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In Situ Environmental Observation of Oxidative Corrosion of Co and Co-Pt Nanocatalysts

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Based on the Kirkendall effect, oxidative corrosion of monometallic and alloy nanoparticles have been used for the creation of hollow and dealloyed nanostructures [1, 2]. This method has been popularized in nanocatalyst synthesis; however spatial-resolved reaction dynamics of the corrosive/oxidative processes, especially in bimetallic systems, remain elusive. Here, we use the state-of-the-art environmental transmission electron microscopy (ETEM) and a custom designed gas flow holder to visualize the oxidative corrosion of Co and Co-Pt nanoparticles *in situ*. Our results allow us correlate the dynamic reaction pathway with the nanoparticles' internal degrees of freedom—size, composition, and initial surface structure. Such *in situ* information uncovers the detailed reaction pathway of the Kirkendall effect for Co and Co-Pt catalysts in particular, and more broadly yields insights into porosity control in the general class of mono-/bi-metallic nanoparticles.

Fig. 1 shows the *in situ* heating experiments of cobalt nanocatalyts in an oxygen environment. Fig. 1a demonstrates *in situ* dynamics of the Kirkendal effect. During heating, metallic cobalt cores in the oxide pockets shrunk anisotropically, one with a unidirectional retraction front (Fig. 1a (upper)) and one with a sweeping retraction front (Fig. 1a (lower)). The formation of voids in an anisotropic fashion is likely due to due to the unsymmetrically distributed diffusion bridges. Fig. 1b shows another oxidation trajectory. In contrast to Fig. 1a, these particles were reduced in hydrogen to be free of surface oxide prior to oxidation. In this case, initial oxidation occurred preferentially on one side of the particle rather than forming a uniform oxidation layer. At the end of the reaction, the particles did not form a round hollow structure. This demonstrates that spatial dependent oxidation pathway of metallic cobalt nanoparticles can be highly dependent on their initial surface structure and oxygen partial pressure, and it does not necessarily always follow the Kirkendall model.

Fig. 2 shows the *in situ* oxidation of three different types of Co-Pt catalysts with selected compositions and sizes. Fig. 2a and Fig. 2b compares the Co:Pt=1:1 catalysts with the catalysts that has a dilute concentration of Pt (Co:Pt=1-δ:δ) (the relatively low intensity areas of the particles). The difference is dramatic: the 1:1 case (Fig. 1a), cobalt segregated out of the Pt-rich core during oxidation. The dark-contrast spots in the particle were Kirkendall voids due to the leaching of cobalt. However, in the case of Co:Pt=1-δ:δ (Fig. 1b), a highly porous skeletal structure of Pt was formed. On the other hand, when the particles were small enough (2-4 nm) as shown in Fig. 2c and 2d, the mass transport is in these particles is not limited by bulk diffusion but surface diffusion. In this regime, the particles are highly dynamic and therefore it is difficult to nucleate voids under heating conditions. As shown in the in situ and ex situ images of these 2-4 nm catalysts, no Kirkendall voids were formed inside. [3]

References

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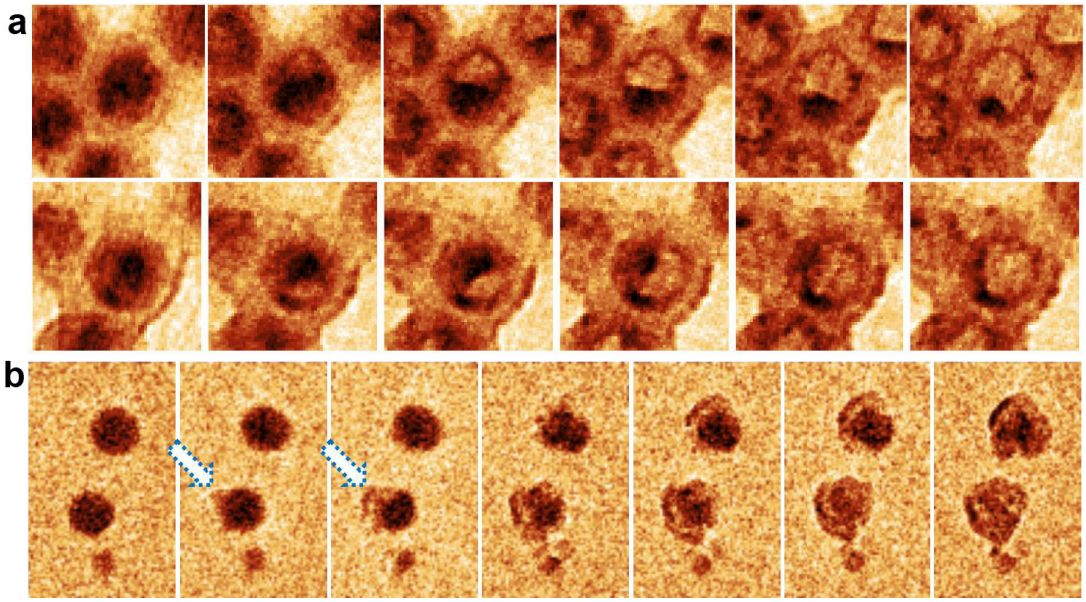

