Composite Materials based on Light Elements for Hydrogen Storage

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In this paper, we review our recent experimental results on hydrogen storage properties of light elements Li, C and Mg based nano-composite materials. The results are summarized as follows: In the Li-N-H system, such as the ball milled 1:1 mixture of Li amide and Li hydride containing a small amount of TiCl_3 (1 mol%), a large amount of hydrogen (~ 6 mass%) is absorbed and desorbed in the temperature range from 150 to 250°C with good reversibility and high reaction rate. Furthermore, in the ball milled mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH , ~ 7 mass% of hydrogen is reversibly stored in the temperature from 140 to 220°C, indicating one of the suitable hydrogen storage materials. In graphite containing a small amount of nanometer sized Fe (~ 2 at.%), a large amount of hydrogen (~ 7 mass%) is chemisorbed by ball milling for 80 h under less than 1 MPa of H_2 -gas pressure. However, the chemisorbed hydrogen capacity decreases with increase in the milling pressure for the 80 h ball milled graphite (down to ~ 4.1 mass% at 6 MPa), while the physisorbed hydrogen capacity in graphite increases with increase in the milling pressure, reaching up to $0.5\sim 1.0$ mass% at 6 MPa. Unfortunately, the desorption temperature of chemisorbed hydrogen is higher than 300°C. Therefore, some break-through is necessary for the development of carbon-based materials as one of the hydrogen storage systems. On the other hand, some nano-composite Mg catalyzed by Ni nano-particle or Nb oxide reveals superior reversible hydrogen storage properties: ~ 6.5 mass% of hydrogen is reversibly stored in the temperature range from 150 to 250°C. Especially, the Nb metals uniformly dispersed in nanometer scale on the surface of MgH_2 , which was produced by reduction of Nb_2O_5 , is the best catalyst we have studied so far. Thus, it seems that some Mg nano-composites catalyzed by nano-particles of d-electron transition metals is acceptable for practical applications.

(Received July 21, 2004; Accepted September 28, 2004)

Keywords: hydrogen storage, mechanical ball milling, lithium amide-imide system, metal nitrogen hydrogen system, ammonia, magnesium hydride, nano-structured graphite, catalyst, d-electron transition metal

1. Introduction

Protection of the earth from pollution is one of the most important issues to be solved by the human race. However, the fast growing world population, increasing globalization and emerging nations on the threshold of becoming highly mobile societies will yield more and more atmospheric pollution. Thus, hydrogen energy systems have been proposed as a means to reduce greenhouse gas and other harmful emissions from stationary and mobile sources. In order to realize hydrogen energy systems in the near future, we have to develop energy storage and transportation technologies. One of the key technologies we need to develop is a high performance hydrogen storage (H-storage) tank, especially, which is to be used in fuel-cell electric vehicles (FCEV). Containers of liquid hydrogen, high-pressure gas hydrogen, and absorbed hydrogen in chemical or metal hydrides with light elements in the periodic table are being investigated all over the world.¹⁻⁵⁾ These methods have advantages and disadvantages, but the method chosen will have to be compact, light, safe and affordable as on-board storage.

Condensation into liquid is particularly attractive from the viewpoint of the energy density. However, the condensation temperature of hydrogen at 0.1 MPa is -253°C and heat transfer through the container leads directly to the loss of hydrogen. Larger containers have a smaller surface to volume ratio than small ones, so that the loss of hydrogen due to evaporation is smaller. Therefore, it is useful for a tanker, truck or bus with huge liquid hydrogen containers, but unsuitable as a hydrogen container for the compact FCEV.

