

**Recent Advances in the Development of
Doped NaAlH₄ as a Hydrogen Storage
Material: X-ray Diffraction and Solid State
¹H, ²⁷Al, and ²³Na NMR Studies**

Craig Jensen,¹ Dalin Sun,¹ Kristin Kumashiro,¹
Walter Niemczura,¹ Keeley Murphy,¹
Tetsu Kiyobayashi,² Hiroyuki Takeshita² and
Nobuhiro Kuriyama²

¹University of Hawaii
Department of Chemistry
Honolulu, HI 96822
USA

²National Institute of Advanced Industrial Science and
Technology
1-8-31 Midorigaoka
Osaka 563-8577
Japan

Recently, Bogdanovic discovered that the elimination of hydrogen from solid NaAlH₄ is markedly accelerated and rendered reversible under moderate conditions upon mixing the hydride with a few mole percent of selected transition metal complexes. This was a revolutionary finding in the area of metal hydrides as hydrogen cycling at moderate temperatures was unprecedented for saline hydrides. The hydrogen cycling performance of doped NaAlH₄ has since been the subject of intensive investigation. These studies have led to considerable practical improvements and it now appears that the doped hydride could possibly be developed as a viable means for the onboard storage of hydrogen. However, the nature of the dopants has remained an enigma. Also a fundamental understanding of why the hydrogen cycling kinetics are enhanced upon doping is lacking. In order to elucidate the structural changes that occur upon doping, we have conducted we have conducted X-ray diffraction and multinuclear solid-state NMR studies. Our results clearly indicate that, contrary to prior speculation, the dopants are not segregated, surface localized species but instead substituted into the bulk hydride lattice. The X-ray diffraction patterns of NaAlH₄ doped with up to 10 mol peaks for the bulk metals or their aluminum alloys. Instead the hydride lattice parameters a and c undergo significant contraction upon 2 mol doping and then expand as the doping level increases from 2 to 5 mol These results can be explained by a model that entails substitution of sodium cations by variable valance transition metal cations and the creation of Na⁺ vacancies in the bulk hydride lattice that will be discussed. In the solid state NMR studies, we have observed unexpected spectral features that will be discussed in the context of structural models.