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Hydrogen reactivity of Li-containing hydrogen storage materials

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Abstract

In hydrogen energy systems, the hydrogen storage alloy is expected as one of important materials for energy storage and transportation. However, they weigh so much for sufficient amounts of hydrogen, therefore, light hydrogen storage materials with much higher storage capacities are required. Alkaline complex hydrides are promising candidates as light hydrogen storage materials. In this study we tried to prepare a sample based on the Na–Li–Al system using the dry process of ball-milling as mechanical synthesis and investigate their hydrogen reaction characteristics. The same study for the sample with 10 wt.% La_2O_3 was also carried out and its hydrogen reactivity compared. The starting materials were $LiAlH_4$, NaH. They were ball-milled with hexane dehydrated in 1 bar Ar. The hydrogen reactivity of the samples obtained were measured by the high-pressure Sievert's type apparatus. For the sample of NaH+LiH+Al, about 1.9~2.0 wt.% of hydrogen was absorbed reversibly within 150 min. The addition of 10 wt.% La_2O_3 improved both the ab/desorption reaction rate and cyclable hydrogen capacity.

Keywords: Hydrogen storage; Alanates; Mechanical alloying; Lanthanum oxide

1. Introduction

In hydrogen energy system, hydrogen storage alloys are expected to play some important roles, such as hydrogen storage and transportation. However, they weigh so much for sufficient amounts of hydrogen absorbed, therefore, lightweight hydrogen storage materials with higher storage capacities are required.

In 1997, Bogdanović and Schwickardi [1] reported some new hydrogen storage materials of Ti-doped alkali metal complex hydrides, $NaAlH_4$, Na_3AlH_6 and Na_2LiAlH_6 prepared by liquid reactions. Especially Ti-doped Na_2LiAlH_6, absorbed more than about 2.6 wt.% of hydrogen at 484 K, under 4.0 MPa H_2 successfully. The plateau pressure of Ti doped Na_2LiAlH_6 is about 1.4 MPa, which is about 2.0 MPa lower than that of Na_3AlH_6. After this report, many studies on $NaAlH_4$ and Na_3AlH_6 as hydrogen storage materials have been carried out from various points of view such as reaction kinetics [2], crystallographic analysis [3], microstructure examination [4] and so on. Sample preparation and catalyst-doping processes have been also explored. The preparation process based on reactions with the use of solvents needs, however, some complicated steps of purification and filtration. Additional severe conditions of high pressure of hydrogen above 100 atm and higher temperature are needed for the activation (1 atm=101325 Pa). A more simplified preparation process is, therefore, desired. From this point of view, some studies on fabricating alkali metal complex hydrides using mechano-chemical synthesis have been reported [5,6].

In this study, we have taken Li as a base metal, which is the lightest metal to form a metal hydride, and tried to prepare the sample based on the non-stoichiometric Na–Li–Al system without any catalytic dopant by ball milling. Some La_2O_3 powder was also given during the milling. Their hydrogen reactivity was investigated using the high-pressure Sieverts' type apparatus.

2. Experimental

The starting materials were NaH and $LiAlH_4$ (Wako Pure Chemical Co. Ltd.), and La_2O_3 (High Purity Chemical Co. Ltd.). At first, NaH was washed by filtration with hexane dehydrated to clear off the preservation mineral oil. Sample materials were weighed for the composition of

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Table 1
Ball milling conditions

Mill type	Rotary mill
Material of vial/balls	SUS 316L/SUS 304
Capacity of vial	70.33 cm^3
Ball diameter	35×0.95 cm
and the number	25×0.60 cm
Total weight of the sample to be milled	1.5 g
Capacity ratio of vial vs. balls	1.7:1
Weight ratio of balls vs. sample	70:1
Dispersion medium	Hexane dehydrated (<0.3 ppm H_2O)
Milling atmosphere	Ar (99.999%)
Rotating velocity	180 rpm
Milling period	30 h

