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Doping effect of Nb species on hydrogen desorption properties of AlH_3

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ABSTRACT:

Hydrogen desorption properties of $\alpha\text{-AlH}_3$ doped with Nb species (Nb, Nb_2O_5 and NbF_5) were investigated. Doping Nb species improved the desorption properties of AlH_3 . In particular, 1 mol% NbF_5 -doped AlH_3 showed the lowest onset desorption temperature at 60 °C. Compared with Nb- or Nb_2O_5 -doped AlH_3 , the fine distribution of dopant was successfully achieved in NbF_5 -doped AlH_3 . The apparent activation energy for hydrogen desorption of AlH_3 was slightly decreased with the dopant of NbF_5 . The improvement of desorption properties might be due to the finely dispersed Nb and/or AlF_3 , which are formed by the reaction between NbF_5 and AlH_3 (surface Al_2O_3).

Keywords: Hydrogen storage; Aluminum hydride, Niobium Fluoride, Niobium oxide, Catalytic effect

Introduction

Aluminum hydride (AlH_3) is an ideal off-board hydrogen storage material because of its high hydrogen capacities (10.1 mass% and 149 g H_2/L) and low desorption temperature ($<100^\circ\text{C}$) [1]. However, its desorption kinetics is not enough to meet the targets for practical applications [2]. Although AlH_3 is thermodynamically metastable at room temperature, it has been suggested that the surface Al_2O_3 film on AlH_3 particle would inhibit the spontaneous decomposition at room temperature [3]. Ball-milling can enhance the desorption kinetics of AlH_3 , likely due to an increase of oxide free surfaces on AlH_3 particles [3,4]. However, the mechanistic study showed that the real reason for the enhancement would be the small amount of desorption during ball-milling [5,6]. The formation of metallic Al particles on the hydride surface would serve as channels for the enhanced desorption and reduce the incubation period [5,6]. In addition, doping additives is one of the common strategies to enhance the kinetics of AlH_3 . For instance, the enhanced desorption properties have been reported for the reactive hydride composites between AlH_3 and other compounds (MgH_2 [7,8], LiBH_4 [9], MgCl_2 [10] *etc.*). Also, Ti is a well-known and effective catalyst for AlH_3 . The measurable enhancement of kinetics was observed by doping TiCl_3 with just a few ppm levels in solution during the AlH_3 synthesis [6].

Nb-based additives have been considered as effective dopants to improve hydrogen sorption reactions of hydrogen storage materials. For instance, Nb_2O_5 is a well-known catalyst for hydrogen absorption and desorption reactions of MgH_2 [11-14]. The composite, MgH_2 and 1 mol% Nb_2O_5 milled for 20 h, was able to absorb -4.5 mass% of hydrogen within 15 s at room temperature under lower pressure than 1.0 MPa and desorb -6.0 mass% of hydrogen at 160°C [12]. Also, NbF_5 is also an effective dopant for various kinds of hydrogen storage materials, such as MgH_2 [15,16], alanate [17,18] and borohydride [19] system. The composite, MgH_2 and 2 mol% NbF_5 milled for 5 h, was able to absorb -5.0 mass% of hydrogen in 12 s and desorb -4.4

mass% of hydrogen in 10 min at 300 °C [15]. Hydrogen desorption properties of MgH₂-AlH₃ nanocomposites were investigated in the previous study, where the addition of just 1 mol% NbF₅ remarkably destabilized γ -AlH₃ in the composite and led to its decomposition at room temperature [8]. Other fluorides, such as CeF₄ [20] and TiF₄ [21], were also effective additives to enhance the kinetics of MgH₂.

Thus, the addition of Nb-based additives showed the improvements of de/absorption properties of hydrogen storage materials. However, the effect of Nb-based additives on α -AlH₃ (the most stable phase of AlH₃) has not been reported. In the present study, Nb, Nb₂O₅, and NbF₅ (hereinafter called “Nb species”) were doped with α -AlH₃. Then, their hydrogen desorption properties and distribution states of Nb species were analyzed. In addition, the chemical bonding states of Nb and F were further investigated in the NbF₅-doped AlH₃ in order to clarify the reaction process.

