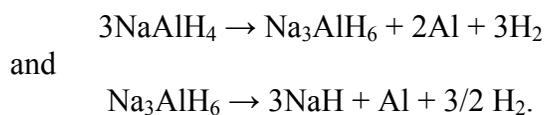


Theoretical Studies of the Structural, Dynamical, and Electronic Properties of NaAlH₄

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NaAlH₄ has recently attracted the attention as a promising solid-state hydrogen storage candidate. With a high theoretical weight-percent hydrogen content of 5.55% and being low cost and readily available in bulk, it would have been a viable candidate for on-board hydrogen storage material. Unfortunately, the hydrogenation reactions are highly irreversible, because thermally activated desorption of hydrogen from NaAlH₄ occurs at an appreciable rate only at temperatures well above its melting temperature of 183 °C. The dehydriding of NaAlH₄ proceeds through a two-step reaction:



In addition, the product can only be rehydrided using complicated (wet) chemical reactions.

The situation has been significantly changed by a recent experiment [1] that demonstrated the effects of doping with a few mole percent of selected titanium compounds such as TiCl₃ as catalysts. The kinetics of both dehydriding and rehydriding processes is greatly enhanced by the catalysts, resulting in a reversible reaction under moderate conditions in the solid state. With catalysts, the temperature required for rapid dehydriding of NaAlH₄ was found to be lowered to 120 – 150 °C. The conditions required for rehydriding were also significantly reduced. Although the rate has not fully reached the values for practical applications, the discovery of the catalysts is considered as a breakthrough in the field.

It would be highly desirable to understand the mechanism of these catalytic reactions, so that proper catalysts can be identified to make the kinetics even faster. If this can be accomplished, NaAlH₄ will become an excellent material that has high hydrogen capacity and moderate temperature for hydrogen exchange in the solid phase.

As a first step to understand this compound, we have performed first-principles calculations for the structural, dynamical, and electronic properties within the density functional theory using pseudopotentials and plane waves. The optimal hydrogen positions are determined by energy and force minimization. This includes a determination of the orientation of the AlH₄⁻ complex relative to the Na⁺ matrix. The binding properties are examined based on the electronic charge distribution and energy bands. A strong bonding is found within the AlH₄⁻ complex. In addition, we will also calculate the hydrogen vibrational modes and possible diffusion paths. Based on these results, we will discuss the possible role of the catalysts in facilitating the motion of hydrogen in this compound.

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[1] B. Bogdanovic and M. Schwickardi, J. Alloys Comp. 1-9, 253 (1997).