ESRF Experimental Report

CH 6450: Investigation of the formation of supported High Entropy Alloy nanoparticles prepared by incipient wetness impregnation

1. Abstract

High entropy alloy nanoparticles (HEA-NP) recently have seen a rise in interest due to their prospect as catalyst materials. Characterization of the synthesized particles is challenging, and the mechanisms of their formation are not yet fully explored. In this work, we investigate the formation of supported HEA-NPs via an incipient wetness impregnation approach. Combining *in situ* XRD and XANES experiments, we follow the reduction of the precursor salts and the subsequent emergence of single-phase HEA-NPs. We uncover both the different reduction behaviors of the individual elements and phase transformations as a function of synthesis temperature.

2. Experiment details

Before arriving at ESRF, the carbon supports (Ketjen black EC300-J) were impregnated and dried at the University of Berne. To that end, aqueous precursor solutions containing chloride salts of the desired elements (IrPdPtRhRu or PtFeCoNiPd) were prepared. The amounts of precursor were determined based on the target catalyst loadings while the solvent volume was calculated based on the pore volume of the deployed precursor. The solutions were then used to impregnate the carbon support which was subsequently dried in an evacuated oven. At ESRF, the impregnated, dried samples were transferred to quartz capillaries. The capillaries were open-ended to provide a reducing atmosphere in the form of a constant flow of H_2 during synthesis. A blow furnace setup provided by BM31 was used to control the synthesis temperature. The temperature program for the measurements consisted of a ramp of 100 °C/h from room temperature to 400° C, followed by a fast ramp of 400 °C/h to 750 °C. Then, the sample was cooled down to 50 °C. During the 100 °C/h ramp XANES and XRD were measured. For the rest of the program, only XRD was recorded. XANES served to track the oxdiation state of the individual metals while XRD was used to gain insight into the evolving crystalline phase.

3. Results

The multimetallic samples with different concentrations could be measured. An example of the time-resolved XRD data recorded during the beamtime is shown in Figure 1 comparing selected XRD datasets of (a) PtFeCoNiPd and (b) IrPdPtRhRu, both with 60% loading.
It is observed that an initial fcc (Fm-3m) phase is formed in the synthesis of PtFeCoNiPd, eventually transitioning to the tetragonal P4/mmm phase at higher temperatures. Further, with increasing temperatures, the unit cell contracts, observed in the shift of the Bragg reflections to higher theta. Our hypothesis is that this is due to the different temperatures at which the precursors are reduced. Figure 2 (a) shows that the larger and noble metals Pt and Pd are reduced first. Whereas, the smaller, less noble metals are reduced later. This could mean that nanoparticles form with larger amounts of Pt and Pd first and the smaller metals are introduced later. The single-phase formation observed in the XRD combined with the XANES analysis in Figure 2 (a) indicates that we were able to form an alloy containing all the five elements.

Likewise, a single fcc phase is formed initially in the synthesis of IrPdPtRhRu. However, the single fcc phase appears to remain throughout the experiment. Without refining the data, one cannot say much more about the formation of the nanoparticle except that the crystallite size grows as expected. This is shown via the peak shape that grows narrower. From the XANES data in Figure 2 (b), the reduction sequence can be compared. Here, it is observed for IrPtRuRHPd that Rh, Ru and Pt reduction appears already at the beginning of the experiment and happens simultaneously. Ir and Pd reduction follows, where Pd appears to reduce slower. As observed for PtFeCoNiPd, the single-phase formation and the reduction of all five metals indicates the formation of an alloy containing all five elements.