Experimental Section

Sample Synthesis

Commercially available Nb (Kojundo Chemical Lab., 99.99 %), Nb₂O₅ (Kojundo Chemical Lab., 99.99 %), NbF₅ (Sigma Aldrich, 98 %) and AlF₃ (Sigma Aldrich, 99.9 %) were used as-received for this research. AlH₃ was prepared by the chemical reaction between LiAlH₄ and AlCl₃ in ether solution [22]. The samples were prepared by ball-milling AlH₃ and Nb species using a planetary ball-mill apparatus (Fritsch Pulverisette 7) with 21 g of stainless balls and 100 mg samples. The milling was performed under 0.1 MPa Ar with 200 rpm for 1 h with two cycles of 30/15 min operation/interval per each cycle. All material handlings were conducted under in a glovebox filled with purified Ar gas in order to avoid oxidation.

Characterization

Hydrogen desorption properties were examined by a thermogravimetry and differential thermal analysis equipment (TG-DTA, Bruker 2000SA) connected to a mass spectrometer (MS, ULVAC, BGM-102). The desorbed gases were carried from TG-DTA equipment to MS through a capillary by flowing high purity He gas as a carrier gas. The flow rate of He gas was set to 300 mL min⁻¹. The samples were heated from room temperature to 200 °C with a heating rate of 5 °C min⁻¹. The crystalline phases of samples were analyzed by powder X-ray diffraction (XRD, PANalytical, X'Pert-Pro with Cu K α radiation). The samples for XRD were placed on a glass plate in a glovebox and then covered with a polyimide sheet and sealed by grease in order to avoid the oxidation during the measurement. SEM-EDS measurements were performed to observe the distribution states of Nb species by using JIB-4600F/HKD, JEOL. The chemical bonding states of samples were studied by using X-ray Photoelectron Spectroscopy (XPS, Thermo Fisher Scientific, ESCALab 250Xi) with Al K α radiation.

Results and discussion

Doping effect of Nb species

Fig. 1 shows the hydrogen desorption properties of as-synthesized, ball-milled, and Nb species-doped AlH₃. As shown in Fig. 1(a) and (b), the hydrogen desorption temperature was reduced after ball-milling and doping with Nb species. The kinetic enhancement in the ball-milled AlH₃ would originate from the formation of metallic Al particles on the hydride surface as shown in the “Introduction” part. In fact, the mass loss of ball-milled AlH₃ (-9 mass%) was lower than that of as-synthesized AlH₃ (-10 mass%), suggesting the formation of metallic Al nuclei during ball-milling. It seemed that Nb- and Nb₂O₅-doped AlH₃ showed the improvement of the desorption kinetics compared with ball-milled one. Among all the samples, NbF₅-doped AlH₃ showed the

