

Mechano-chemical Synthesis of NaAlH₄ : Optimization of Reaction Conditions

Won-Bi Han^{1,a}, Ki-Kwang Bae^{1,b}, Kyoung-Soo Kang^{1,c}, Seoung-Uk Jeong^{1,d}, Won-Chul Cho^{1,e} Chang-Hee Kim^{1,f} and Chu-Sik Park^{1,g,*}

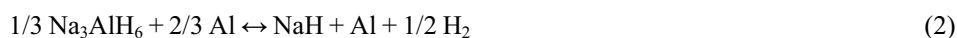
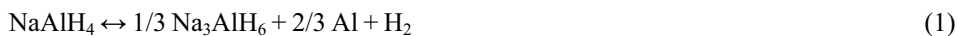
¹Hydrogen Energy Research Center, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

^awbhan@kier.re.kr, ^bkkbae@kier.re.kr, ^ckskang@kier.re.kr, ^dsujung@kier.re.kr, ^emizkeec@kier.re.kr, ^fchk14@kier.re.kr, ^{g,*}cspark@kier.re.kr (Corresponding author)

Abstract. NaAlH₄ was mechano-chemically synthesized with high energy ball-milling method. The effect of synthesis conditions such as milling time, H₂ pressure, chloride catalysts, and solvents was investigated to enhance the synthesis of NaAlH₄. Among the chloride catalysts, TiCl₄ showed the highest H₂ pressure decrease which means the highest NaH conversion to NaAlH₄. Furthermore, when the NaAlH₄ was synthesized with THF solvent, it exhibited the higher H₂ pressure decrease than that of sample prepared without THF solvent. This is mainly due to the synergy effect of TiCl₄ 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]. NaAlH₄ has been studied due to its reversibility when it is synthesized with suitable catalyst [2]:



Bogdanovic and Schwickardi discovered that desorption kinetics of NaAlH₄ 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 NaAlH₄. Effect of milling conditions such as pressure, temperature, and catalyst has been studied [4].

* Corresponding author: cspark@kier.re.kr

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 NaAlH₄ doped with Ti [4, 8]. Srinivasan et al. reported that the NaAlH₄ 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 NaAlH₄. After the optimization of milling conditions (milling time and pressure), chloride catalysts (TiCl₄, NiCl₂, MgCl₂, GaCl₃) were studied to replace the Ti chloride catalyst. Furthermore, NaAlH₄ was prepared in solvent to check the effect of solvent. The effect of each parameter has been interpreted through the H₂ pressure change.

2 Experimental

2.1 High Energy Ball-milling

NaAlH₄ 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 TiCl₄ (99%, Kanto chemical), MgCl₂ (98%, Sigma aldrich), NiCl₂ (98%, Sigma aldrich), GaCl₃ (98%, Sigma aldrich). The powder to Cr ball ratio was fixed as 1:30. After putting the power and Cr balls in the reactor, H₂ 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. H₂ pressure was checked with pressure indicator connecting with valve, before and after the ball-milling reaction. The difference of H₂ pressure (ΔP) 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 α 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. H₂ adsorption and desorption properties were conducted under 80 bar of H₂ and vacuum condition at 120 °C respectively.

3 Results and Discussion

3.1 Optimization of Reaction Conditions

NaAlH₄ milled for 60 hr without catalyst showed no NaAlH₄ peak in XRD and H₂ pressure change. Therefore, 3 mol.% TiCl₄ catalyst was chosen to optimize the reaction conditions. NaH and Al powders with 3 mol.% TiCl₄ catalyst were milled for 0 to 120 hr. Fig.1 shows the H₂ pressure after the high energy ball-milling reaction with time change. NaAlH₄ shows the dramatic H₂ pressure decrease at 60 hr of milling time. The H₂ pressure increases after 60 hr of milling due to the partly decomposition of NaAlH₄.

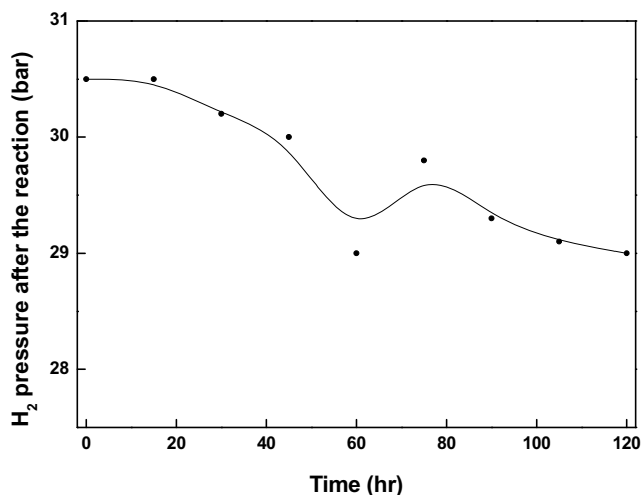


Fig.1. H₂ pressure with ball-milling time change

Fig.2 depicts the reacted NaH amount with H₂ pressure change from 30 to 70 bar after the 30 hr of milling. The mol of reacted NaH increases linearly with an increase of H₂ 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 H₂ pressure has positive effect in increase the reaction rate of conversion of NaH to NaAlH₄. Based on these results, the remaining high energy ball-milling reactions were carried out for 60 hr under 30 H₂ bar. To clarify the effect of catalyst clearly, 30 bar of H₂ was chosen instead of 70 bar of H₂.