In most countries, classical high-pressure tanks made of cheap steel are regularly filled up to 15 or 20 MPa. In order to run a compact FCEV for 400 km, it needs a tank that can store 4 kg of hydrogen. This means that, an internal volume of

0.225 liters is required, but this is too large a volume for a compact car. Recently, novel high-pressure tanks made of carbon-fiber-reinforced composite materials are being developed; these are tested up to 60 MPa and filled up to 35 MPa for regular use. The novel high-pressure tanks would contain about ~ 4 kg hydrogen by weight, but still has the disadvantage that the fuel tank would be too large by volume for a compact FCEV. In order to overcome this disadvantage, a very-high-pressure tank of up to 70 MPa has been considered for FCEV. However, there is considerable risk in using very-high-pressure vessels. The compression itself is the most dangerous and complicated part. There are still problems remaining that need to be solved for high-pressure containers.

It is well known that metal hydride systems can store more hydrogen in a safe and efficient way than liquid hydrogen or high-pressure hydrogen. However, materials with good storage capabilities and reversibility only desorb hydrogen at relatively high temperatures, which are too high for fuel cell application, while materials fitting these requirements are too heavy or too expensive for commercial application.

In these situations, H-storage research projects have been initiated all over the world. In 2003 in Japan, the New Energy and Industrial Technology Development Organization (NEDO) has set a target to develop reversible H-storage media capable of delivering 5.5 mass% H at less than 150°C as a research and development program on H-storage materials. In USA, the Department of Energy (DOE) has set a target to develop and verify on-board H-storage systems achieving 2 kWh/kg (6 mass%) at less than 100°C by 2010. Internationally, the International Energy Agency (IEA) has set a target to achieve a reversible H-storage medium with 5 mass% H_2 recoverable at $T < 80^\circ\text{C}$. In recent years, in order to achieve the above targets, new materials with lighter elements, such as lithium (Li), sodium (Na), carbon (C) or

magnesium (Mg) based materials, have been developed to overcome the disadvantage of heavy weight in conventional metal hydrides.

In this paper, we review our recent experimental results on the H-storage properties of light elements Li, C and Mg based nano-composite materials, which were designed by a mechano-chemical method.

2. Hydrogen Storage Properties of Lithium Based Materials

To overcome the disadvantage of too heavy weight of conventional metal hydrides for H-storage, some chemical hydrides composed of light elements such as Li and Na have been attracted as new H-storage materials in these days. In particular, the H-storage properties of some alanate systems have been studied by many researchers till now,^{6–34)} in which hydrogen is desorbed by the following 2-step reactions:

Here, the total hydrogen capacities for $\text{M} = \text{Na}$ and Li are theoretically calculated to be 5.6 and 8.0 mass%, respectively. Both the enthalpy changes of the reactions (1) and (2) for $\text{M} = \text{Na}$ were estimated to be endothermic and the reversibility of both the reactions were experimentally confirmed. Then, some catalysts containing Ti or Zr-elements were doped to improve the reaction rate. On the other hand, the enthalpy changes of the reactions (1) and (2) for $\text{M} = \text{Li}$ have been estimated to be respectively exothermic and endothermic by DTA measurements. Therefore, only the second reaction (2) for $\text{M} = \text{Li}$ should be reversible for H-storage. However, the hydrogenating reaction could not be confirmed so far, because the reaction rate might be too slow for realizing the hydrogenating reaction under moderate temperature and H_2 gas pressure.

Concerning with chemical hydrides composed of lithium and boron, many data have been also accumulated. The lithium tetrahydroborate (LiBH_4) was first synthesized in 1940³⁵⁾ by the reaction of the ethyl lithium with diborane (B_2H_6). Until now, direct synthesis from Li or LiH, B and H_2 at elevated conditions up to 650°C and 15 MPa of H_2 pressure has been tried by many researchers, but all the attempts failed. Quite recently, Orimo *et al.* have succeeded to synthesize LiBH_4 from LiH and B at 500°C and under 35 MPa of H_2 gas pressure.³⁶⁾ On the other hand, the hydrogen desorption (HD) process from LiBH_4 was examined by Fedneva *et al.* in 1964.³⁷⁾ Three endothermic reactions at ~110, ~280 and ~480°C were observed in the TDS spectra. The first peak corresponds to polymorphic transformation, the second one to the fusion of LiBH_4 and the third one starts at 380°C and liberates 80% of the hydrogen in LiBH_4 . Recently, Züttel *et al.* showed that a slight amount of hydrogen was desorbed during the structural transformation around 100°C and major hydrogen desorption of 13.5 mass% started at ~200°C when the SiO_2 -powder was added to the LiBH_4 .³⁸⁾

On the Li-N-H systems, there have been new developments for H-storage in recent years. We have also started to study their H-storage properties in ball milled mixture of

metal hydrides and amides prepared by a mechano-chemical method. About our recent development on Li-N-H systems for H-storage, we will review in the following session.