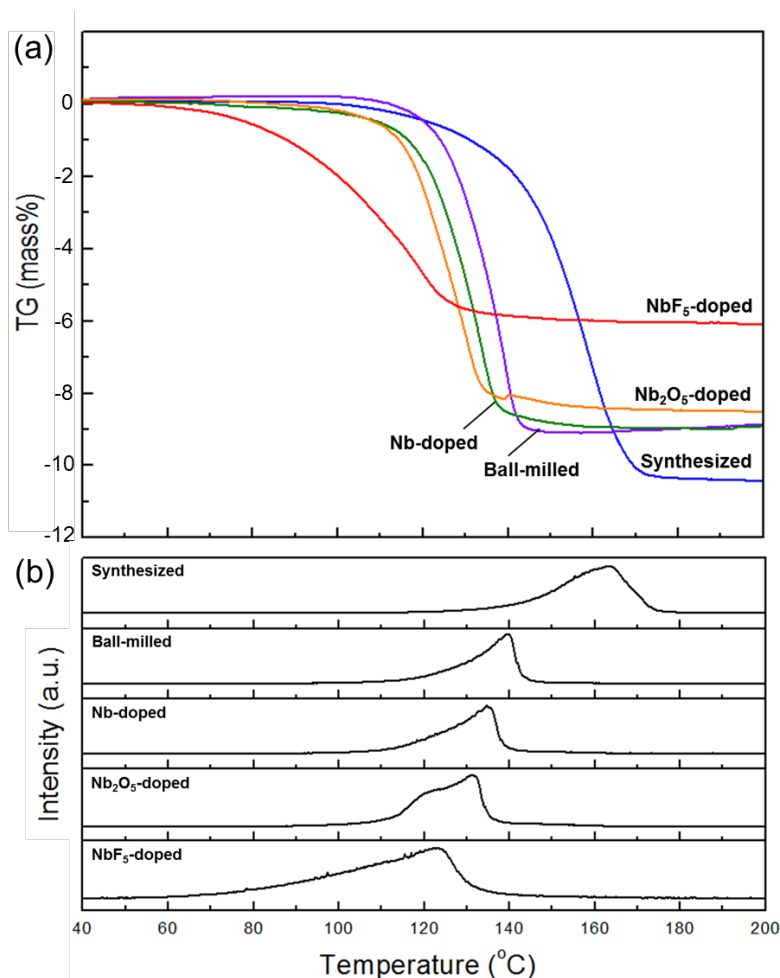


Fig. 1 (a) TG profiles and (b) MS ($m/z = 2$, H_2) profiles of as-synthesized, ball-milled, and Nb-, Nb_2O_5 -, NbF_5 -doped AlH_3 . The amount of Nb species was 1 mol% in each doped sample. The heating rate was $5\text{ }^{\circ}\text{Cmin}^{-1}$. The mass loss value was calculated by using the total system mass.

lowest desorption temperature. It started to desorb hydrogen from $60\text{ }^{\circ}\text{C}$ with a peak temperature at $122\text{ }^{\circ}\text{C}$ (Fig.1(b)). However, the hydrogen mass loss of NbF_5 -doped AlH_3 was only -6 mass%, whose value was the smallest among all the samples. We also measured the sample with 5 mol% NbF_5 doping, but most of the hydrogen was released during ball-milling (The desorbed hydrogen amount during heating was only -1 mass%). Thus, doping a large amount of NbF_5 promoted the decomposition during ball-milling.

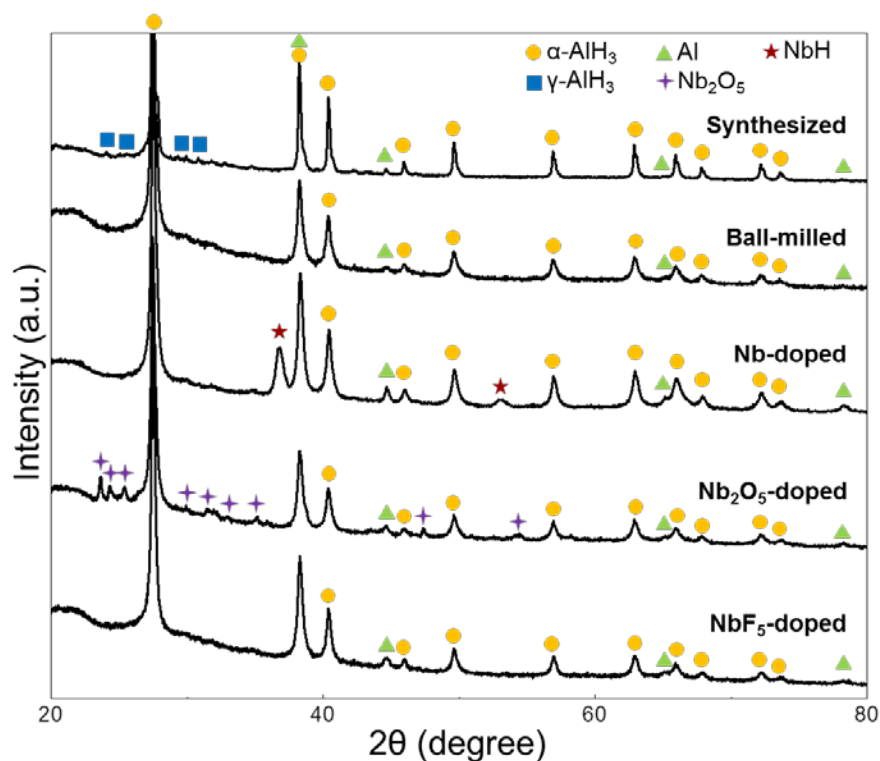


Fig. 2 XRD patterns of as-synthesized, ball-milled, and Nb-, Nb₂O₅-, NbF₅-doped AlH₃. The amount of Nb species was 1 mol% in each doped sample.