NaH:$LiAlH_4$=1:1 ($NaLiAlH_5$) and additionally 10 wt.% of La_2O_3, then ball-milled under the same conditions as shown in Table 1. The mill we used was laboratory-scale one, which was a rotary mill from Irie Shokai Co. Ltd., not a planetary one. The milled samples obtained of 0.2 g each were loaded in the reaction bed attached with a stop valve under a glove box. All the processes mentioned above were carried under an inert gas atmosphere with low moisture content in a glove box. Their hydrogen reactivity was measured after setting on a high-pressure Sieverts' type apparatus. To confirm the phases and structure of the sample, X-ray diffraction (XRD) measurements were carried out by Miniflex (Rigaku Co.) with a Cu Kα X-ray source. Microstructural observation was carried out using scanning electron microscopy (SEM; Hitachi S-3200N+ Horiba EMAX5771W).

Because each sample obtained was hydride, before the absorption and desorption measurements, they were initially dehydrogenated by heating up to 543 K under a 0.15 MPa He atmosphere and then evacuated to 0.1 Pa. After the dehydrogenation, samples were cooled to 484 K under 0.3 MPa of He.

3. Results and discussion

The first dehydrogenation curve of the sample without La_2O_3 and XRD results are shown in Figs. 1 and 2, respectively. During heating up from room temperature to 543 K, the curve showed two steps. The first step began from 423 K, and the second from 483 K, which correspond to well-known thermal decomposition as shown as follows:

$$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \qquad (1)$$

$$1/3Na_3AlH_6 \leftrightarrow NaH + 1/3Al + 1/2H_2 \qquad (2)$$

In spite of the fact that the starting materials were NaH and $LiAlH_4$, aiming for the composition of $NaLiAlH_5$, this result suggests that the milled product contains mainly $NaAlH_4$ phase. However, if considering the loss of hydrogen amount in the sample induced by collision during ball milling, the ratio of released hydrogen amount does not correspond to the reaction expressed above, that is, some of hydrogen was possibly released during milling, while the ratio of hydrogen amount derived from the first step

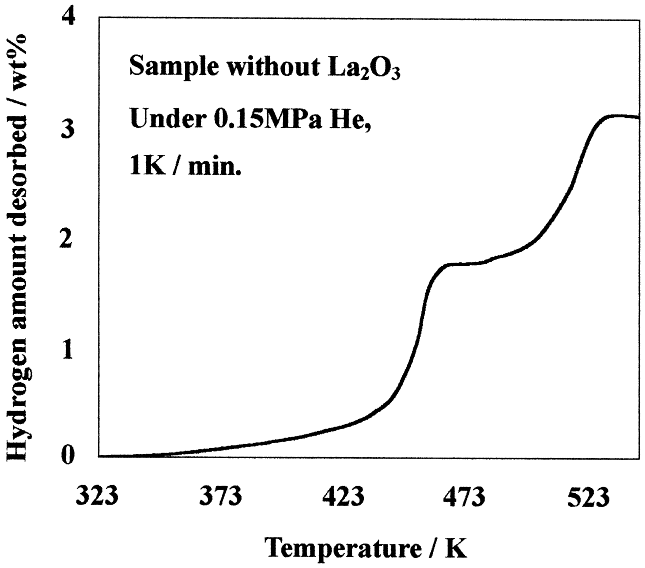

Fig. 1. The first dehydrogenation curve of the sample without La_2O_3.