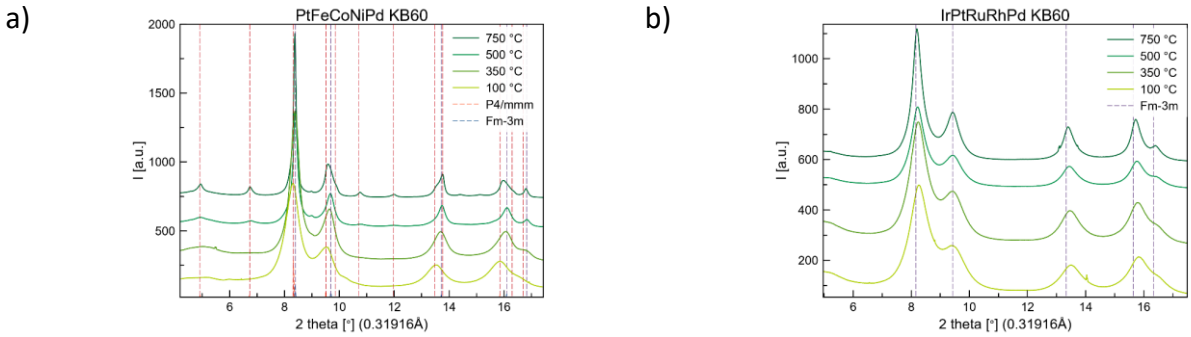

Figure 1. Overview of the selected in situ XRD dataset recorded during the synthesis of (a) PtFeCoNiPd, here for comparison with an Fm-3m phase from the binary alloy PtFe and the tetragonal P4/mmm of also a PtFe alloy. (b) IrPtRuRhPd NPs with the Fm-3m phase of Pd.

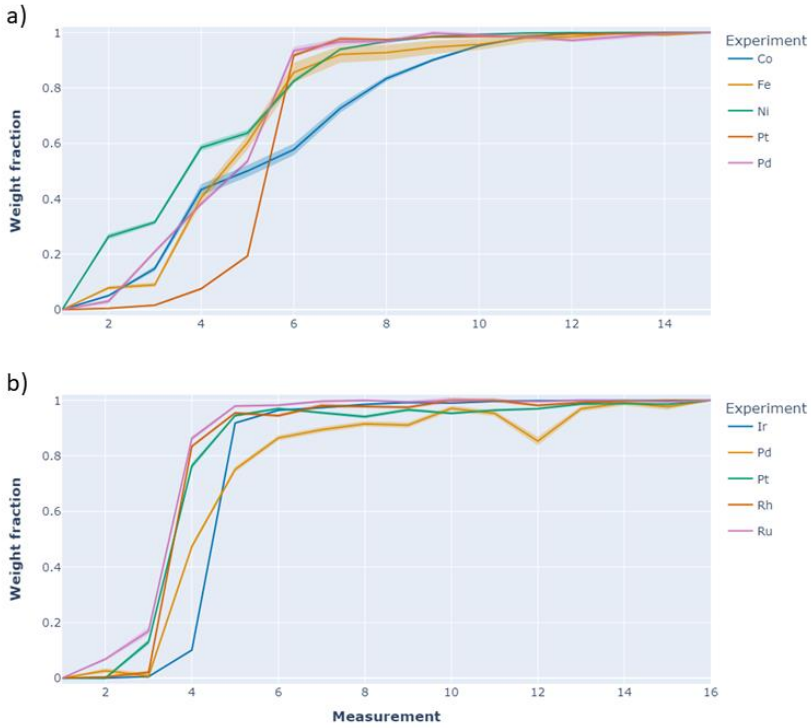

Figure 2. Analysis of the reduction of metal ion species in the formation of (a) PtFeCoNiPd and (b) IrPdPtRhRu NPs extracted from the XANES data.

4. Conclusions and future work

Overall, the beamtime was successful. Currently, we are in the process of refining the XRD data and analyzing the XANES data. In order to completely understand the formation of these HEA with this synthesis approach, the results of this analysis will be combined with electron microscopic measurements, EDS analysis, ICP-MS analysis as well as theoretical calculations.

5. Publications resulting from this work

Once the analysis is complete and we achieved a proper understanding, we are planning to publish the results in a joint paper with the ESRF staff.