Fig. 2 shows the XRD patterns of samples. Although as-synthesized sample contained α -AlH₃ and a small amount of γ -AlH₃, ball-milled one did not contain γ -AlH₃, probably due to its transformation to α -AlH₃ during milling [23]. The formation of NbH was observed in the Nb-doped AlH₃, indicating Nb reacted with AlH₃ during ball-milling. In the Nb₂O₅-doped AlH₃, Nb₂O₅ was observed after milling. In the case of MgH₂ doped with Nb₂O₅, reduced Nb₂O_{5-x} phase was found on the surface of the samples [24]. Thus, the surface state of Nb₂O₅ could be also changed in the Nb₂O₅-doped AlH₃ system. On the other hand, Nb- or F-containing phases were not observed in any of the diffraction patterns of the NbF₅-doped AlH₃. In order to investigate the distribution states of Nb dopants, SEM-EDS measurements were conducted for NbF₅- and Nb₂O₅-doped AlH₃ (Fig. 3). As shown in Fig. 3(a), micron-particles containing Nb or F were not observed from the EDS mapping images. Similar results were obtained in the case of

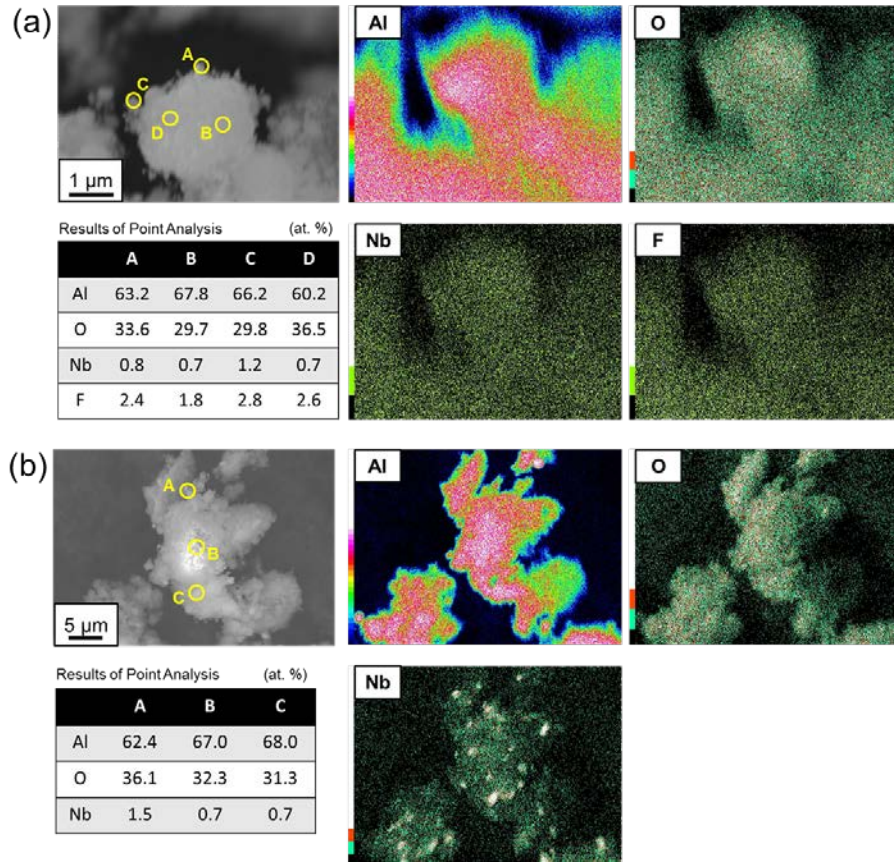


Fig. 3 SEM-EDS results of (a) 1 mol% NbF₅-doped AlH₃ and (b) 1 mol% Nb₂O₅-doped AlH₃. Secondary-electron images and EDS results (point analysis and mapping images) are shown.

5 mol% NbF₅ doping. On the other hand, the micron-particles containing Nb and O were clearly observed in the Nb₂O₅-doped AlH₃. Thus, it seemed that Nb and F distributed uniformly on the surface of AlH₃ in the NbF₅-doped AlH₃. The fine distribution of Nb and F was also observed in other NbF₅-doped hydride systems [8,25,26]. For instance, Kim *et al.* suggested that NbF₅ will melt during ball-milling and this promoted the presence of extremely fine Nb/NbH film on the surface of MgH₂ particles in NbF₅-doped MgH₂ system [25,26]. Thus, compared with Nb- or Nb₂O₅-doped AlH₃, the fine distribution of dopant was successfully achieved in the NbF₅-doped AlH₃.

