Dehydrogenation Properties and Catalytic Mechanism of the K2NiF6-Doped NaAlH4 System

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ABSTRACT: The K2NiF6 catalytic effect on the NaAlH4 dehydrogenation properties was studied in this work. The desorption temperature was studied using temperature-programmed desorption and exhibited a lower onset hydrogen release after doped with different wt % of K2NiF6 (5, 10, 15 and 20 wt %). It was found that the NaAlH4 doped with 5 wt % K2NiF6 showed the optimal value that can reduce the onset desorption temperature of about 160 °C compared to 190 °C for the milled NaAlH4. The NaAlH4 + 5 wt % K2NiF6 sample showed faster desorption kinetics where 1.5 wt % of hydrogen was released in 30 min at 150 °C. In contrast, the milled NaAlH4 only released about 0.2 wt % within the same time and temperature. From the Kissinger analysis, the apparent activation energy was 114.7 kJ/mol for the milled NaAlH4 and 89.9 kJ/mol for the NaAlH4-doped 5 wt % K2NiF6 indicating that the addition of K2NiF6 reduced the activation energy for hydrogen desorption of NaAlH4. It is deduced that the new phases of AlNi, NaF, and KH that were formed in situ during the dehydrogenation process are the key factors for the improvement of dehydrogenation properties of NaAlH4.

INTRODUCTION

Hydrogen has been considered to be the most promising candidate as a suitable energy carrier as it produces only water as a byproduct of the energy generation. As an energy carrier, hydrogen holds the potential to fundamentally secure our future energy supply and draw it more environmentally favorable. However, both hydrogen production and storage are the most important issues to realize for the development of hydrogen economy, especially for the transportation application.1−25 According to the latest US Department of Energy (DOE) targets for 2020, the fuel cell demands hydrogen storage materials with more than 4.5 wt % of hydrogen capacity and faster sorption kinetics.4 Storing hydrogen in the solid state form benefits the onboard applications in the aspects of safety, economy, and efficiency as compared to the gas or cryogenic liquid form.5,6 Complex metal hydride, which is NaAlH4 has become a promising candidate material for the solid-state hydrogen storage because of the high gravimetric and volumetric hydrogen densities. It is well-known that the dehydrogenation of NaAlH4 consists of three steps based on the reactions as follows

$$\text{Na}_3\text{AlH}_6 \rightarrow 3\text{NaH} + \text{Al} + 1.5\text{H}_2 \quad (2)$$
$$3\text{NaH} \rightarrow 3\text{Na} + 1.5\text{H}_2 \quad (3)$$

The hydrogen content for NaAlH4 is 7.4 wt % of which 5.5 wt % can be released under moderate temperature for two dehydrogenation steps.7 However, the operation temperature is still high and sluggish de/rehydrogenation kinetics limit NaAlH4 for practical applications.8 A lot of methods have been used to improve the performance of NaAlH4 such as by ball milling,9 adding the catalyst,10−13 and destabilizing with other hydrides.14−16 Among them, the hydrogen storage properties of NaAlH4 greatly enhanced by the addition of catalyst. Different types of catalysts such as metal,10,17 metal oxide,11,18 and metal halide19,20 have been doped into NaAlH4. Recently, Khan and Jain21 reported that TiO2-doped NaAlH4 showed faster desorption kinetics with improved hydrogen capacity (3.6−5.1 wt %) at 250 °C, while the study on the effect of Nb2O5 on the dehydrogenation kinetics of NaAlH4 revealed that the amount of desorbed hydrogen varied between 4.8 and

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5.0 wt % at 250 °C following the catalyst content. In the other study on the effect of metal chlorides (TiCl3, PdCl2, and CeCl3) on the hydrogen desorption of NaAlH4, Khan and Jain found that the amount of hydrogen desorbed at a temperature below 150 °C was less than 1 wt %. The amount of hydrogen desorbed increased as the dehydrogenation temperature rose and 2 wt % CeCl3 gave the higher amount of hydrogen desorbed which was 5.4 wt % at 250 °C. However, a total comprehension of the effects of catalysts on the improvement of the NaAlH4 dehydrogenation properties is insufficient and there is room for improvements. In addition, different complex metal hydride requires a different catalyst because it will give different roles and effects. Thus, it is essential to find another type of catalyst that has a potential to enhance the NaAlH4 dehydrogenation properties without sacrificing its hydrogen storage capacity, especially at a lower operating temperature.