Fig. 1. In situ heating of cobalt nanocatalyts in an oxygen environment. (a) Oxidation of cobalt catalyst with their passivation surface oxide (p_{ox}~1 bar). (b) Oxidation of cobalt catalysts that have been reduced to remove surface oxide (p_{ox}~0.1 mbar).

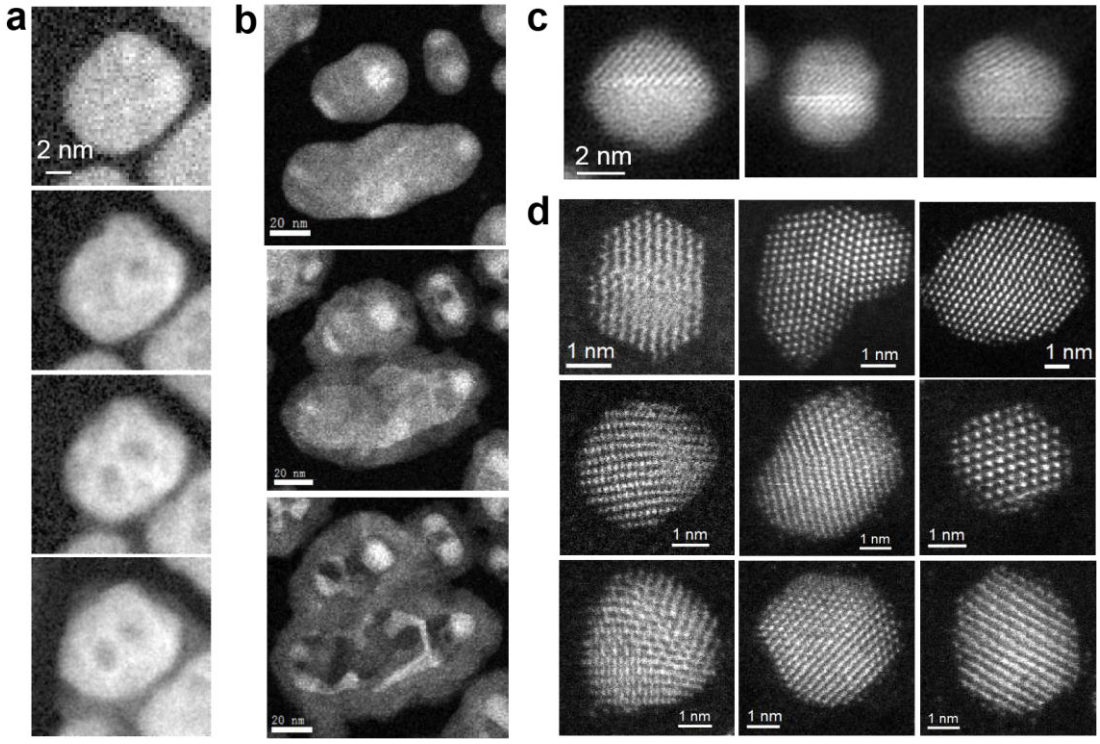

Fig. 2. Oxidation of Co-Pt nanoparticles. (a) In situ oxidation trajectory of 10 nm $Co_{0.5}Pt_{0.5}$ nanocatalyts. (b) In situ oxidation of $Co_{1-\delta}Pt_{\delta}$ nanocatalyts (the low intensity areas of the particles). (c) In situ and (d) ex situ ADF-STEM image of oxidized 2-4 nm $Co_{0.5}Pt_{0.5}$ particles.

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