Investigation of NbF₅-doped AlH₃

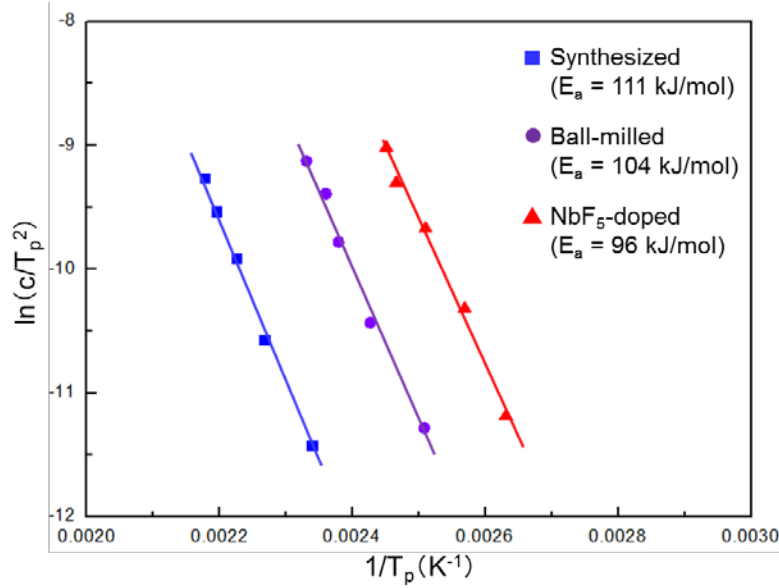


Fig. 4 Kissinger plots for hydrogen desorption of as-synthesized, ball-milled and 1 mol% NbF₅-doped AlH₃.

In order to get an insight on the desorption mechanism, further investigation was conducted for the NbF₅-doped AlH₃, which showed the lowest onset temperature among all the samples. The activation energy for hydrogen desorption was analyzed for the NbF₅-doped AlH₃. Fig. 4 shows the Kissinger plots for the hydrogen desorption of AlH₃ and NbF₅-doped AlH₃. The apparent activation energy for hydrogen desorption is calculated by using Kissinger equation [27],

$$\ln \frac{c}{T_p^2} = -\frac{E_a}{RT_p} + \ln \frac{RA}{E_a}$$

where E_a is the apparent activation energy for hydrogen desorption, c is the heating rate, T_p is the peak temperature, R is gas constant, and A is the frequency factor. The activation energies of as-synthesized AlH₃, ball-milled AlH₃, and NbF₅-doped AlH₃ were calculated to be 111, 104, and 96 kJ/mol, respectively. The values for as-synthesized and ball-milled AlH₃ were similar to those

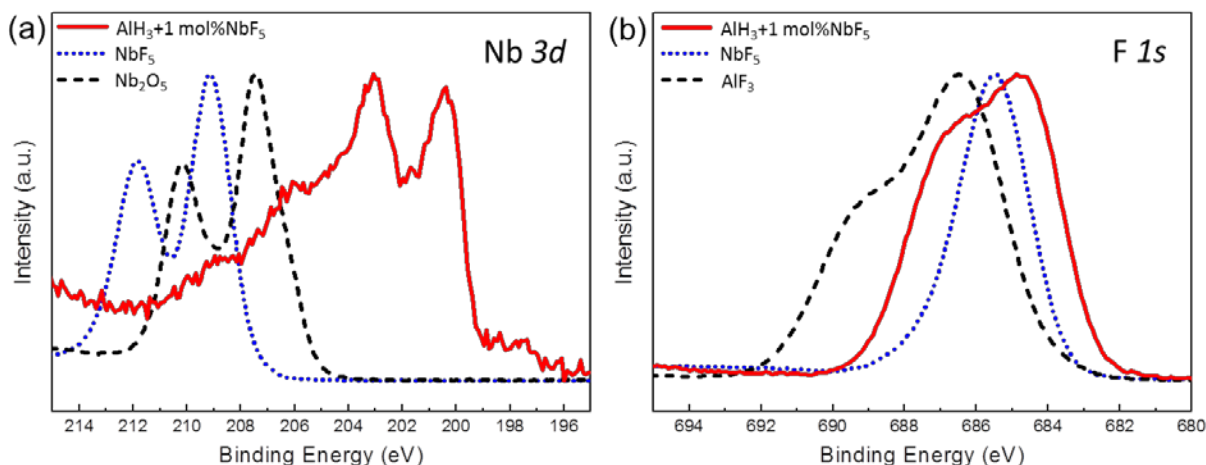
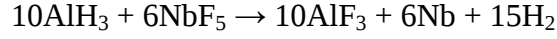


Fig. 5 XPS spectra of (a) Nb 3d and (b) F 1s regions of 1 mol% NbF₅-doped AlH₃. The spectra of NbF₅, Nb₂O₅ and AlF₃ are also shown as references.

