

Research Article

An Investigation on Hydrogen Absorption/Desorption in Metal Hydride

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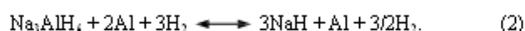
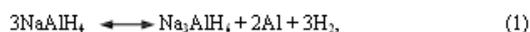
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Abstract. To alleviate the problem that the release of hydrogen from NaAlH₄ is not up to what has been expected, some transition metals have been added into the medium in order to increase the hydrogen absorption capacity and speed up the kinetics of hydrogen desorption from NaAlH₄. In this project, NaAlH₄ was purified by dissolving in THF and was precipitated by pentane. The purified NaAlH₄ was modified by adding TiCl₃, HfCl₄ and ZrCl₄ with different ratios (0-9 mol%). The hydrogenation was carried out at 125 °C and 13.8 MPa and dehydrogenation was in the temperature range of 25-225 °C. The desorption capacity was observed through thermal volumetric analysis in the range of 25-225 °C. The results show that the higher metal loading, the better kinetic rate but the lower capacity. The optimum metal loading is 6 mol%. In case of desorption, ZrCl₄ seems to enhance the release of hydrogen the most followed by HfCl₄ and TiCl₃; however, they affect the dehydrogenation in different reaction, i.e. TiCl₃ promotes the first decomposition step while ZrCl₄ and HfCl₄ promote the second one. For absorption, TiCl₃ is the most effective species in hydrogenation/rehydrogenation.

Keywords: NaAlH₄, Metal Transition, Hydrogen Absorption, Hydrogen Desorption, Dehydrogenation, Rehydrogenation.

Introduction

Hydrogen is a renewable energy source that is abundant, clean and environmentally friendly. It is aimed as a fuel source for onboard fuel cell applications. A major difficulty in such the utilization is hydrogen has low energy density. High pressure and cryogenic hydrogen storage systems have been used but they are impractical for vehicular applications due to safety concerns, weight, volumetric constraints and economic point of view. From these reasons, solid stage method for hydrogen storage especially hydrogen storage in complex hydride of light metal (NaAlH_4) is expected to be hydrogen storage medium for onboard fuel cell. It has high enough hydrogen capacity and lower price per unit of stored hydrogen. The decomposition of NaAlH_4 occurs on two steps, Eqs. (1)-(2),



Stoichiometrically, the first step releases 3.7 wt% hydrogen at temperature about 185 °C and the second step occurs at 260 °C and releases 1.8 wt% hydrogen. However, their disadvantages include high temperature for desorption of hydrogen from hydrides, low kinetics and non-reversibility [1]. Until 1997, Bogdanovic and Schwickardi found that NaAlH_4 can be modified to improve hydrogen absorption/desorption kinetics by adding ($\text{Ti}(\text{O}^\text{n}\text{Bu})_4$ and $\text{Fe}(\text{OEt})_2$) [2]. After this discover, NaAlH_4 has been modified by doping with other catalysts such as $\text{Zr}(\text{OPr})_4$, TiCl_3 , ZrCl_4 [3-4] with different doping methods (wet doping, semi-doping, dry doping) [5] to improve the kinetics [6]. Moreover, the amount of doping catalysts [7] and the mixing time of catalysts and hydrides [8] affects to the hydrogen desorption/absorption.

The objective of this study was to modify NaAlH_4 by doping metal transition (TiCl_3 , ZrCl_4 , HfCl_4) in order to investigate their effects on the hydrogen absorption/desorption kinetics.

Experimental Details

NaAlH_4 , HfCl_4 (99.5%) and ZrCl_4 (99.5%) were obtained from Aldrich Chemical. Hydrogen gas (99.99%) was used in sorption kinetics. THF (99.5%) and n-pentane (98%) were obtained from Aldrich Chemical. NaAlH_4 was purified by THF in order to remove aluminum residuals [9] and re-crystallized by n-pentane under nitrogen atmosphere. The purified NaAlH_4 was mixed with one of three metals (TiCl_3 , HfCl_4 , ZrCl_4) by a mortar for 25 min.

Amount of dopants (TiCl_3 , ZrCl_4 , HfCl_4) was varied between 0-9 mol%. Immediately after milling by mortar, approximately 1 g of the modified samples was placed into the thermovolumetric apparatus, evacuated to 0.133 Pa. For hydrogen desorption, the reactor was compressed with 0.35 MPa helium gas. The high pressure reactor was heated from room temperature to 280 °C at a heating rate of 4 °C per min via heating tape that was controlled temperature by a PID temperature controller. Hydrogen absorption was carried out

at 125 °C with hydrogen pressure 13.8 MPa. The pressure transducer (Setra Co., Ltd., model 206) was used to measure the changing of pressure. Amount of released hydrogen was calculated by using constant volumetric method (Equation of state).

