

# Mechano-chemical Synthesis of NaAlH<sub>4</sub> : Optimization of Reaction Conditions

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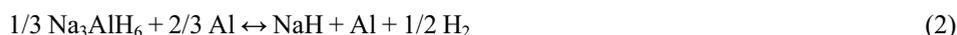
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**Abstract.** NaAlH<sub>4</sub> was mechano-chemically synthesized with high energy ball-milling method. The effect of synthesis conditions such as milling time, H<sub>2</sub> pressure, chloride catalysts, and solvents was investigated to enhance the synthesis of NaAlH<sub>4</sub>. Among the chloride catalysts, TiCl<sub>4</sub> showed the highest H<sub>2</sub> pressure decrease which means the highest NaH conversion to NaAlH<sub>4</sub>. Furthermore, when the NaAlH<sub>4</sub> was synthesized with THF solvent, it exhibited the higher H<sub>2</sub> pressure decrease than that of sample prepared without THF solvent. This is mainly due to the synergy effect of TiCl<sub>4</sub> catalyst and THF solvent.

## 1 Introduction

Hydrogen has been attracted as a clean energy carrier. One of the important issues in hydrogen usage is to establish safe and reliable hydrogen storage method [1]. Complex hydride is safer than the commercial storage methods storing the hydrogen in compressed or liquid form. In addition, due to the large hydrogen storage capacities, complex hydride has been attracted in recent years [2,3]. NaAlH<sub>4</sub> has been studied due to its reversibility when it is synthesized with suitable catalyst [2]:



Bogdanovic and Schwickardi discovered that desorption kinetics of NaAlH<sub>4</sub> can be enhanced, when it is used with ball-milling method and catalysts [2,3]. The advantage of ball-milling method is it can directly prepare the catalysts doped NaAlH<sub>4</sub>. Effect of milling conditions such as pressure, temperature, and catalyst has been studied [4].

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Among various transition and rare earth metals, Ti chloride showed the most effective [5]. Recently, Anton studied various form of chloride catalysts in dehydrogenation step [6,7]. Some researchers studied the synthesis of NaH and Al in tetrahydrofuran (THF) in order to prepare the NaAlH<sub>4</sub> doped with Ti [4, 8]. Srinivasan et al. reported that the NaAlH<sub>4</sub> synthesized with Ti catalyst in solvent shows better dehydrogenation property than that of sample prepared by dry milling method. [8]

In the present work, high energy ball-milling method was used as a mechano-chemical synthesis of NaAlH<sub>4</sub>. After the optimization of milling conditions (milling time and pressure), chloride catalysts (TiCl<sub>4</sub>, NiCl<sub>2</sub>, MgCl<sub>2</sub>, GaCl<sub>3</sub>) were studied to replace the Ti chloride catalyst. Furthermore, NaAlH<sub>4</sub> was prepared in solvent to check the effect of solvent. The effect of each parameter has been interpreted through the H<sub>2</sub> pressure change.

## 2 Experimental

### 2.1 High Energy Ball-milling

NaAlH<sub>4</sub> was prepared by a high energy ball-milling method. NaH (95%, Sigma aldrich) and Al (99%, Samchun chemicals) powders (1:1) were combined with 3 mol.% of chloride catalysts. The catalysts were TiCl<sub>4</sub> (99%, Kanto chemical), MgCl<sub>2</sub> (98%, Sigma aldrich), NiCl<sub>2</sub> (98%, Sigma aldrich), GaCl<sub>3</sub> (98%, Sigma aldrich). The powder to Cr ball ratio was fixed as 1:30. After putting the power and Cr balls in the reactor, H<sub>2</sub> was added through the valve up to 70 bar. The high energy ball-milling method was carried out in a planetary Fritsch Pulverisette 5. Milling of powders was carried out under the 300 rpm for 15 to 120 hr. H<sub>2</sub> pressure was checked with pressure indicator connecting with valve, before and after the ball-milling reaction. The difference of H<sub>2</sub> pressure ( $\Delta P$ ) represents the activity of reaction in this study. 100 mL of THF (99.5%, Samchun chemicals) and diethyl ether (99%, Sigma aldrich) were used to check the effect of solvent. Powder handling was done in the glove box (99.999%, Ar) to prevent the exposure of oxygen and water.

### 2.2 Characterization

XRD patterns were recorded using a Rigaku D/MAX-IIIC diffractometer (Ni filtered Cu K $\alpha$  radiation, 40 kV, 150 mA). The samples were covered by Kapton film to avoid any exposure to oxygen and water. The crystallite size was calculated using the Debye-Scherrer equation. H<sub>2</sub> adsorption and desorption properties were conducted under 80 bar of H<sub>2</sub> and vacuum condition at 120 °C respectively.

