

Size and Composition Dynamics of bimetallic nanoparticle electrocatalysts probed using in-situ Small Angle X-ray Scattering (SAXS)

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Introduction

Surface Science approaches in catalysis on single crystal alloy surfaces have resulted in a tremendous amount of insight into how structure and surface composition affects catalytic surface reactivity. As monometallic or bimetallic model systems, single crystal surfaces have provided much understanding of structure-property relationships and reaction mechanisms of metal and metal alloy particle catalysts. To a large extent during mechanistic single crystal studies, especially at gas-solid interfaces, the catalytic surface was assumed to be stable in time with respect to surface composition or surface structure. Irreversible changes to the catalytic surface were intentionally kept to a minimum.

However, on solid-liquid (electrocatalytic) interfaces, in particular on bimetallic nanoparticles, surface composition and surface structure (and size) are often strongly dependent on the detailed reaction conditions, e.g. electrode potential or electrolyte. Irreversible changes in composition are the rule rather than the exception due to surface metal dissolution¹. In addition bimetallic electrocatalytic nanoparticles typically experience coarsening (Ostwald growth) and coalescence resulting in a change in their particle size distribution during the course of the reaction. Both effect can also be coupled, as severe surface metal dissolution (compositional change) may affect the particle size distribution as well.

The ability to characterize particle size and particle composition distributions in real time is therefore critical for an *understanding and prediction of the stability behavior* of alloy nanoparticle catalyst ensembles. To date, the study of changes in size and composition of nanoparticle catalysts has been largely relying on ex-situ Transmission Electron Microscopy (TEM) and related compositional studies such as Energy Dispersive X-ray Analysis (EDX). Statistically more relevant scattering techniques which allow in situ modes are therefore desirable.

Materials and Methods

To better understand structural dynamics of alloy nanoparticles, we have been proposing synchrotron-based Small Angle X-ray scattering (SAXS)^{2, 3}. SAXS is a reciprocal-space method that is suited for the in-situ investigation of particles in the 1-100 nm diameter range with a time resolution on the minute scale. The information obtained from SAXS is generated

over a large sampling volume; hence, the number of particles probed is very large, and in contrast to TEM an excellent statistical representation of the ensemble is attained.

Our group has reported bimetallic Pt-Cu nanoparticle electrocatalyst systems where selective dissolution of Cu surface atoms was deliberately introduced (dealloying) to activate the nanoparticles for electrocatalysis, for instance for the Oxygen Reduction Reaction (ORR)⁴. During this treatment the nanoparticles underwent a severe change in composition. We hypothesized that a severe change in particle size accompanies the change in composition.

Results and Discussion

To check our hypothesis we have combined synchrotron in-situ SAXS with in-situ XRD techniques in order to follow the selective dissolution of Cu surface atoms (initial activation through Cu dealloying) of our bimetallic alloy nanoparticles. Using three electrode arrangements in spectroelectrochemical flow cells, we monitor the atomic scale structural parameters such as particle size (SAXS), and the unit cell parameter (XRD) and its corresponding alloy composition of the catalytic particle as function of time, voltage, and electrode potential.

Pure Pt nanoparticles with mean diameters of 2-3 nm showed rapid particle growth over the first 120 minutes, while heat treated Pt particles (5-7 nm) were very resistance to growth and coarsening under the chosen conditions. Alloy particles decreased their mean size due to metal dissolution and then increased their size due to coarsening of the dealloyed particles. Generally, holding the electrode potential constant had less severe effects on particle size than continuous potential sweeps.

We were able to obtain detailed kinetic information on the dealloying processes, which serves as input to theoretical descriptions⁵ of metal dissolution/corrosion in order to extract kinetic parameters or establish predictive models.

Significance

Structural and Compositional stability of individual nanoparticles severely impact the stability/durability characteristics of real supported catalysts. For the first time, we present an synchrotron based in situ study of the particle size and particle composition dynamics of a bimetallic electrocatalysts under reaction conditions. Our study highlights the complex nature of bimetallic nanoparticle electrocatalysts under a variety of potential control protocols.

References

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