To date, no research has been found that surveyed the effect of the K2NiF6 additive on the hydrogen storage properties of NaAlH4. So far, only Sulaiman et al. 24,25 reported the applications of K2NiF6 as the additive for the MgH2 system. They claimed that the formed species, KF, KH, and MgNi were acting synergistically and were responsible for the enhancement of the MgH2 sorption properties. Moreover, the combination of three elements of K, Ti, and F on NaAlH4 has been reported by Liu et al.26 They found that the NaAlH4−0.025 K2TiF6 sample can release about 4.4 wt % of hydrogen within 40 min at 140 °C. Therefore, it can be speculated that the K2NiF6 may also give a similar effect on NaAlH4. In addition, Ni is one of the good catalysts for MgH2.27−51 The doping effect of the Ni element is more notable than Ti because of the hardness of Ni that can help to reduce the particle size of MgH2, thus reduced the initial dehydrogenation temperature as studied by Zhang et al.28 Meanwhile, Yahya and Ismail in their current study reported the effect of Ni on the hydrogen storage properties of the MgH2−SrTiO3 composite. Their result showed that the decompensation temperature was reduced to 260 °C for the MgH2−10 wt % SrTiO3−5 wt % Ni composite with a total of 6 wt % hydrogen released. Thus, it was hypothesized in this present study that K2NiF6 may play a vital part as a dopant precursor which can give a synergetic catalytic impact on the hydrogen storage properties of NaAlH4. Therefore, the aim of this work is to investigate the dehydrogenation properties of NaAlH4 with the addition of the K2NiF6 catalyst and the possible catalytic mechanism will also be discussed.

RESULTS AND DISCUSSIONS
The curves of the temperature-programmed desorption (TPD) of the undoped NaAlH4 and NaAlH4 doped with various amounts of K2NiF6 (5, 10, 15, and 20 wt %) is shown in Figure 1. Pure NaAlH4 starts to release hydrogen at around 190 °C. The dehydrogenation reaction for the first two steps has completed at 300 °C with a total hydrogen release of about 5.7 wt %. This result is very close to the theoretical value and in good agreement with a previous study.34 On the other hand, the milled NaAlH4 has a close onset desorption temperature as the pure NaAlH4. This outcome shows that the 1 h ball milling process has a minimal impact on the dehydrogenation properties of NaAlH4. However, the dehydrogenation process completed at a lower temperature than the pure NaAlH4 for two-step decomposition (280 °C) with a total hydrogen release of 5.5 wt %. Compared to the undoped sample, the onset desorption temperature for different wt % of K2NiF6-doped NaAlH4 compounds show a lower dehydrogenation temperature. The NaAlH4 + 5 wt % K2NiF6 sample starts to release hydrogen at 160 °C and completed at around 260 °C for the two-step dehydrogenation process. For the 10 wt % doped sample, the dehydrogenation temperature starts to decompose at about 150 °C and completes at 250 °C. The addition of 5 and 10 wt % K2NiF6 has reduced the onset desorption temperature of NaAlH4 by 30 and 40 °C, respectively, as compared with the milled NaAlH4. However, the total value of hydrogen released is slightly reduced to 5.1 wt %. Meanwhile, the desorption temperature has reduced to 145 °C after increasing the doping value of K2NiF6 to 15 and 20 wt %. The dehydrogenation process for 15 and 20 wt % doped samples was completed at 245 and 237 °C with a total hydrogen capacity at about 4.9 and 4.5 wt %, respectively. This result indicates that a higher amount of doping further reduces the onset desorption temperature and decreases the hydrogen capacity. This phenomenon is believed because of the high level of the added amount of K2NiF6 that led to the excessive catalytic effect and it is almost similar to our previous work.24,35

Figure 2 shows the hydrogen desorption curves of the milled NaAlH4 and NaAlH4 doped with 5, 10, 15, and 20 wt % of K2NiF6 at 150 °C. The hydrogen released of the milled NaAlH4 is only at about 0.5 wt % after 120 min, demonstrating poor dehydrogenation kinetics of the undoped sample. The hydrogen has released about 1.5 wt % at 30 min after being doped with 5 wt % K2NiF6. Further increasing the doping amount to 10, 15, and 20 wt %, the result shows faster
desorption rate in which the hydrogen released about 2.1, 2.5, and 2.2 wt %, respectively within 30 min dehydrogenation. The total hydrogen capacity for the all doped NaAlH4 is at about 3.0 wt % after 120 min dehydrogenation. Therefore, the remarkable improvement in the dehydrogenation kinetics of NaAlH4 can be achieved by the addition of the K2NiF6 additive. These results indicated that the addition of minimum amount of K2NiF6 (5 wt %) can reduce the onset decomposition temperature and improve the dehydrogenation kinetics of NaAlH4. Thus, the NaAlH4 + 5 wt % K2NiF6 sample was selected for further analysis.