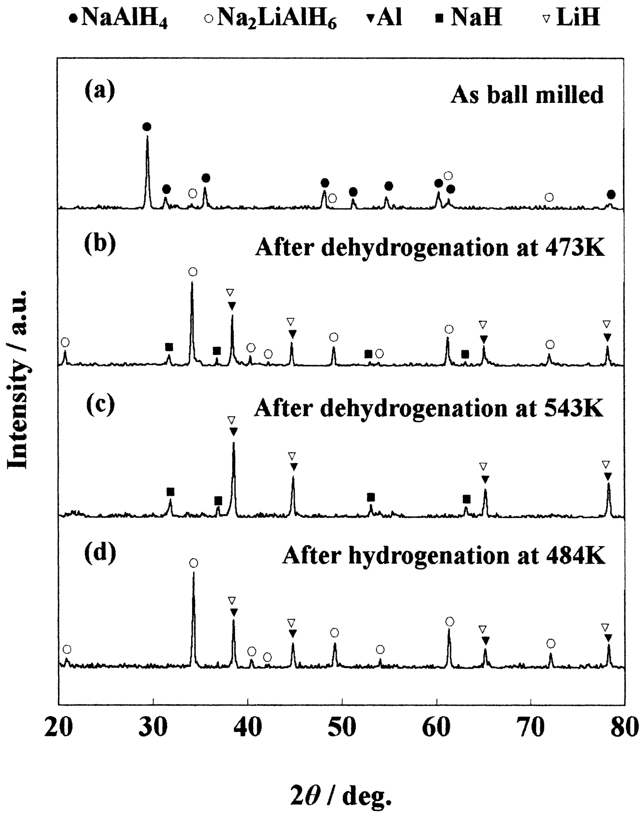

Fig. 2. X-Ray diffraction patterns for the sample without La_2O_3; (a) as ball milled, (b) after the first dehydrogenation at 473 K, (c) after the first dehydrogenation at 543 K, (d) after hydrogenation at 484 K.

and second step was not 2:1. The XRD results (Fig. 2a) also suspend this consideration. In the case of the sample with 10 wt.% La_2O_3, first dehydrogenation was yielded in the same manner.

After the first dehydrogenation, hydrogenation measurements were carried out under the same conditions at 484 K and 3.9 MPa of applied hydrogen pressure. Fig. 3 shows the first hydrogenation curves for the sample with and without La_2O_3. The hydrogen amounts absorbed for the sample with and without La_2O_3 were 1.98 wt.% each, which corresponds to $H/NaH+LiH+Al=1.13$. For the sample with 10 wt.% La_2O_3, the absorbed amount is expressed without the weight of La_2O_3. Comparing the curves of each sample, the initial reaction rate of the sample with 10 wt.% La_2O_3 is higher than that without La_2O_3.

After removing the residual hydrogen from the reaction bed, 0.15 MPa of He was introduced subsequently, then H_2 desorption measurement was carried out. Fig. 4 shows the second desorption curves for the sample with and without La_2O_3 at 484 K under 0.15 MPa of He atmosphere. The sample with 10 wt.% La_2O_3 also showed better kinetics than that without La_2O_3 in dehydrogenation as it did in hydrogenation.

The results of XRD measurements for the sample without La_2O_3 at each stage of ‘‘As ball milled’’, ‘‘After the first dehydrogenation at 473 K’’, ‘‘After the first dehydrogenation at 543 K’’ and ‘‘After the first hydrogenation’’ are shown in Fig. 2. As previously mentioned, milled products contained some different hydride phases, such as $NaAlH_4$ and Na_2LiAlH_6 (see Fig. 2a). Some of their decomposition products, NaH, LiH, and Al react during the first dehydrogenation resulting in Na_2LiAlH_6 phase (see Fig. 2b and c). As some of the reasons why there are no obvious peaks containing lithium, e.g. LiH in Fig. 2a, it should be considered that the decrease of grain size and introduction of defects by ball milling [7]. These factors could weaken the peak intensity and broaden the peak width. Therefore it is possible to suggest that LiH exists behind the background as a result of these effects. It can be followed by a result that the observed peak width of $NaAlH_4$ also seems to be relatively wide. The reappearance of LiH phase in Fig. 2b can be due to an effect of recovery and recrystallization caused by subsequent heating.

