

X-RAY ABSORPTION SPECTROSCOPY FOR INVESTIGATING STRUCTURAL EVOLUTION IN COMPLEX METAL HYDRIDES: Ti K-edge Spectra for Various Milling Times

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We report studies concerning the time scale for catalytic reactions between NaAlH_4 and TiCl_3 during the milling cycle. A structural transition from Ti^{3+} to Ti^0 is observed within the first 5 minutes of milling. After 5 minutes, the Ti^0 structure persists. When milled for 1 minute and 5 minutes, the Ti K-edge absorption spectra exhibits features related to transitional states. Analysis of spectral features show that the first coordination sphere around the Ti^{3+} absorber shifts to larger distances as milling time increases. Previously reported x-ray absorption spectroscopy studies have demonstrated the structural transition from in TiCl_3 to Ti^0 (determined by others to be TiAl_3). For samples milled for 1 minute, a shift in the Ti-K edge position occurs after a single adsorption/desorption milling cycle. Here, we report on the structural evolution in the local environment of TiCl_3 introduced to NaAlH_4 at a variety of milling times. Finally, we propose that XAS study of the local environment of Al will further elucidate catalytic mechanisms for improved reaction kinetics and reversibility.

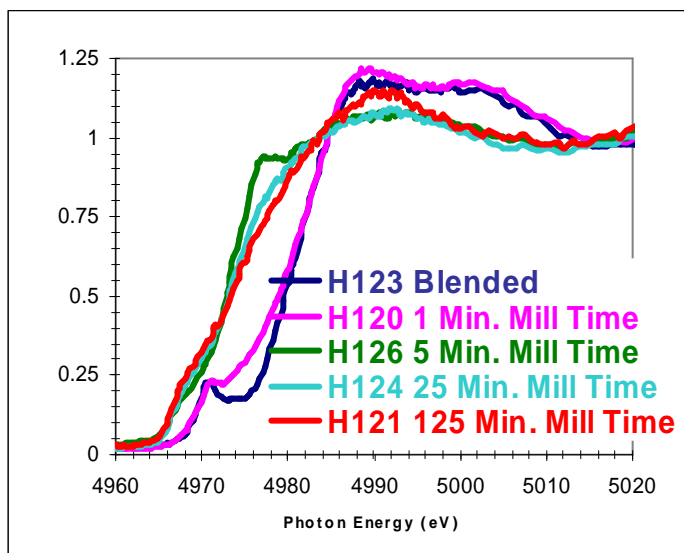


Figure shows Absorption edge position changed at mill time between 1 and 5 minutes.

- K-edge for Ti^0 occurs at 4966 eV.
- The edge shifts depending on the oxidation state.
- Valence state shifted from Ti^{3+} to Ti^0 .
- Maybe a little Ti^{3+} remnant after 5 minutes