To compare the thermal properties of the doped and undoped composite, Figure 3 shows the differential scanning calorimetry (DSC) curves of the milled NaAlH4 and NaAlH4 + 5 wt % K2NiF6 samples. The samples were measured at 100−350 °C with a heating rate of 25 °C/min. Three endothermic peaks are shown by the DSC curves of the undoped sample curve. The decomposition of NaAlH4 is signified by the first strong endothermic peak at approximately 195 °C. Meanwhile, the phase transition of α-Na3AlH6 to β-Na3AlH6 is signified by the weaker peak at 278 °C. The third endothermic peak at approximately 310 °C is ascribed to the decomposition of NaH into Na and Al. The pattern of this result is almost the same as reported in the previous study by Mao et al. In contrast, the K2NiF6-doped sample has shifted to lower temperature with only two endothermic peaks appeared. These two endothermic peaks decomposed at approximately 179 and 277 °C correspond to the decomposition of NaAlH4 and Na3AlH6, respectively. The reduction in the peak temperature of the DSC results revealed that the dehydrogenation properties of NaAlH4 have improved with the addition of K2NiF6.

The activation energy for the dehydrogenation of NaAlH4 + 5 wt % K2NiF6 was calculated to investigate the impact of the introduction of K2NiF6 on the kinetic property of NaAlH4. In this context, the Kissinger plot was prepared based on the Kissinger equation as follows

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + A$$

where β is the heating rate, \(T_p\) is the peak temperature obtained from the DSC curve, R is the gas constant, and A is the linear constant. Thus, the activation energy can be achieved from the slope in a plot of \(\ln(\beta/T_p^2)\) versus 1000/\(T_p\). Figures 4 and 5 show the DSC traces at various heating rates and Kissinger plot for the first-step and second-step dehydrogenation of doped and undoped NaAlH4, respectively. From the Kissinger plot of the DSC data for the first-step dehydrogenation as shown in Figure 4c, the apparent activation energy of the milled NaAlH4 and NaAlH4 + 5 wt % K2NiF6 was found to be 114.7 and 89.9 kJ/mol.

Meanwhile, Figure 5c shows the second step dehydrogenation apparent activation energy of the doped and undoped NaAlH4. The NaAlH4 + 5 wt % K2NiF6 sample gives an
activation energy value of about 99.6 kJ/mol, while the undoped sample has an activation energy of 125.2 kJ/mol. The activation energies for the NaAlH₄ + 5 wt % K₂NiF₆ are reduced by 24.8 and 25.6 kJ/mol for the first and second step dehydrogenation, respectively, which are significantly lower compared to those of undoped NaAlH₄. This result indicated that the dehydrogenation behavior of NaAlH₄ has remarkably improved by the addition of K₂NiF₆ with the reduction of the 𝐸ₐ value.

Table 1 shows the comparison of activation energy of the undoped and different catalysts doped to NaAlH₄. Referring to this table, all the catalysts have effectively reduced the apparent activation energy of the NaAlH₄ for the first and second step dehydrogenation. As can be seen from the table, K₂NiF₆-doped NaAlH₄ does not have the best reduction in the 𝐸ₐ value as compared to the other catalysts. The NaAlH₄-doped with NiFe₂O₄ shows the lowest 𝐸ₐ value which is 54.3 and 73.1 kJ/mol, for the first and second step dehydrogenation specifically. However, the addition of K₂NiF₆ still gives the positive effect on the reduction of the apparent activation energy of NaAlH₄.

Figure 6 shows the morphologies of the pure NaAlH₄, pure K₂NiF₆ milled NaAlH₄, and NaAlH₄ + 5 wt % K₂NiF₆. The scanning electron microscopy (SEM) image shows an irregular shape with the average particle size was in the range of 100 μm for the pure NaAlH₄ (Figure 6a). The pure K₂NiF₆ without further treatment had a smaller particle size which is smaller than 100 μm (Figure 6b). In addition, after the milling process,

