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# Reversible hydrogen decomposition of KAlH<sub>4</sub>

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## Abstract

We report that potassium aluminum tetrahydride, KAlH<sub>4</sub>, exhibits a rapid reversible hydrogen decomposition reaction without any aid of external catalysts. This is significantly different from the reaction mechanism of NaAlH<sub>4</sub> and LiAlH<sub>4</sub>, in which the homogeneous doping of the transition metal catalyst is essential for the reversibility and fast kinetics. The reversible dehydrogenation and hydrogenation were clearly observed without a catalyst over a temperature range 250-340 °C under <10 bar of hydrogen. Hydrogen storage ability was above 3.5 wt.% (81.4% of the theoretical value of 4.2 wt.%). KAlH<sub>4</sub> may be a competitive option with a lightweight but high-temperature metal hydride system such as Mg<sub>2</sub>NiH<sub>4</sub>. These findings will also provide renewed guidelines for understanding the reaction mechanism of the catalyzed alanates as reversible hydrogen storage materials.

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## 1. Introduction

Intermetallic compounds, such as in BCC, Laves, and AB<sub>5</sub> phases, are well known as hydrogen storage materials. However, for practical use under ambient temperature and pressure, their low energy density per unit weight is recognized as a fatal disadvantage. For instance, the hydrogen capacity of the most popular LaNi<sub>5</sub>-based alloys operating at moderate temperature does not exceed 1.4 wt.%. Whereas an Mg-based alloy, for example Mg<sub>2</sub>Ni, shows a hydrogen capacity as high as 3.6 wt.% but its operating temperature is too high (ca. 330 °C). In conventional hydrogen storage metal alloys, the reversible hydrogenation and dehydrogenation is based on the topotactic reaction, in which the structure of the host metal framework is allowed to change only by atomic displacement, with no diffusive rearrangement. The host must be stable enough to tolerate repeated hydrogen insertion and extraction over a finite range of solid solution.

In 1997, NaAlH<sub>4</sub> was introduced as a novel lightweight reversible hydrogen storage material by Bogdanovic and

Schwickardi [1]. The reaction mechanism is based on reversible decomposition, in which all of the elements migrate during the reaction. Jensen and Gross [2] have proposed that neutral cluster of AlH<sub>3</sub>, leaving the (NaH) neutral clusters, are the main mobile species. This is significantly different from the reaction mechanisms of conventional metal hydrides using interstitial crystallographic sites for hydrogen atoms, hydrogen being the only mobile species. Another feature of interest in Bogdanovic and Schwickardi's pioneering work is that they added a catalyst to NaAlH<sub>4</sub> to enhance the kinetics and reversibility of the reaction. The major role of the catalyst is believed to be to cut  $Al^{3+}-H^-$  ionic bonds to form an Al-rich surface and H<sub>2</sub>. These findings reported in 1997 spurred the interest of the scientific community and a number of groups have started to work on this material [1-21].

Thermolysis of  $NaAlH_4$  releases hydrogen and it consists of three steps of dehydrogenation. The first two steps are used for the reversible hydrogen releasing reaction.

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 (H_2: 3.7 \text{ wt.\%})$$
 (1)

$$Na_3AlH_6 \rightarrow 3NaH + Al + 3/2H_2 (H_2: 1.9 \text{ wt.\%})$$
 (2)

$$3NaH \rightarrow 2Na + 3/2H_2 \ (H_2: 1.9 \text{ wt.\%})$$
 (3)

In step 1, NaAlH<sub>4</sub> decomposes to  $Na_3AlH_6$ , followed by

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decomposition to NaH in step 2. Due to its high binding energy, NaH is not applicable for a reversible hydrogen source. Before the decomposition of NaH, theoretically 5.6 wt.% of hydrogen is reversibly discharged from NaAlH<sub>4</sub>. Other alanates, such as Na<sub>2</sub>LiAlH<sub>6</sub>, LiAlH<sub>4</sub>, and Li<sub>3</sub>AlH<sub>6</sub>, were also reported to exhibit reversible hydrogenation/ dehydrogenation upon doping with a titanium catalyst for kinetic enhancement. However, potassium aluminum tetrahydride, KAlH<sub>4</sub>, which is also in the family of  $A^{+}(AlH_{4})^{-}$ -type ionic complex hydrides, has not yet been explored with an eye to hydrogen storage applications. Although  $KAlH_4$  shows an apparent disadvantage in terms of its gravimetric hydrogen capacity as compared to  $NaAlH_4$  and  $LiAlH_4$ , the thermodynamic and kinetic parameters for KAlH<sub>4</sub> will shed light on the reaction mechanism of the catalyzed alanates.

The purpose of our work is to investigate KAlH<sub>4</sub> as a possible reversible hydrogen storage material and this led us to the discovery that this material has an easy and reversible hydrogenation/dehydrogenation reaction over a temperature range of 250–300 °C under <10 bar of H<sub>2</sub>. The emphasis is on reactions proceeding without any assistance from the transition metal catalyst.