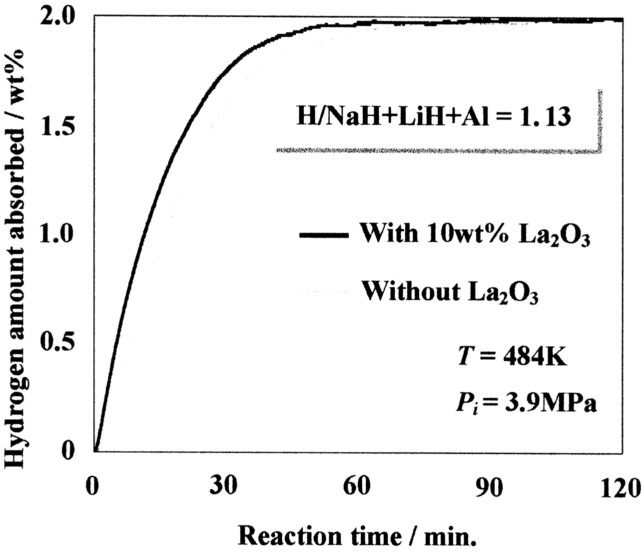

Fig. 3. The first hydrogenation curves of the sample with and without La_2O_3.

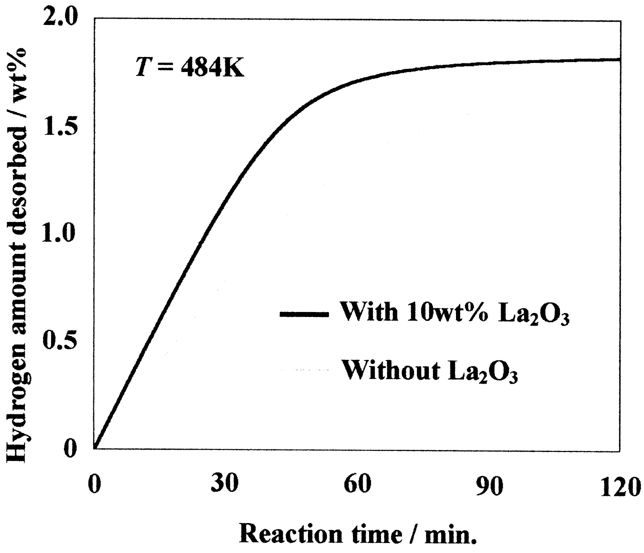

Fig. 4. The second dehydrogenation curves of the sample with and without La_2O_3.

Fig. 5 shows a SEM image of the sample powder ball milled with 10 wt.% La_2O_3. The white color indicates the existence of La_2O_3. An almost homogeneous dispersion of La_2O_3 caused by ball milling was confirmed from the image.

A remarkable effect by addition of La_2O_3 was shown in cycling behavior. Fig. 6 shows the hydrogen capacity in the course of four de/rehydrogenation open cycles and its

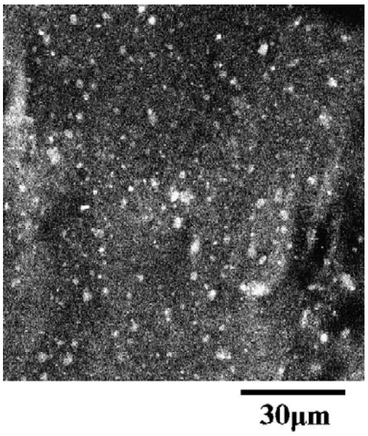

Fig. 5. SEM image of the sample powder ball milled with 10 wt.% La_2O_3, shown as white color.