Table 1. Comparison of Activation Energy (𝐸ₐ) of NaAlH₄ Doped with Different Catalysts

| samples                          | 1st-step 𝐸ₐ (kJ/mol) | 2nd-step 𝐸ₐ (kJ/mol) |
|----------------------------------|-----------------------|----------------------|
| pristine NaAlH₄                  | 116.2                 | 149.3                |
| pristine NaAlH₄                  | 114.2                 | 156.8                |
| as-received NaAlH₄              | 113.7                 | 142.5                |
| as-milled NaAlH₄ (this work)    | 113.8                 | 142.6                |
| NaAlH₄ + TiB₂                    | 106.5                 | 105.5                |
| NaAlH₄ + Cr₂O₃                  | 98.9                  | 119.1                |
| NaAlH₄ + TiN                    | 91.7                  | 99.9                 |
| NaAlH₄ + K₂NiF₆ (this work)     | 89.9                  | 99.6                 |
| NaAlH₄ + NbF₄                   | 88.2                  | 102.9                |
| NaAlH₄ + CeAl₄                 | 80.93                 | 98.94                |
| NaAlH₄ + CeCl₃                 | 80.76                 | 97.27                |
| NaAlH₄ + TiO₂                  | 73.5                  | 101                  |
| NaAlH₄ + Nb₂O₅                 | 65.3                  | 85.6                 |
| NaAlH₄ + MnFe₂O₄               | 57.7                  | 75.1                 |
| NaAlH₄ + NiFe₂O₄               | 54.3                  | 73.1                 |

Figure 5. DSC traces for the second-step dehydrogenation of (a) NaAlH₄, (b) NaAlH₄ + 5 wt % K₂NiF₆, and (c) Kissinger plot for the second-step dehydrogenation of NaAlH₄ and NaAlH₄ + 5 wt % K₂NiF₆.
the particles size of the doped and undoped sample reduced drastically. However, the particle size of the milled NaAlH₄ (Figure 6c) was inhomogenous and agglomerated. This may be the reason for the slightly reduced onset temperature in the TPD results for milled NaAlH₄ as shown in Figure 1. It can be observed that the particles of the NaAlH₄-doped with 5 wt % K₂NiF₆ (Figure 6d) were dispersed more homogeneously and less agglomeration than those of the undoped NaAlH₄. The particle size appeared to have a finer surface and reduced drastically as compared with the undoped sample.

The particle sizes of the pure NaAlH₄ and NaAlH₄ + 5 wt % K₂NiF₆ are determined by Image J software and the particle size distributions are plotted in histograms as shown in Figure 7. On the basis of the histograms, the estimated average of particle sizes are 21.86 and 0.14 μm for the pure NaAlH₄ and NaAlH₄ + 5 wt % K₂NiF₆, respectively. This indicates that the milling process and the addition of catalyst remarkably reduced the particle size of the compound. The particle size reduction can increase the specific surface area and reduce the diffusion length of hydrogen within the particles which can lead to the increment of the kinetic rates as reported by previous studies.42,43

Figure 8 presents the X-ray diffraction (XRD) patterns of the pure NaAlH₄ and pure K₂NiF₆. The purity of the NaAlH₄ and K₂NiF₆ compounds are corroborated by the XRD patterns of the as-received NaAlH₄ (JCPDS card no. 22-1337), as well as the as-received K₂NiF₆ (JCPDS card no. 22-837). This result is correlated with data previously reported.39,44

The XRD patterns as in Figure 9 exhibit the milled NaAlH₄ and the milled K₂NiF₆-doped with 5 and 20 wt % K₂NiF₆ after 1 h ball milling. Figure 10. FTIR spectra of the milled NaAlH₄, NaAlH₄ + 5 wt % K₂NiF₆, and NaAlH₄ + 20 wt % K₂NiF₆ after 1 h ball milling.

K₂NiF₆ peaks appeared. This demonstrates that the K₂NiF₆ additive does not react with NaAlH₄ and remains stable throughout the whole process of milling. The present finding seems to be consistent with the result reported by Huang et al.,11 which found that no reaction had occurred between NaAlH₄ and NiFe₂O₄ throughout the ball milling process in their study.

