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Atomistic Reaction Kinetics and Chemistry Revealed using In Situ STEM

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The process of learning the kinetic pathways in chemical reactions can be complex and expensive because probing the beginning and ending compound products do not reveal the intermediate species and stages, which are critical to depict the entire reaction processes. In situ techniques can monitor the materials dynamical behavior in response to the environmental conditions and stimuli in a confined space, producing a time-resolved understanding, in turn offering insights on the control over the resulting end products and their morphology. With its high spatial resolution and capability to perform spectroscopic analysis, scanning transmission electron microscopy (STEM) has been applied to the study of dynamic processes for a diverse range of materials. However, revealing reaction mechanisms in chemistry at the atomic scale remains challenging. Here we show in situ imaging of the reaction pathways of two materials systems using aberration corrected STEM, demonstrating the capture of entire chemical processes in real space in real time at atomic resolution.

First, using integrated differential phase contrast (iDPC) imaging coupled with high angle annular dark field (HAADF) imaging in aberration corrected STEM (Thermo Scientific Titan 80-300), we directly determine the nature of the intermediate phases in the decomposition process of a precursor salt of Pt, K_2PtCl_4. The temporal and spatial relationship among all compounds involved in the chemical reaction are revealed at the molecular level. Especially, fluctuations of the Pt-Cl bond angles were imaged directly, reflecting the evolving bonding characteristics that are critical to understand the reaction pathway.

Second, with an atmospheric gas cell system (Protochips Atomsphere 210), we characterize the formation process of high entropy oxides (HEO), an emerging family of materials with large configurational space and have applications in catalysis, energy storage, and environmental and thermal barrier coating. Starting from an amorphous sol-gel precursor, a high entropy fluorite oxide, Ce_2(Er, La, Sm, Y, Yb)O_7, has been successfully synthesized in the gas cell. In situ STEM imaging performed simultaneously has permitted the observation of the dynamics of precursor oxidation, the temperature-dependent grain growth, liquification, and recrystallization of the high entropy oxide. At the lower critical temperature of 400 °C, the precursor is pyrolyzed and the nucleation of the HEO nanoparticles begins. At the high critical temperature of 900 °C, a temperature far below the melting point of any of the constituent oxides, liquefaction begins followed by recrystallizing the liquid phase to form a large HEO single crystal, driven by entropy stabilization.

Both studies show that it is possible to control the morphology and phase of the ending materials by tuning the parameters used in the chemical reaction and crystal growth. Details of the in situ experiments, analysis using energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS), and new insights from the results in combination with density functional theory (DFT) calculations will be discussed in the presentation. [1]

References:

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