## 3 Results and Discussion

### 3.1 Optimization of Reaction Conditions

NaAlH<sub>4</sub> milled for 60 hr without catalyst showed no NaAlH<sub>4</sub> peak in XRD and H<sub>2</sub> pressure change. Therefore, 3 mol.% TiCl<sub>4</sub> catalyst was chosen to optimize the reaction conditions. NaH and Al powders with 3 mol.% TiCl<sub>4</sub> catalyst were milled for 0 to 120 hr. Fig.1 shows the H<sub>2</sub> pressure after the high energy ball-milling reaction with time change. NaAlH<sub>4</sub> shows the dramatic H<sub>2</sub> pressure decrease at 60 hr of milling time. The H<sub>2</sub> pressure increases after 60 hr of milling due to the partly decomposition of NaAlH<sub>4</sub>.

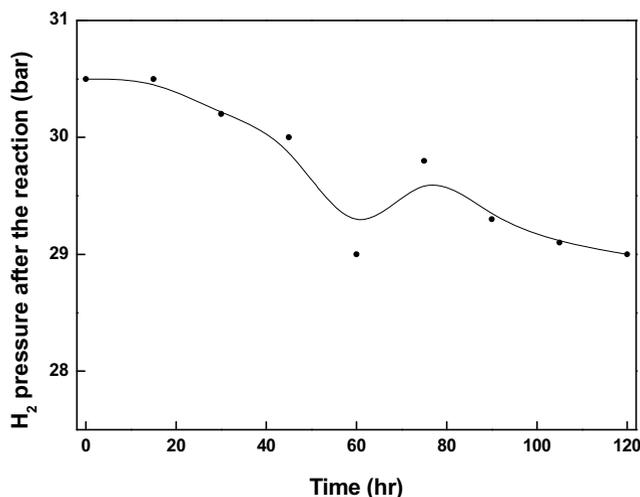


Fig.1. H<sub>2</sub> pressure with ball-milling time change

Fig.2 depicts the reacted NaH amount with H<sub>2</sub> pressure change from 30 to 70 bar after the 30 hr of milling. The mol of reacted NaH increases linearly with an increase of H<sub>2</sub> pressure. The reacted NaH mol increases in the following order: 30 bar (0.028 mol) < 40 bar (0.031 mol) < 50 bar (0.039 mol) < 70 bar (0.044 mol). This suggests that the H<sub>2</sub> pressure has positive effect in increase the reaction rate of conversion of NaH to NaAlH<sub>4</sub>. Based on these results, the remaining high energy ball-milling reactions were carried out for 60 hr under 30 H<sub>2</sub> bar. To clarify the effect of catalyst clearly, 30 bar of H<sub>2</sub> was chosen instead of 70 bar of H<sub>2</sub>.

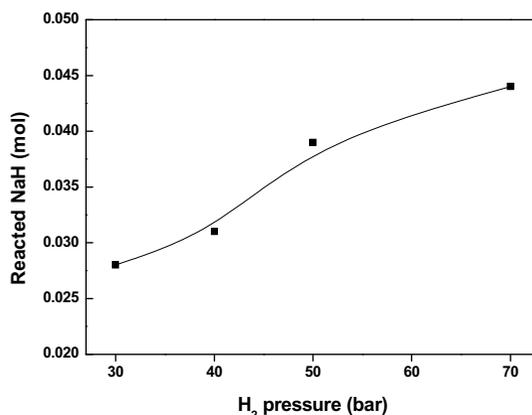


Fig.2. Reacted NaH amount with H<sub>2</sub> pressure change

### 3.2 Optimization of Chloride Catalyst

Fig.3 depicts the XRD patterns of synthesized samples with 3 mol.% chloride catalysts. The bottom pattern is the XRD peak of kapton film. According to the XRD patterns, sample synthesized with TiCl<sub>4</sub> catalyst shows the NaAlH<sub>4</sub> peak (PDF #. 85-0374). However, Al and

$\text{Na}_3\text{AlH}_6$  (PDF #. 42-0786) peaks are found on the other samples synthesized with chloride catalysts ( $\text{MgCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{GaCl}_3$ ). The crystallite size of  $\text{NaAlH}_4$  synthesized with  $\text{TiCl}_4$  catalyst is 22.4 nm. This suggests that the only  $\text{TiCl}_4$  catalyst is effective in synthesis of  $\text{NaAlH}_4$ .

