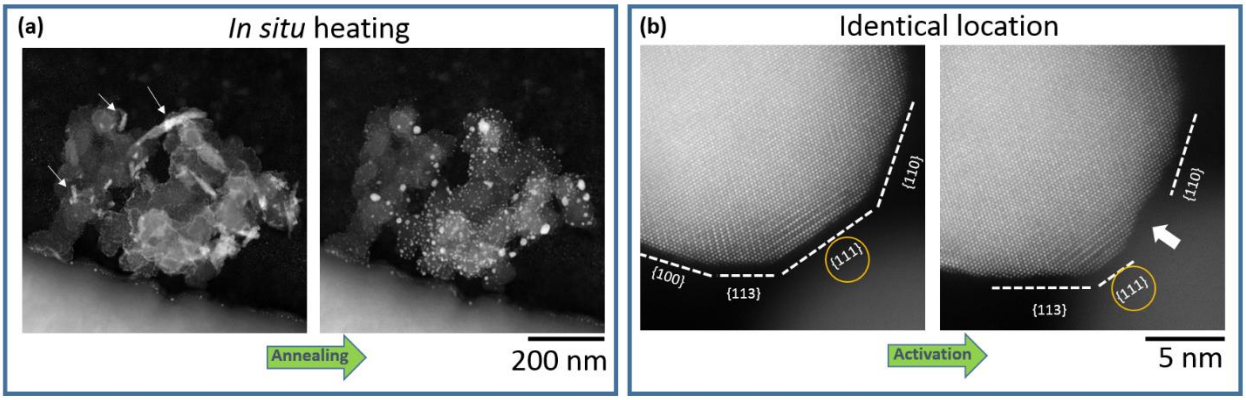

Fig.1. (a) Formation of $PtCu_3$ nanoparticles during the *in situ* heating STEM experiment. Left, CuPt nanoparticles at room temperature with Cu needles (marked with arrows). In the right, CuPt nanoparticles after the annealing process at 500 °C and further 800 °C. (b) Neighboring facets of {111} get preferentially dealloyed, observed by identical location STEM after the activation protocol.