#### 2. Experimental

## 2.1. Synthesis of $KAlH_4$

 $\text{KAlH}_4$  powder was synthesized based on the method proposed by Dymova et al. [22]. Under high pressure of hydrogen (>175 bar) at high temperature (270 °C), the following reaction proceeds.

$$KH + AI \xrightarrow[>175 \text{ bar}]{270 °C} KAIH_4$$
(4)

KH in mineral oil was purchased from Aldrich Co. and was filtered and washed several times with hexane to separate KH from the oil, followed by evaporation of the solvent. The filtration process was done in a glove box filled with argon. The mixture of KH and Al (>99.5% Wako Co.) was mechanically milled in 35-ml milling containers with three steel balls with a diameter of 10 mm and 40 steel balls with a diameter of 5 mm for 30 min at 500 rev./min (Fritsch Pulverisette 7). The mixture was then transferred to a 100-ml autoclave (Taiatsu techno<sup>®</sup> TVS-N2), and the autoclave was filled with approximately 135 bar of hydrogen gas at room temperature, followed by heating to 270 °C. This resulted in increasing the pressure of the autoclave to more than 175 bar. The temperature was maintained for 3 days.

#### 2.2. Phase identification

X-ray diffraction measurement was performed with RINT2000 (Rigaku Co.) using  $CuK\alpha$  radiation to identify

the phases. Because of the hygroscopic nature of  $KAIH_4$ , the sample was set in an argon environment and was placed in a small sealed container with clear plastic windows that allowed X-rays to irradiate the sample.

## 2.3. Gas identification

Prior to the following experiments, a thermal programmed desorption (TPD) measurement was performed in a high vacuum to confirm that desorbed gas is hydrogen. The gas was identified using a quadrupole mass spectrometer equipped in an RGA detector (SRS RGA100). The temperature of the sample was increased at a rate of 2 °C/min during the measurement.

#### 2.4. Dehydrogenation monitoring

The degree of dehydrogenation of  $\text{KAlH}_4$  under ambient pressure of hydrogen was measured using a TPD measurement system of original design. The desorbed hydrogen gas in the sample holder is vented through a mass flow meter (Lintec MC-3102E 10SCCM) and a check valve to outside of the system so that the internal pressure is kept constant. The quantity of desorbed gas from the sample was obtained by measuring the positive deviation from the background flow rate, measured using the mass flow meter. The sample was heated at a rate of 2 °C/min from room temperature to 500 °C. The background data were accumulated without sample.

#### 2.5. Rehydrogenation monitoring

KAlH<sub>4</sub> was heated to 390 °C, so it decomposed into KH, Al, and H<sub>2</sub>, and then naturally cooled down to room temperature in H<sub>2</sub> at 1 bar. For the hydrogenation, the decomposed compound of KH and Al were exposed to approximately 9 bar of hydrogen gas. The pressure change in the sample holder was then monitored while the compound was heated from room temperature to 500 °C at rate of 0.5 °C/min. The negative deviation from blank data indicates the onset of rehydrogenation.

#### 2.6. Cycle tolerance test

In the dehydrogenation cycle,  $KAlH_4$  was heated at 1 bar from room temperature to 370 °C at a rate of 2 °C/min to dehydrogenate the sample to decompose it into KH, Al, and H<sub>2</sub>. The amount of desorbed hydrogen gas was recorded, as described in Section 2.4.

In the hydrogenation cycle, after each dehydrogenation process, 10 bar of hydrogen gas were slowly induced into the sample holder at room temperature, and the sample was heated for 10 h at two different constant temperatures. In the first three hydrogenation cycles, the sample was heated at  $250 \,^{\circ}$ C, and in the fourth hydrogenation cycle, the sample was heated at  $330 \,^{\circ}$ C.



Fig. 1. X-ray powder diffraction measurement of  $KAlH_4$ , synthesized from KH and Al at 270 °C at >175 bar of hydrogen (reaction (4)).

The overall dehydrogenation and hydrogenation cycle was repeated five times.

#### 3. Results and discussion

Fig. 1 shows the result of X-ray diffraction measurement of the synthesized compound indicating that  $KAlH_4$  was formed by reaction (4), though a small amount of unreacted residual aluminum was included.

Fig. 2 shows the dehydrogenation behavior of KAlH<sub>4</sub>. The expected decomposition processes are as in reactions (5)-(7), in analogy with the decomposition process of NaAlH<sub>4</sub>.

$$3KAlH_4 \rightarrow K_3AlH_6 + 2Al + 3H_2 (H_2: 2.9 \text{ wt.\%})$$
 (5)



Fig. 2. TPD measurement of KAlH<sub>4</sub> dehydrogenation. The sample was heated from room temperature to 500 °C at the rate of 2 °C/min. Please refer to reactions (5)–(7) for the decomposition reaction.

$$K_3AlH_6 \rightarrow 3KH + Al + 3/2H_2 \ (H_2: 1.4 \text{ wt.\%})$$
 (6)

$$3KH \rightarrow 3K + 3/2H_2 \ (H_2: 1.4 \text{ wt.\%})$$
 (7)

The first dehydrogenation occurred at approximately 300 °C to decompose to  $K_3AlH_6$  and Al (reaction (5)), and 2.4 wt.% of hydrogen was released, which is comparable to its theoretical value of 2.9 wt.%. The second and third dehydrogenation steps, reactions (6) and (7), occurred approximately at 340 and 430 °C, respectively, and 1.3 and 1.2 wt.% of hydrogen was released. These values agree reasonably well with the theoretical values, 1.4 wt.% for both steps.