2.1 Novel reaction of LiNH_2 and LiH for hydrogen storage

As early as 1910, Dafert and Miklauz³⁹⁾ had reported that the reaction between Li_3N and H_2 proceeded at 200–300°C and generated Li_3NH_4 . However, the product was proved to be a mixture of lithium amide and lithium hydride by Ruff and Goerges⁴⁰⁾ as follows;

Furthermore, they had claimed that the mixture was decomposed into lithium imide and released H_2 on heating as follows;

These were the first reports concerning hydrogen absorption and desorption reactions on Li-N-H systems. After that, there had been no researches on H-storage properties in Li-N-H systems for almost one century.

In recent years, Chen *et al.*⁴¹⁾ and Hu and Ruckenstein⁴²⁾ demonstrated that Li_3N reversibly absorbed and desorbed hydrogen by the following 2-step reactions at relatively low temperatures under moderate pressures;

They reported that a high capacity of hydrogen (~9.4 mass%) was reversibly stored in the above system. Since that, some alkali and alkali earth metal nitrides or their imides have become one of the promising families for H-storage media.^{41–48)}

The enthalpy change of the first step of the reaction (5) could be estimated to be 148 kJ/mol H_2 and that of the second step to be 45 kJ/mol H_2 .⁴¹⁾ Since the second reaction has a much smaller enthalpy change for hydrogen release than the first one and has a potential for storing still a large amount of hydrogen (6.5 mass%), we focused on the second step of the reaction (5), which is expressed as follows;

In the above reaction, we could commercially buy both of LiNH_2 and LiH except Li_2NH .

So, first of all, we started to study HD properties from the 1:1 mixture of purchased LiNH_2 and LiH .⁴⁶⁾ To achieve a good contact between LiNH_2 and LiH in nanometer scale, the mixture was ball-milled by a planetary mill equipment (Fritsch P7) under a H_2 -gas atmosphere of 1 MPa for 2 h. A profile of thermal desorption mass spectroscopy (TDMS) for the ball milled mixture are shown in Fig. 1. We notice that the NH_3 gas in addition to hydrogen gas is desorbed from the ball milled mixture at higher temperature region around 350°C, where the hydrogen desorption synchronizes with the NH_3 desorption. Usually, it is known that the NH_3 gas is emitted by the following decomposition reaction on heating process;

Here the enthalpy change for releasing NH_3 is endothermic

Fig. 1 TDMS profiles for H_2 and NH_3 gases from the mixture of $LiNH_2$ and LiH in the 1:1 mole ratio prepared by mechanically milling under 1 MPa H_2 atmosphere for 2 h.

and is estimated to be 84 kJ/mol NH_3 . Therefore, the NH_3 emission from the mixture at higher temperatures might be due to thermal decomposition of remaining $LiNH_2$ that could not react with LiH because of slow reaction speed between $LiNH_2$ and LiH .

