Correlation between particle size and hydrogen generation properties on ammonia and lithium hydride system

Hiroki Miyaoka [a,*], Kyoichi Tange [b], Hikaru Yamamoto [b], Satoshi Hino [c], Takayuki Ichikawa [d], Yoshitsugu Kojima [b,c]

[a] Institute for Sustainable Sciences and Development, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8530, Japan
[b] Graduate School of Advanced Sciences of Matter, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8530, Japan
[c] Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8530, Japan
[d] Graduate School of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima, 739-8521, Japan

ARTICLE INFO

ABSTRACT

For the ammonia (NH_3) and lithium hydride (LiH) system, which is one of the promising hydrogen storage materials, the correlation between particle size of LiH and reactivity with NH_3 is investigated to understand the kinetic properties of the system. The pristine LiH shows low reaction yield of less than 10% due to the slow kinetics even after the reaction for 24 h. The activation by the ball-milling drastically improved both of reaction rate and yield, and then more than 80% of reaction proceeded for 24 h in the case of the LiH with the smallest particle size. Thus, the particle size strongly affects the kinetic properties. Furthermore, a thickness of possible NH_3 diffusion into the LiH surface for the 24 h reaction is estimated to be 20 nm assuming that the LiH particles are an ideal spherical shape. Therefore, the rate-determining step of the system would be the NH_3 diffusion process.

Introduction

Hydrogen (H_2) has high gravimetric energy density and can be produced from various kinds of primary energy. Thus, H_2 is recently considered as an attractive energy medium. However, H_2 is difficult to be compactly stored because H_2 is gaseous phase under ambient conditions and has to be cooled down to below 33 K, which is a critical point, for liquefaction. Thus, the various types of solid hydrogen storage materials have been investigated to realize the compact storage state so far [1,2]. Among them, the light elements based chemical materials such as amides, borohydrides, alanates, and ammonia borane have especially been investigating because of the high

gravimetric density [3—5]. Ammonia (NH_3) is recently recognized as a liquid state hydrogen storage material because of the high gravimetric and volumetric hydrogen density [6,7]. The gravimetric density of NH_3 is 17.8 mass%, which is the higher value among conventional hydrogen storage materials. The volumetric hydrogen density is 10.7 kg H_2/100 L under about 1.0 MPa at room temperature, which is higher than 3.9 kg H_2/100 L of a compressed hydrogen under 70 MPa of pressure and 7.1 kg H_2/100 L of a liquefied hydrogen at 20 K. However, utilization of NH_3 as the hydrogen carrier would be limited by requirements of a high temperature for decomposition processes even though effective catalysts are used [8,9]. Previously, we have proposed and investigated the NH_3 and alkali metal hydride (MH = LiH, NaH, KH) systems as the hydrogen storage system operated under moderate conditions compared with NH_3 itself [10,11]. The reaction is expressed as follows.

$$NH_3 + MH \leftrightarrow MNH_2 + H_2, \qquad (1)$$

The hydrogen desorption reaction of all the systems proceeds at room temperature without catalysts. The reaction products MNH_2 can be recycled back to NH_3 and MH below 573 K under the H_2 flow condition. Although the hydrogen capacity is reduced by the combination with MH, the NH_3—LiH system still has the high gravimetric and volumetric density, which are 8.1 mass% and 4.5 kg H_2/100 L, respectively, where it is assumed that packing density of the solid LiH is 60% [10]. Thus, the NH_3—LiH system is also attractive as hydrogen storage techniques. For development of the system, the main issue is the improvement of kinetics on the hydrogen generation reaction because the reaction yield of the H_2 generation of the Li system at room temperature is only 10% after the reaction for 24 h. Generally, the kinetic properties of gas—solid reactions are controlled by surface reaction and atomic diffusion processes, where this common understanding is adapted to the reaction between NH_3 and LiH. Actually, the mechanical ball-milling is reduced the crystalline size of LiH, resulting in the higher reaction yield [10—12]. Moreover, when the reaction of LiH with gaseous NH_3 is mechanochemically performed by the ball-milling, LiH is completely changed to $LiNH_2$ phase by the dynamic destruction of $LiNH_2$ layers on the surface and the simultaneous reduction of the crystalline size [13].