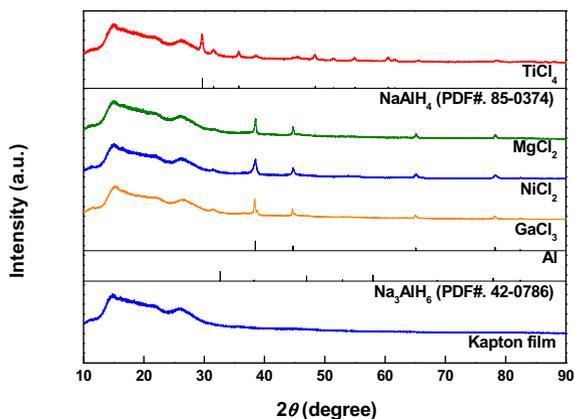
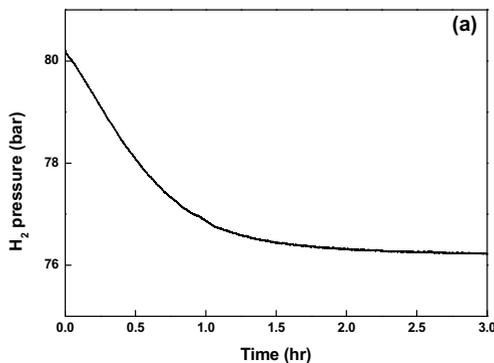


Fig.3. XRD patterns of samples synthesized with chloride catalysts

$\text{H}_2$  adsorption and desorption properties are shown in Fig.4.  $\text{NaAlH}_4$  prepared with  $\text{TiCl}_4$  was degassed at 120 °C under a vacuum and adsorbed  $\text{H}_2$  at 120 °C under  $\text{H}_2$  80 bar. 4 bar of  $\text{H}_2$  adsorbed in 2 hr and 3.6 bar of  $\text{H}_2$  degassed in 6 hr. This suggests that the  $\text{NaAlH}_4$  prepared with  $\text{TiCl}_4$  has a hydrogen storage property.



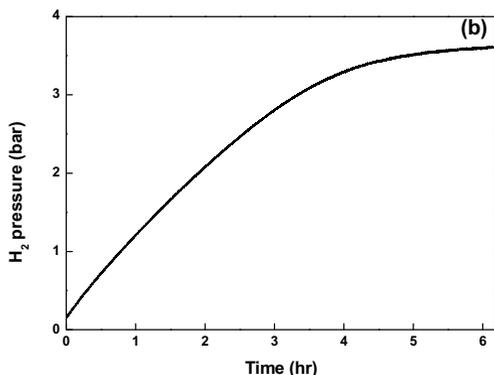


Fig.4. H<sub>2</sub> adsorption and desorption pattern of NaAlH<sub>4</sub> synthesized with TiCl<sub>4</sub> catalyst  
 ((a) adsorption, (b) desorption)

### 3.3 Effect of Solvent

Table 1 summarizes the reacted NaH amount with solvents. To compare the effect of solvent, the result in Fig.2 which was milled for 30 hr under 70 bar H<sub>2</sub> was chosen as a criteria. In the case of addition of diethyl ether as a solvent, 0.039 mol of NaH reacted. This suggests that diethyl ether has the negative effect in synthesis of NaAlH<sub>4</sub>. In contrast, sample prepared in THF solvent exhibits higher reacted NaH mol (0.057 mol) than that of sample prepared without solvent (0.044 mol). Therefore, it suggests that the THF has the synergy effect in NaH conversion to NaAlH<sub>4</sub> when it is used with TiCl<sub>4</sub> catalyst.

Table 1. Reacted Nah Amount With Solvents

Solvent	Diethyl ether	None	THF
Reacted NaH (mol)	0.039	0.044	0.057
Difference (mol)		- 0.005	+ 0.013

### 4 Conclusion

NaH and Al powders were milled under various reaction conditions (milling time, H<sub>2</sub> pressure, chloride catalyst, solvent) to synthesize the NaAlH<sub>4</sub>. Among the reaction conditions, 60 hr of milling time and 30 bar of H<sub>2</sub> pressure were chosen to prepare the NaAlH<sub>4</sub>. XRD results showed that the TiCl<sub>4</sub> plays a key role in synthesis of NaAlH<sub>4</sub>. Furthermore, NaAlH<sub>4</sub> prepared with TiCl<sub>4</sub> showed the 4 bar of H<sub>2</sub> adsorption and desorption properties at 120 °C. The improved TiCl<sub>4</sub> catalyst activity was shown when it is used with THF solvent under 70 bar H<sub>2</sub> with 30 hr of milling. Therefore, the THF has the synergy effect in synthesis of NaAlH<sub>4</sub> with TiCl<sub>4</sub>.

### 5 Acknowledgements

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