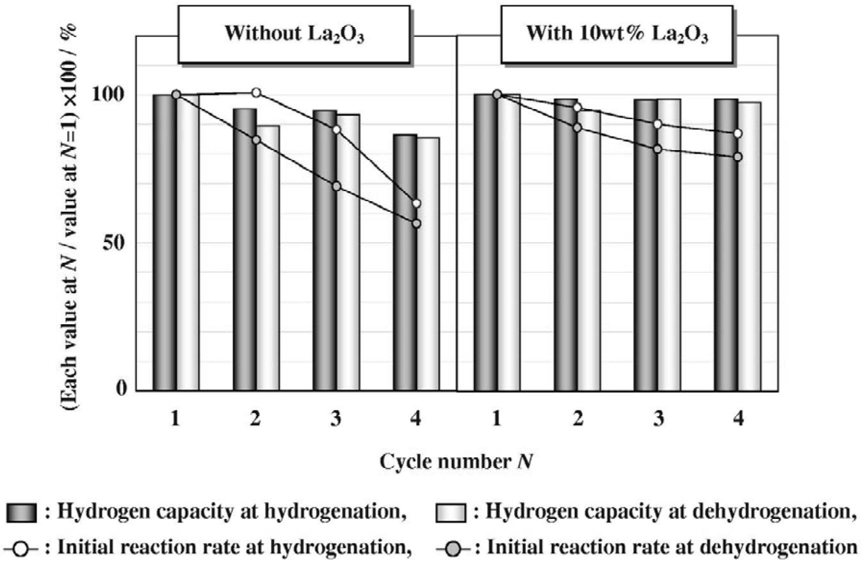

Fig. 6. Comparison of hydrogen capacity and reaction rate in the course of four re/dehydrogenation open cycles for the sample with and without La_2O_3.

initial reaction rate at each reaction. After the fourth cycle, the hydrogen capacity at hydrogenation decreased to 86% for the sample without La_2O_3, while the sample with 10 wt.% La_2O_3 remained at 98% of hydrogen capacity. A similar effect was also shown in the initial reaction rate.

From the pressure dependence of initial reaction rate, the rate determining step can be investigated [8]. The dependence coefficient; n of $v \propto p^n$ indicates the rate determining step of the molecular dissociation ($n=1$) or permeation/diffusion of atomic hydrogen ($n=0.5$). For samples with and without La_2O_3, H_2 dissociation seems to be the rate determining step as shown in Fig. 7. Additionally, the sample with La_2O_3 shows a higher dissociation rate, i.e., La_2O_3 seems to act as a catalytic substance in alkali-Al hydrogenation. The catalytic effect of La_2O_3 was also reported elsewhere [9].

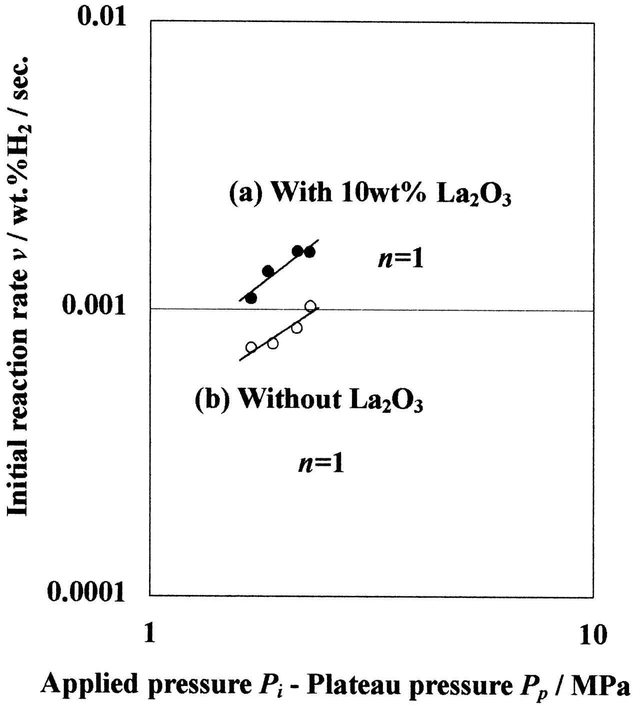

Fig. 7. Pressure dependence of initial reaction rate for the sample (a) with 10 wt.% La_2O_3 and (b) without La_2O_3.

4. Conclusion

In this paper the hydrogen reactivity of alkali metal complex hydrides prepared by ball milling $NaH+LiAlH_4$ as the starting material, and the effect of the addition of La_2O_3 powder were investigated. The hydrogen capacity of the sample at 484 K and 3.9 MPa of hydrogen pressure was about 1.9~2 wt.%, which decreased to 1.7 wt.% at several cycles without La_2O_3 powder. This small value is caused by the absorption reaction of Na_2LiAlH_6. This phase was confirmed by XRD, although initially we intended a non-stoichiometric Na–Li–Al system for obtaining higher concentration of H. The addition of La_2O_3 resulted in enhancing the dissociative reaction rate and keeps hydrogen capacity and reaction rate in the sorption cycles.

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