It seems, therefore, that the decompositions followed reactions (5)–(7) and the initial content of KAlH<sub>4</sub> in the sample was more than 80%. The rest of the content is assumed to be aluminum, based on the XRD data shown in Fig. 1.

Fig. 3 shows the process of rehydrogenation to KAIH<sub>4</sub> from KH and Al. The measurement was carried out under 9 bar of hydrogen while the temperature of the sample was slowly increased to 500 °C starting from a room temperature. The gradual rehydrogenation of the sample started below 200 °C. The rate of rehydrogenation increased until the hydrogenation reaction stopped at around 340 °C.

The preceding experiments lead to the important conclusion that, even without a catalyst, potassium alanate exhibits reversible decomposition under much less hydrogen pressure than Ti-doped sodium alanate, whereas the operating temperature is much higher (Ti/NaAlH<sub>4</sub> 150–250 °C; KAlH<sub>4</sub> 300–400 °C).

A repeated-cycle-test showed that the reaction is essen-



Fig. 3. The full line indicates the reduction of hydrogen gas pressure in the sample holder, indicating the hydrogenation from KH and Al to potassium alanate, and the dashed line is the result of a blank measurement. After dehydrogenation of KAlH<sub>4</sub> to KH and Al at 390 °C, the sample was cooled down to room temperature under 1 bar of H<sub>2</sub> gas and heated at a rate of 0.5 °C/min to 500 °C under 9 bar of hydrogen, and the pressure changes in the sample holder were monitored.



Fig. 4. Repeated-cycle-test of KAlH<sub>4</sub>. For dehydrogenation, the sample was heated to 370 °C at a rate of 2 °C/min. For hydrogenation the sample was hydrogenated under 10 bar of hydrogen while heating the sample at a constant temperature.

tially reversible but the amount of absorbed hydrogen decreases as the number of cycle increases, except in the fifth cycle (Fig. 4 and Table 1). The absorption temperatures for the first through third hydrogenation cycles were 250 °C and for the fourth hydrogenation cycle, 330 °C. The charging condition was 10 h under 10 bar of hydrogen for all experiments. The only difference in the fifth dehydrogenation cycle was the charging temperature. Therefore, the hydrogenation was completed at 330 °C but not at 250 °C, which meant that the capacity decrease up to four cycles was not critical but was a kinetic problem, e.g. 10 h of hydrogenation to be completed.

The formation energy for KH and NaH is similar (-56.3 and -56.3 kJ/mol, respectively), while that for KAlH<sub>4</sub> and NaAlH<sub>4</sub> differs by about 30 kJ/mol ( $\Delta H_f$  for KAlH<sub>4</sub> and NaAlH<sub>4</sub> is -183.7 and -155.5 kJ/mol, respectively) [23]. This shows that for the reaction MAlH<sub>4</sub> $\rightarrow$ MH+Al+ 3/2 H<sub>2</sub>, the enthalpy change with M=K would also be about 30 kJ/mol more endothermic than with M=Na. This accounts for the higher decomposition temperature of KAlH<sub>4</sub> (300–400 °C) than NaAlH<sub>4</sub> under ambient H<sub>2</sub> pressure. What is remarkable is that with a slight increase

Table 1 A summary of the cycle tests

Peak	Dehydrogenation (wt.%)				
	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
First	2.34	2.01	1.77	1.40	2.47
Second	1.22	1.28	1.27	1.23	1.26

The amount of hydrogen released for each peak is shown. The first peak started at about 300  $^\circ\!C$  and the second peak started at about 340  $^\circ\!C$ .

in  $H_2$  pressure from 1 to 10 bar, at the temperature of decomposition, the reaction can be driven to the reverse direction for the potassium case. In addition, considering Figs. 3 and 4, kinetic enhancement is abrupt at a higher temperature (>300 °C). Such a situation makes KAIH<sub>4</sub> active as a high-temperature reversible hydrogen storage medium without the aid of an external catalyst and rechargeable at low pressure. Further thermodynamic investigations based on the data accumulated for the Pressure–Composition–Temperature (PCT) diagrams will lead to more quantitative understanding.

## 4. Conclusion

The reversible hydrogen decomposition of KAlH<sub>4</sub> is demonstrated. The hydrogen ability was above 3.5 wt.%. Under 10 bar of hydrogen in a temperature range of 250-330 °C, the reversible reaction smoothly proceeds without any catalyst, which is different from the reactions of NaAlH<sub>4</sub> and LiAlH<sub>4</sub>, in which homogeneous doping of a transition metal catalyst is essential for reversibility and good kinetics. These findings provide new guidelines for a systematic understanding of the reversible hydrogen decomposition of the alanate family.

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