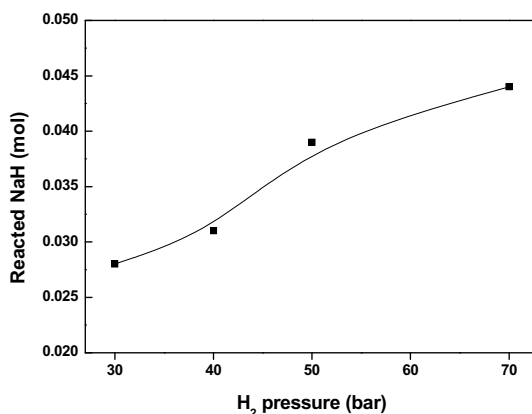


Fig.2. Reacted NaH amount with H₂ pressure change

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 TiCl₄ catalyst shows the NaAlH₄ peak (PDF #. 85-0374). However, Al and

Na_3AlH_6 (PDF #. 42-0786) peaks are found on the other samples synthesized with chloride catalysts (MgCl_2 , NiCl_2 , GaCl_3). The crystallite size of NaAlH_4 synthesized with TiCl_4 catalyst is 22.4 nm. This suggests that the only TiCl_4 catalyst is effective in synthesis of NaAlH_4 .

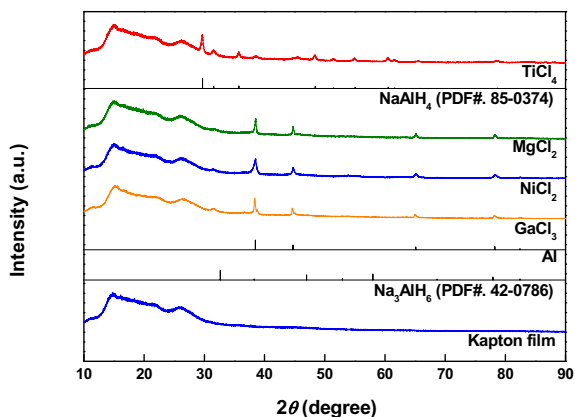
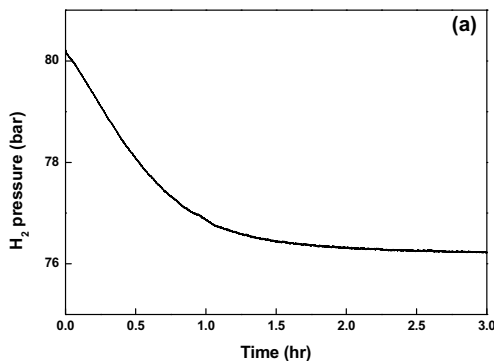


Fig.3. XRD patterns of samples synthesized with chloride catalysts

H_2 adsorption and desorption properties are shown in Fig.4. NaAlH_4 prepared with TiCl_4 was degassed at 120°C under a vacuum and adsorbed H_2 at 120°C under H_2 80 bar. 4 bar of H_2 adsorbed in 2 hr and 3.6 bar of H_2 degassed in 6 hr. This suggests that the NaAlH_4 prepared with TiCl_4 has a hydrogen storage property.



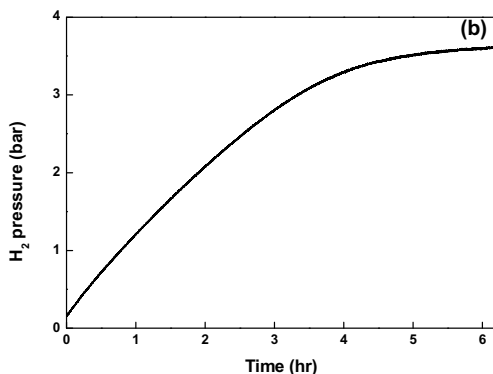


Fig.4. H₂ adsorption and desorption pattern of NaAlH₄ synthesized with TiCl₄ catalyst
 ((a) adsorption, (b) desorption)

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 H₂ 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 NaAlH₄. 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 NaAlH₄ when it is used with TiCl₄ 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, H₂ pressure, chloride catalyst, solvent) to synthesize the NaAlH₄. Among the reaction conditions, 60 hr of milling time and 30 bar of H₂ pressure were chosen to prepare the NaAlH₄. XRD results showed that the TiCl₄ plays a key role in synthesis of NaAlH₄. Furthermore, NaAlH₄ prepared with TiCl₄ showed the 4 bar of H₂ adsorption and desorption properties at 120 °C. The improved TiCl₄ catalyst activity was shown when it is used with THF solvent under 70 bar H₂ with 30 hr of milling. Therefore, the THF has the synergy effect in synthesis of NaAlH₄ with TiCl₄.

5 Acknowledgements

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