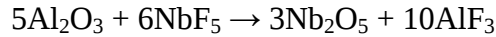
of the previous study (104 kJ/mol [5], 102 kJ/mol [28]). The activation energy of NbF₅-doped AlH₃ was just slightly decreased compared with as-synthesized and ball-milled AlH₃. As shown in the “Introduction” part, Ti is known as an effective catalyst for AlH₃. It was reported that a decrease of the activation energy by at least 50 % is possible with the addition of Ti [6]. Thus, the effect of Nb on the decomposition kinetics would be less pronounced than that of Ti. The effect of cation species on the kinetics should be further clarified to understand the catalytic mechanism of hydrogen desorption from AlH₃.

The bonding states of Nb and F elements were studied by using XPS. For comparison, the standard materials of NbF₅, Nb₂O₅ and AlF₃ were also measured. Fig. 5(a) shows the XPS spectra of Nb 3d region. In the NbF₅-doped AlH₃, the binding energies of Nb 3d_{3/2} and 3d_{5/2} shift towards to the chemical states of Nb, suggesting the reaction between NbF₅ and AlH₃ would occur to form Nb. Also, shoulder peaks appeared between 204.0-212.0 eV, suggesting the presence of Nb oxide species *e.g.*, Nb₂O₅ and/or NbO. Fig. 5(b) shows the XPS spectra of F 1s region. In the NbF₅-doped AlH₃, the binding energies of F 1s peaks were observed at 686.5 eV

(AlF₃) and a new peak at 684.8 eV. The new peak position is similar to the previously reported AlF_xO_y species [29], suggesting such kind of AlF_xO_y phase could exist. The broad peak at 688.9 eV in the starting material of AlF₃ might be attributed to the contamination of C-F species [30]. The XPS results suggest that the following reaction would occur during the milling process:



whose Gibbs free energy $\Delta G^\circ = -3570.4$ kJ [31,32] is possible from the thermodynamic potentials. The Nb spectrum in the NbF₅-doped AlH₃ (Fig.5 (a)) was similar to that of NbF₅-doped MgH₂ system [15]. In this system, MgF₂ and Nb were formed by the reaction between MgH₂ and NbF₅. Thus, the chemical state of Nb was similar between AlH₃ and MgH₂ system. However, the existence of oxide species (Nb oxide, AlF_xO_y) could be one of the characteristics in the AlH₃ system. It is known that amorphous- or χ -Al₂O₃ film exists on the surface of AlH₃ particles [33,34]. Due to the lack of the standard Gibbs free energy of formation for amorphous- or χ -Al₂O₃, we considered the reaction with the most stable phase, α -Al₂O₃, as follows:



whose Gibbs free energy $\Delta G^\circ = -1442.2$ kJ [31] is thermodynamically possible. Thus, NbF₅ could also react with surface Al₂O₃ film in the NbF₅-doped AlH₃ system. In order to clarify the detailed catalytic mechanism, *e.g.*, *in-situ* measurements on the reaction process between NbF₅ and surface Al₂O₃ film should be conducted. As the summary of XPS results, the formation of finely dispersed Nb species and/or AlF₃ could have the catalytic effect for hydrogen desorption of AlH₃. According to the previous study, AlF₃-doped AlH₃ led to the decomposition of AlH₃ at room temperature [35], suggesting AlF₃ may have such catalytic effect.

Conclusion

In summary, the addition of Nb species (Nb, Nb₂O₅, NbF₅) enhanced the hydrogen desorption properties of α -AlH₃. In particular, 1 mol% NbF₅-doped AlH₃ started to desorb hydrogen from 60 °C with a peak temperature at 122 °C. Compared with Nb- or Nb₂O₅-doped AlH₃, the fine distribution of dopant was observed in the NbF₅-doped AlH₃. The activation energy for hydrogen desorption was slightly decreased by doping NbF₅. From the XPS analysis, the reactions between NbF₅ and AlH₃ (surface Al₂O₃ film) were suggested. The improvement in the NbF₅-doped AlH₃ might be ascribed to the formation of finely distributed Nb and/or AlF₃.

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