Then, in order to improve the reaction rate, we examined the catalytic effect on the HD properties in the ball milled 1:1 mixture of $LiNH_2$ and LiH .⁴⁶⁾ A small amount (1 at%) of Fe, Co, or Ni metal with several nanometers diameter, and the chloride of VCl_3 or $TiCl_3$ (1 mol%) was added to the 1:1 mixture as a catalyst before ball milling and then ball milled for 2 h under 1 MPa of H_2 -gas at room temperature. In Fig. 2, the TDMS profiles for H_2 and NH_3 gases are shown for all the doped mixtures. The mixture containing a small amount of $TiCl_3$ (1 mol%) shows the most superior HD properties among all the doped mixtures; the product shows the sharpest desorption curve and desorbs a large amount of hydrogen (5.5–6.0 mass%) in the temperature range from 150 to 250°C at a heating rate of 5°C/min. This indicates that the reaction speed is dramatically improved by doping 1 mol% of $TiCl_3$ as a catalyst and the doping leads to lower activation energy for the HD reaction (4) than in the mixture with no catalyst. Here, it is noteworthy that no NH_3 gas emission was detected at all in the TDMS measurement up to 450°C for the mixture doped 1 mol% $TiCl_3$ as a catalyst within our experimental accuracy. This result indicates that all of the $LiNH_2$ were completely consumed by reacting with LiH until 300°C and transformed into Li_2NH and H_2 , leading to no NH_3 gas emission at all.

Next, we examined the reversibility of the hydrogen desorption and absorption reactions for the ball milled 1:1 mixture with the 1 mol% $TiCl_3$ catalysts.⁴⁶⁾ The reversibility was tested by the following cyclic processes; the hydrogen desorption was performed by keeping the product at 220°C for 12 h under high-vacuum and then the hydrogen absorption was done under pure hydrogen gas up to 3 MPa. In Fig. 3, are shown the TDMS profiles after several cycles. The amount of desorbed hydrogen slightly decreases after 2nd cycle, suggesting that a small amount of stable compounds like Li_2O , TiN or $LiCl$ has been produced during the first heating process. However, since the effective hydrogen capacity was still higher than 5 mass% after the initial dehydrogenation reaction and the reaction rate did not change after 2nd cycle

Fig. 2 TDMS profiles for H_2 and NH_3 gases from the ball milled 1:1 mixture of $LiNH_2$ and LiH with 1 mol% of catalysts (Ni^{nano} , Fe^{nano} , Co^{nano} , VCl_3 and $TiCl_3$) by mechanically milling under 1 MPa H_2 atmosphere for 2 h.

Fig. 3 H_2 desorption spectra from 1:1 mixture of $LiNH_2$ and LiH with 1 mol% $TiCl_3$ catalyst prepared by mechanically milling under H_2 atmosphere for 2 hrs and corresponding weight loss. The solid, dotted and dashed lines correspond to the first, second and third cycles, respectively.

until 10th cycle (almost same as 3rd cycles data), we conclude that the cycle retention is excellent.⁴⁶⁾

Furthermore, we investigated the kinetics of the HD reaction. Figure 4 shows the logarithmic plot of the residual

Fig. 4 Logarithmic plots of normalized remaining hydrogen amount, $X_{H_2}(t)/X_{H_2}(0)$, and linear plots of measuring temperature as a function of time for the 1:1 ball milled powders with and without 1 mass% $TiCl_3$ catalyst.

hydrogen content ratio $X_{H_2}(t)/X_{H_2}(0)$ as a function of time for the desorption process from the ball milled 1:1 mixtures with and without 1 mol% $TiCl_3$ catalyst. Here, $X_{H_2}(t)/X_{H_2}(0)$ was determined by the thermo-gravimetric analysis (TGA), which were performed under no partial pressure of hydrogen and NH_3 using He gas as a flow gas. In this figure, the temperature fluctuations from a programming temperature are also plotted as a function of time. We notice that the reaction rate of the product with 1 mol% $TiCl_3$ as a catalyst is much faster than that without catalyst and almost 90% of hydrogen is desorbed within 20 min from the catalyzed mixture at $210^\circ C$. In addition, one can see that both the logarithmic plots are linear against time after measuring temperatures reached at the programming ones, indicating that both the HD reactions are of first order.⁴⁶⁾