Results and Discussion

Hydrogen desorption

Effect of purification

Figure 1 shows the temperature program desorption of the as-received NaAlH₄ and the purified NaAlH₄. The purified NaAlH₄ has higher hydrogen capacity than the as-received NaAlH₄, but the hydrogen desorption occurs at higher temperature than the unpurified one.

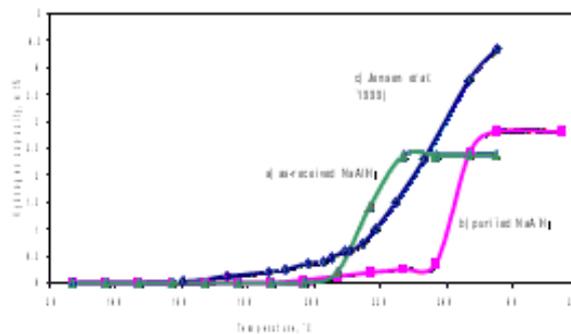


Fig. 1 Temperature program desorption of a) as-received NaAlH₄ b) purified NaAlH₄ c) Jensen *et al.* (1999).

This may be because the purified NaAlH₄ has more crystalline phase, which is difficult to decompose. However, the obtained hydrogen capacity is less than that from the theoretical value (5.6 wt%) [2] and that reported by Jensen *et al.* (1999) as shown in Figure 2. This is probably due to the different techniques and in the NaAlH₄ purification that causes the contamination of water and oxygen residue and obstruct the desorption/absorption kinetics.

Effect of metal loading types

With the metals in the same group from the periodic table, it was discovered that different metals contribute differently to the kinetics as shown in Figure 2. The hydrogen desorption from the 1st reaction of TiCl₃, ZrCl₄, and HfCl₄ doped NaAlH₄ occur at 170 °C. The second reaction takes place at 190 °C with TiCl₄, at 210 °C with ZrCl₄ and HfCl₄. On the other hand, ZrCl₄ doped NaAlH₄ shows the best kinetic important and the highest released hydrogen followed by HfCl₄ and TiCl₄ doped NaAlH₄.

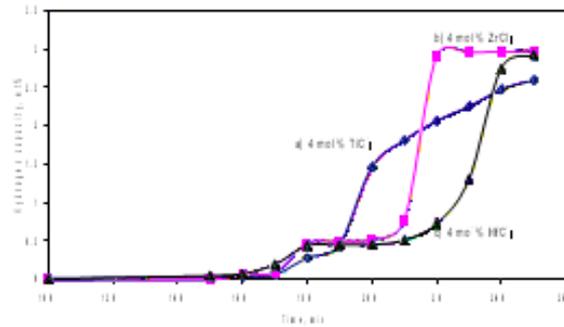


Fig. 2 Progression of the hydrogen desorption with time for NaAlH₄ doped with a) 4 mol% TiCl₃ b) 4 mol% ZrCl₄ c) 4 mol% HfCl₄ at room temperature to 270 °C.

Effect of metal loading amount

Figures 3 and 4 show the hydrogen desorption capacity in different amount of ZrCl₄ doping in NaAlH₄. It was found that ZrCl₄ doped NaAlH₄ results in the hydrogen desorption at lower temperature than those with the amount of ZrCl₄ higher than 6 mol%. It can be hypothesized that this may be caused by the lattice distortion (atomic substitution in formation of Zr²⁺ and Zr³⁺ instead of Zr⁴⁺) [10].

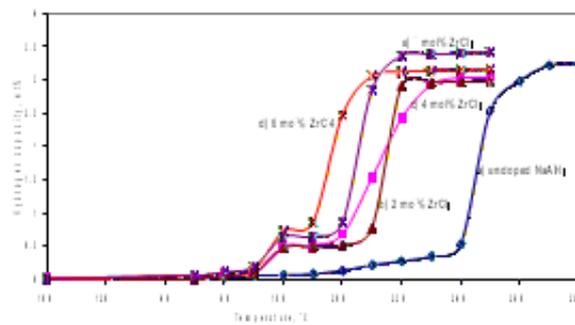


Fig. 3 Hydrogen desorption as a function of temperature on NaAlH₄ a) undoped NaAlH₄ b) 2 mol%ZrCl₄ c) 4 mol% ZrCl₄ d) 6 mol% ZrCl₄ e) 9 mol% ZrCl₄.