In order to confirm whether there is a reaction occurring or not after the ball milling process, Fourier transform infrared spectra (FTIR) measurement was performed for milled NaAlH₄ and NaAlH₄-doped with 5 and 20 wt % K₂NiF₆ as shown in Figure 10. For milled NaAlH₄, two intense bands appeared at 1654 and 900 cm⁻¹ which represent the characteristic stretching mode and the bending mode of the Al−H vibration in the AlH₄ group, respectively. The pattern is almost closed with the previous studies.12 Interestingly, after being doped with 5 and 20 wt % of K₂NiF₆ similar stretching and bending mode are observed but slightly reduced in
intensity. This indicated that increasing the wt % of the additive weakening the Al–H bonds of NaAlH₄. All the bands are still of NaAlH₄ and no Na₃AlH₆ band is observed. Thus, it can be deduced that there is no reaction occurring between the K₂NiF₆ and the host material of NaAlH₄ throughout the ball milling process. The XRD measurement was carried out on the K₂NiF₆-doped NaAlH₄ sample in order to verify the phase structure after the dehydrogenation process. Figure 11 presents the XRD pattern of the NaAlH₄-doped with 5 and 20 wt % K₂NiF₆ after dehydrogenation at 300 °C. The decomposition temperature and dehydrogenation which significantly accelerates the disintegration of NaAlH₄ as suggested by previous studies.²⁰,⁴⁷ It is likewise recommended that the in situ formed catalyst indicates higher catalytic activity and superior stability than those of the externally added catalyst in view of the better homogeneity and finer particle sizes.⁴⁸ Hence, it is evidence from the SEM result that the NaAlH₄-doped K₂NiF₆ compound has smaller and finer particle sizes. These smaller particle sizes give larger surface areas which can reduce the diffusion length and improved the dehydrogenation kinetics as well as lowering the onset decomposition temperature as reported in the literature.⁴⁹,⁵⁰ Furthermore, it is believed that, the establishment of the new active species may facilitate the dehydrogenation process by functioning as the active sites for nucleation and growth of the dehydrogenated product associated with the shortening of the diffusion paths among the reaction ions and thus decreasing the kinetic barriers and improving the dehydrogenation kinetics.⁵¹ Therefore, it is reasonable to believe that the in situ formed active species; AlNi, KH, and NaF will work simultaneously and work synergistically for a significant enhancement on the hydrogen storage properties of NaAlH₄.

### CONCLUSIONS

As a conclusion, the addition of K₂NiF₆ has successfully lowered the decomposition temperature and boosts the kinetic performance of NaAlH₄. The 5 wt % K₂NiF₆-doped compound gave the optimal value for the improvement of the dehydrogenation properties of NaAlH₄. The sample doped with 5 wt % K₂NiF₆ started to release hydrogen at 160 °C, which is 30 °C lower as compared to the milled NaAlH₄. The dehydrogenation kinetic revealed that the doped sample showed faster hydrogen released, with 5 wt % K₂NiF₆ can release about 1.5 wt % of hydrogen in 30 min and at 150 °C. While the milled NaAlH₄ only released about 0.2 wt % within the same time and temperature. The apparent activation energy calculated from Kissinger plots were reduced from 114.7 and 125.2 kJ/mol for undoped NaAlH₄ to 89.9 and 99.6 kJ/mol after being doped with K₂NiF₆ for the first and second-step of dehydrogenation, respectively. In addition, the particles size also reduced and less agglomerated with the addition of K₂NiF₆. This can help to improve the hydrogen sorption of NaAlH₄. These result demonstrated that the active species that formed in situ, the AlNi, KH, and NaF are responsible for the enhancement of the dehydrogenation properties of NaAlH₄.

### EXPERIMENTAL DETAILS

The commercial starting materials, NaAlH₄ (purity ≈ 98%) and K₂NiF₆ (purity ≈ 99%) were obtained from Sigma-Aldrich and were utilized without further treatment. All handling of the samples were operated in a glovebox (MBraun Unilab) with an argon atmosphere to avoid from humidity and oxygen. NaAlH₄-doped with different wt % of K₂NiF₆ (5, 10, 15 and 20 wt %) were prepared via the planetary ball mill (NQM-0.4). This process was conducted for 1 h with a rotation speed of 400 rpm for three cycles in a different direction. Each of the sample was sealed in stainless steel jars together with stainless steel balls. Similarly, milled NaAlH₄ was also prepared in the same manner as a reference. The decomposition temperature and dehydrogenation kinetics of the samples were investigated using a Sievert-type pressure-composition-temperature equipment from Advanced
Material Corporation. For the TPD experiment, all the samples were heated to 300 °C at a heating rate of 5 °C/min. The isothermal dehydrogenation kinetics was conducted at 150 °C under 30 atm hydrogen pressure. The DSC measurement was conducted on Mettler Toledo TGA/DSC 1. The samples were operated at four different heating rates starting from room temperature to the desired temperature with the influence of 50 mL/min of an argon flow.

Characterizations of the samples were carried out using a SEM (JEOL JSM-6360LA). The phase compositions were characterized using an XRD method with Cu Kr radiation (Rigaku MiniFlex X-ray diffractometer). The diffraction angle of the samples were scanned between 20 and 80° at a scan speed of 2.00°/min. The FTIR measurement of the samples after ball milled was recorded on the IRTTracer-100 spectrophotometer using attenuated total reflection in the transmission mode. The spectral resolution was 4 cm⁻¹ and the scans were taken from 750 to 4000 cm⁻¹.

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Notes

The authors declare no competing financial interest.

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