As is described above, it was clarified that the HD reaction is of first order and very fast, although it is considered to be solid-solid reaction. In order to make clear the origin of such unusual reaction behaviors, we examined the TDMS profiles of NH_3 and hydrogen gaseous emissions from a single-layered sample of ball milled $LiNH_2$ and a two-layered sample composed of ball milled $LiNH_2$ and LiH ,⁴⁷⁾ where the ball milled LiH layer is placed on the ball milled $LiNH_2$ layer as schematically shown in Fig. 5. The detected TDMS profiles for hydrogen and the NH_3 gases are shown in Fig. 6 for single-layered $LiNH_2$ with a 1 mol% $TiCl_3$ catalyst (A) and without any catalyst (B), and two-layered samples with the $TiCl_3$ catalyst (C) and without any catalyst (D) as well. We can see that the emission of NH_3 from $LiNH_2$ itself starts from $\sim 220^\circ C$, and takes a broad peak at $330^\circ C$, while the desorption of H_2 from the two-layered sample synchronizes with NH_3 emission from $LiNH_2$, irrespective of doping a 1 mol% $TiCl_3$. This indicates that NH_3 emitted from $LiNH_2$ immediately reacts with LiH and releases H_2 . That is, either

Fig. 5 Schematic figure for sample arrangements of (i) an alone $LiNH_2$ and (ii) a two-layered sample with LiH on $LiNH_2$ used for TDMS analysis, and both were put in the sample pan. Here, ammonia is emitted by decomposition of $LiNH_2$ to Li_2NH .

the reaction,

or the reaction,

would be realized in this experiment. If the reaction (8) is realized, the reaction is calculated to be exothermic (~ 42 kJ/mol) from the literature. Therefore, the reaction (8) should progress in the milling process under NH_3 -gas atmosphere even at room temperature. Then, we performed ball mill treatment of LiH (~ 40 mg) under NH_3 -gas atmosphere of 0.4 MPa for 2 h, which corresponds to the 1:1 molar ratio of LiH and NH_3 . The examined X-ray diffraction (XRD) profile indicated that the product is assigned to be a single phased $LiNH_2$ after milling. Thus, we clarified that the reaction (8) is one of the elemental reactions in the HD reaction (6). From the above results, we conclude that the following 2-step elemental reactions mediated by ammonia are essential for the HD reaction (6):

and

In Fig. 6, we notice two other interesting points to be considered. One is that H_2 -releasing temperature from the two-layered sample is lower than that of NH_3 from the single layered sample. The other is that the doping of $TiCl_3$ in $LiNH_2$ and LiH gave no strong influence on both of the NH_3 and H_2 emission processes.

It is of interest to point out that the onset of hydrogen desorption from the $TiCl_3$ -doped 1:1 mixture of LiH and $LiNH_2$ prepared by ball milling method is much lower temperature than that in two-layered sample composed of LiH and $LiNH_2$ with a small amount of $TiCl_3$ (1 mol%). This indicates that $TiCl_3$ acts as an excellent catalyst on the H_2 desorption from the ball milled 1:1 mixture, but not acts as a catalyst on both of the NH_3 and H_2 emissions in both elemental reactions (7) and (8) themselves. Therefore, it seems likely that the catalyst $TiCl_3$ acts as a role for the transfer of NH_3 molecule from $LiNH_2$ to LiH in nanometer scale. Moreover, the above results suggest that LiH plays a role of something like a catalyst for the decomposition of $LiNH_2$ in the ball milled mixture, because the HD temperature from the 1:1 mixture is actually much lower than the NH_3 emission temperature from $LiNH_2$ itself. A preliminary

Fig. 6 TDMS profiles for hydrogen and the NH_3 gases from single-layered LiNH_2 with 1 mol% TiCl_3 catalyst (A) and without any catalyst (B), and two-layered samples with the TiCl_3 catalyst (C) and without any catalyst (D).

Raman scattering experiment for LiNH_2 indicated that a quite small amount of NH_3 molecule started to be liberated from the LiNH_2 particle surface around 70°C , while the decomposition of LiNH_2 into Li_2NH and NH_3 normally started from more than 200°C .