In this work, the correlation between the reaction properties of LiH and the structural properties such as particle and crystalline sizes is investigated to understand the reaction parameters for the improvement of the hydrogen generation properties.

Experimental section

300 mg of LiH (99.4%) powder purchased from Alfa Aesar Co. was put into a Cr steel vessel (SKD-11, 30 cm^3, Umetoku Co. Ltd.) with 20 steel balls (SUJ-2, 7 mm in diameter), and then ball-milling was performed for 10 h under 1.0 MPa of H_2 by a planetary ball-mill apparatus (P7, Fritsch) at 370 rpm. The obtained sample is denoted as LiH*. To further reduce the crystalline size, the sample is synthesized by following procedures. As a pre-treatment, LiH reacted with 0.5 MPa of NH_3 gas for 10 min and a small amount of $LiNH_2$ was then formed at only surface part (several mol% for LiH). After that, the ball-milling was performed by the same conditions in the case of LiH*, where the synthesized sample is denoted as LiH-A*. The hydrogen generation reaction of the samples was statically performed under about 0.5 MPa of NH_3 pressure at room temperature, where the molar ratio of NH_3 to LiH is fixed to be 1: 1. The reaction yield was estimated by measuring a weight gain of the solid product after the reaction. For the experiments, the samples were handled in a glove box (MP-P60W, Miwa MFG), where the moisture and oxygen contents in the glove box are maintained to be less than 0.1 and 1 ppm, respectively. The solid samples were identified by X-ray diffraction (XRD) measurements (RINT-2100, CuKa radiation, Rigaku). For the measurements, a poly-imide sheet (Kapton®, Du pont-Toray Co. Ltd.) was used to protect the samples from the moisture and oxygen in air. The morphology and particle sizes are analyzed by a transmission electron microscope (TEM, 300 kV, Phylips). Specific surface area of the samples is evaluated by a BET method using N_2 gas adsorption at 77 K (Yuasa Corp.).

Results and discussion

Fig. 1 shows XRD patterns of the pristine LiH, LiH*, and LiH-A*. The clear diffraction peaks corresponding to LiH were observed in the XRD pattern of the pristine LiH. The peak intensity and shape were weakened and broadened, respectively, in the case of LiH*. The reduction of the crystalline size and the induction of lattice distortion and/or defects proceeded by the mechanical ball-milling. For LiH-A*, the $LiNH_2$ phase was not detected because the amount of $LiNH_2$ generated by the short time reaction with NH_3 was very small. The peak intensity of LiH was significantly decreased compared with other two samples while the peak shape was similar.
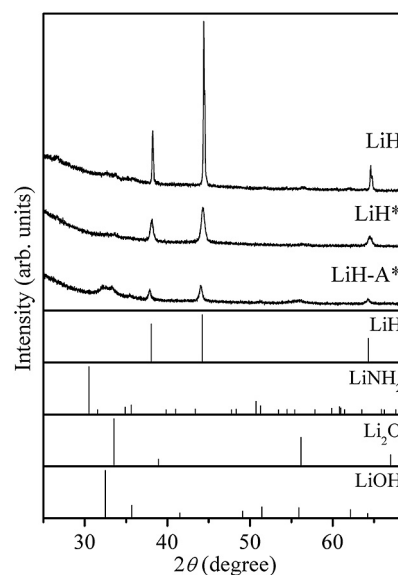

Fig. 1 — XRD patterns of LiH, LiH*, and LiH-A*. LiH (PDF#65—2897), $LiNH_2$ (PDF#71—1616), LiOH (PDF#32—0564), and Li_2O (PDF#65—2972) as references from database.