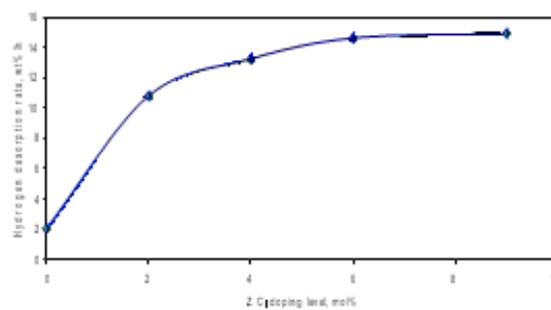


Fig. 4 Hydrogen desorption rate as a function of doped ZrCl₄.

Hydrogen absorption

The hydrogen capacity of absorption on doped NaAlH₄ with various halide compounds is shown in Figure 5. TiCl₃ doped NaAlH₄ has the highest hydrogen absorption rate in the 1 hour. That the ionic radius plays an important role on hydrogen absorption can be quoted [8]. It was expected that the low rate of hydrogen discharge is observed for doped metals with radii significantly larger or smaller than 0.74 Å, the midpoint between Na⁺ (0.97 Å) and Al³⁺ (0.51 Å). Likewise, there is a range of ionic radius (0.73-0.8 Å) that holds the highest potential to enhance hydrogen charge rate. Because Ti³⁺ (0.76 Å) has smaller ionic radius than that of Zr⁴⁺ (0.86 Å) and Hf⁴⁺ (0.85 Å) [11], this formulation can easily substitute into the lattice on the surface of material. A reason why the hydrogen uptake rate of HfCl₄ doped NaAlH₄ is lower than the ZrCl₄ doped one may be because of the symmetry of orbital. Hf⁴⁺ has less proper electronic configuration for activation than Zr. The sample rendered by ZrCl₄ sustains hydrogen at higher capacity so it can be interpreted that activity of HfCl₄ as a catalyst is considerably lower than that of ZrCl₄.

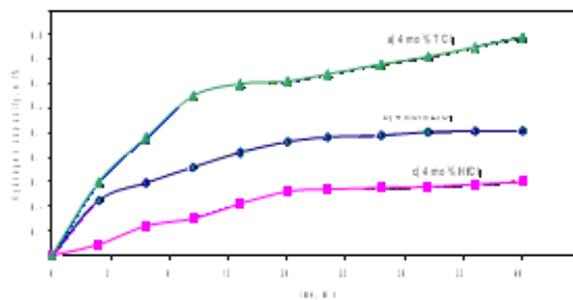


Fig. 5 Hydrogen absorption of NaAlH₄ doped with a) 4 mol% TiCl₄ b) 4 mol% ZrCl₄ c) 4 mol% HfCl₄.

Table 1 summarizes the rehydrogenation or the recycle ability of the doped materials degree of rehydrogenation [8], a portion of absorption to desorption capacity. Nevertheless, all doped samples are not entirely reversible and generally show lower absorption capacity than the desorption capacity. A major reason may be the incomplete absorption owing to the formation of large metallic aluminum particles hampering the mass transfer problem [11].

Table 1 Total the hydrogen capacity measured by absorption and desorption; the estimated degree of rehydrogenation at different types of doped metals

Type of metal loadings	Hydrogen capacity (wt%)*		Degree of rehydrogenation (%)
	Desorption	Absorption	
TiCl ₃	3.05	1.93	63.3
ZrCl ₄	3.14	1.78	56.7
HfCl ₄	2.88	1.42	49.3

Conclusions

Adding some transition metal halides on NaAlH_4 can promote the dehydrogenation/hydrogenation rate and decrease the temperature of hydrogen desorption. TiCl_3 shows the good kinetics in the first decomposition while ZrCl_4 and HfCl_4 assist the second decomposition. For hydrogen absorption, TiCl_3 results in better kinetics than ZrCl_4 and HfCl_4 .

Acknowledgements

This work was supported UOP LLC; The Petroleum and Petrochemical College, Research Unit for Petrochemical and Environmental Catalysts, Ratchadapisek Somphot Endowment Fund, and The Petroleum and Petrochemical Technology Consortium, Chulalongkorn University.

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