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Phase transition and atomic scale dynamics in chemical reactions revealed in the solid state by electron microscopy

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Optimization and control over the outcome of a chemical reaction in the solid-state demands a complete understanding of its reaction kinetics and pathways. While the start and end products of such a process can easily be obtained using conventional means, observing the reaction process at an atomic resolution can provide additional information that may reveal any rate limiting steps or opportunities to modify the end product by adjusting a variable. Previous studies have demonstrated the viability of using transmission electron microscopy (TEM) to observe transitions in the atomic structure of a beam sensitive material.[1,2] In this study, we explore K_2PtCl_4, a beam sensitive crystalline precursor of Pt that undergoes rapid decomposition into a metallic state upon exposure to high energy electrons.

The K_2PtCl_4 salt was dissolved in Millipore water and re-dispersed on the surface of a holey carbon grid. Upon drying, it forms solid crystallites. Atomic resolution scanning transmission electron microscopy (STEM) was performed using an aberration corrected Titan operated at 200kV. The solid-state decomposition kinetics of K_2PtCl_4 have been observed using low dose STEM. The dynamic process was imaged with a segmented annular detector and a high angle annular dark field (HAADF) simultaneously. Of the two, the integrated differential phase contrast (iDPC) image shows robust image contrast from light elements and operates efficiently in a low dose environment; HAADF imaging provides high contrast from the more massive Pt atoms, differentiating Pt from the light elements K and Cl. The sequential experimental images acquired at different stages of the chemical reaction processes were then analyzed and compared to images simulated using a multislice algorithm to aid in the interpretation of the data.

In this presentation, it will be demonstrated that as a consequence of its exposure to electron irradiation, the K_2PtCl_4 decomposes into a combination of Pt metal, KCl salt, and Cl gas, the same as the results of the reduction of the precursor. The intermediate steps in this process were revealed at atomic resolution, showing different materials phases that can be correlated with the atomic models and chemical formula, providing a deeper understanding of the reaction kinetics. The kinetics are reliant on the ionic and covalent species-dependent atomic bonds and observed crystalline phases, including a novel intermediate phase that appears immediately after the pristine precursor is exposed to irradiation. An example of the intermediate phase adjacent to the pristine precursor, K_2PtCl_4, is seen in Figure 1. The Pt and KCl within the final product can also be resolved, as shown in Figure 2. These findings using electron microscopy provide valuable insight on the decomposition and chemical processes with atomistic understanding of the dynamic changes in relative distribution and orientation of the phases.[3]

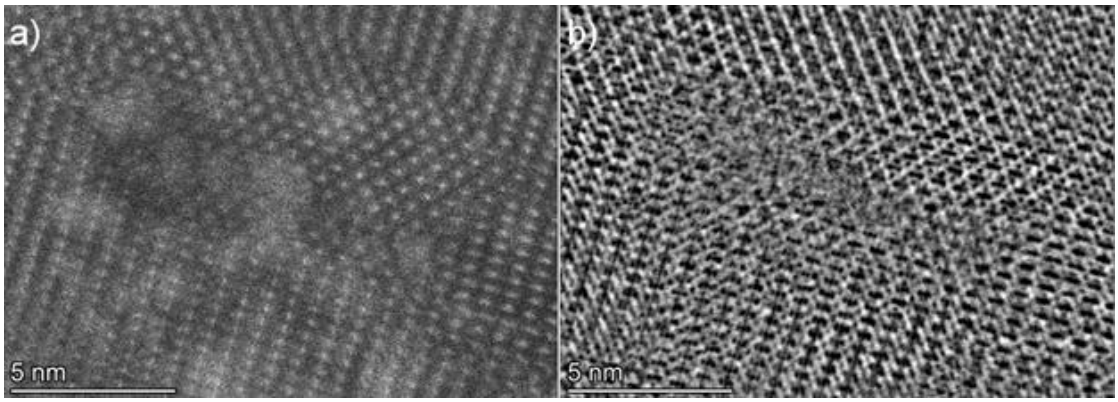

Figure 1. a) HAADF and b) iDPC images of K_2PtCl_4 and the intermediate phase under electron irradiation.

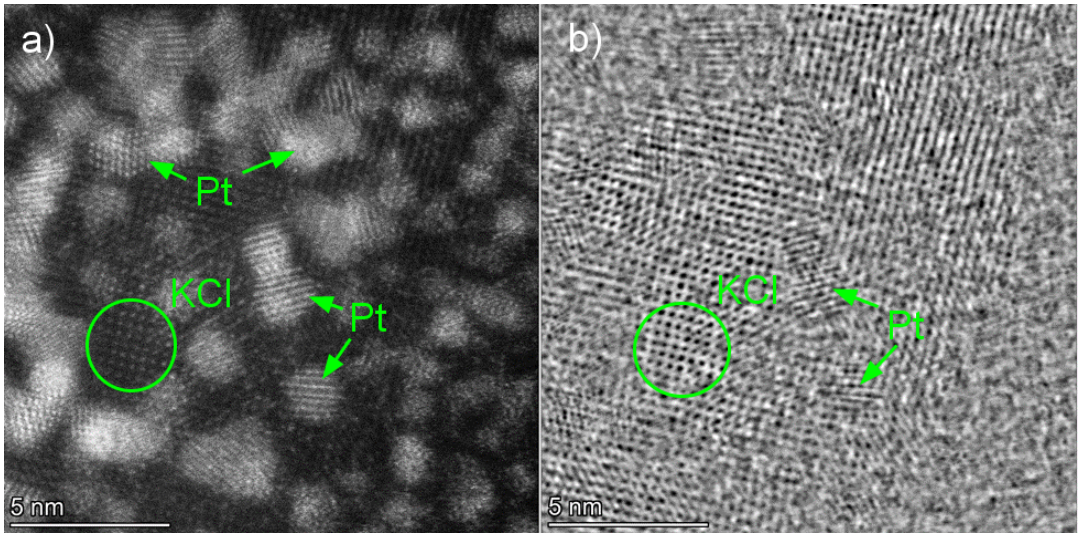

Figure 2. a) HAADF and b) iDPC images of KCl and Pt nanoparticles observed in the fully decomposed product.

References

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