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In situ study of highly active PtNi octahedral ORR electrocatalysts at the atomic scale

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PtNi octahedral nanoparticles (NPs) represent an evolving class of electrocatalysts, which are expected to show improved oxygen reduction reaction (ORR) activities. A full understanding of such reactions requires a knowledge of the structural and chemical evolution of the NPs. In situ techniques are increasingly important for closing this gap in material characterization. In particular, in situ transmission electron microscopy (TEM) can now be performed using specimen holders that are based on micro-electro-mechanical systems (MEMS) technology and allow catalysts to be analysed under controlled conditions. Previous studies have shown that PtM (M = transition metal) NPs demonstrate enhanced catalytic performance after thermal annealing. This improvement is thought to result from the creation of specific surface atomic configurations.[1],[2] For shaped NPs, high temperature thermal annealing can result in undesired morphological shapes, as reported in previous TEM studies on the thermal annealing of shaped Pt nanoparticles..[3] A recent study by Pan et al.[4] reported changes in Ni content at the surfaces of octahedral NPs during heating, while Gan et al.[5] showed that octahedral PtNi NPs largely maintain their octahedral shapes during annealing up to 500 °C. Here, we use a MEMS-based *in situ* specimen holders to observe structural and compositional changes of active PtNi octahedral catalysts under controlled reducing and oxidizing conditions using high-resolution TEM, high-angle annular dark field scanning TEM (HAADF-STEM) and energy dispersive x-ray spectroscopy (EDX). We follow the dynamic evolution of NP morphology, faceting and elemental segregation under working conditions. We successfully follow changes to the octahedral catalysts from segregated structures (Fig. 1a) to alloy configurations and finally shapeless structures (Fig. 1b) at different temperatures under reducing and oxidizing conditions.

References:

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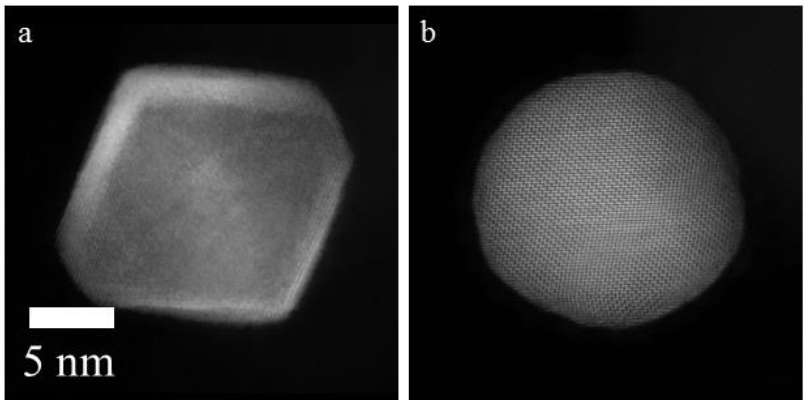

Figure 1. HAADF-STEM images of (a) an octahedral PtNi NP with a segregated structure under reducing conditions at 300 °C; (b) the same NP shapeless after examination at 600 °C under reducing conditions.