From the above results, we conclude that the HD reaction (6) is controlled by the two-step gas-solid elemental reactions (7) and (8) mediated by ammonia. Thus, we can understand that the HD reaction (6) is first order and shows the fast reaction rate. Then, the HD reaction in reaction (6) can be expressed as follows;

That is to say: At the first step, LiNH_2 decomposes into $\text{Li}_2\text{NH}/2$ and $\text{NH}_3/2$, and then the emitted $\text{NH}_3/2$ quickly reacts with $\text{LiH}/2$, transforming into $\text{LiNH}_2/2$ and $\text{H}_2/2$. At the second one, the produced $\text{LiNH}_2/2$ decomposes into $\text{Li}_2\text{NH}/4$ + $\text{NH}_3/4$ and then $\text{NH}_3/4$ + $\text{LiH}/4$ transform to $\text{LiNH}_2/4$ + $\text{H}_2/4$, and such successive steps continue until LiNH_2 and LiH completely transform into Li_2NH and H_2 . These successive multi step reaction might progress at low temperature by doping some appropriate catalysts like TiCl_3 .⁴⁷⁾

2.2 Novel reaction of $\text{Mg}(\text{NH}_2)_2$ and LiH for hydrogen storage

As discussed in the above section, we clarified that the HD reaction between LiNH_2 and LiH was controlled by the gas-solid 2-step elemental reactions mediated by ammonia. Similarly, we can expect that the reaction between magnesium amide $\text{Mg}(\text{NH}_2)_2$ and LiH would also proceed through NH_3 -mediating gas-solid reactions as well.

Unfortunately, we can not commercially obtain $\text{Mg}(\text{NH}_2)_2$ yet. So, we first synthesized $\text{Mg}(\text{NH}_2)_2$ by ball milling MgH_2 in a gaseous NH_3 atmosphere of 0.4 MPa using a rocking mill with a frequency of 10 Hz for 13 h at room temperature, according to the following reaction:

Then, a mixture of $\text{Mg}(\text{NH}_2)_2$ and LiH with a molar ratio of 3:8 was mechanically milled under a hydrogen gas atmosphere of 1 MPa at 400 rpm for 2 h and the HD properties were examined. The TDMS and TGA profiles of the ball milled mixture without any catalysts are shown in Fig. 7. The results indicate that a large amount of hydrogen (~ 7 mass%) start to be desorbed at 140°C and the desorption peaks at 190°C at a heating rate of $5^\circ\text{C}/\text{min}$ almost without emitting NH_3 . Here, it is noteworthy that the HD properties of the ball milled mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH are much better than those of LiNH_2 and LiH ²⁻⁴³⁾ from the viewpoint of both the hydrogen capacity and the desorption temperature. The reason may be due to the fact that $\text{Mg}(\text{NH}_2)_2$ is less stable and more easily decomposes into the corresponding imide and nitride than LiNH_2 because of the smaller enthalpy change or larger entropy change in the dehydrogenation reaction.

The XRD profile of the mixture after releasing hydrogen at 400°C is shown in Fig. 8(a). This shows that the product is the mixed phases of Li_2NH and Mg_3N_2 . Therefore, the HD reaction from the ball milled mixture of $3\text{Mg}(\text{NH}_2)_2$ and 8LiH can be expressed by the following chemical formula;

From the reaction (12), we can theoretically calculate the amount of H-storage capacity to be ~ 7 mass%, which is in good agreement with the experimental amount of desorbed

Fig. 7 (a) Hydrogen desorption mass spectrum and (b) weight loss percent due to thermal gravimetry analysis for the mixture of 3Mg(NH₂)₂ and 8LiH in the heating process up to 400°C under a helium flow at a 5°C/min heat rate. Here, the hydrogen desorption mass spectrum for the 1:1 mixture of LiNH₂ and LiH with a small amount (1 mol%) of TiCl₃,¹³⁾ is also shown by dotted line.

Fig. 8 XRD patterns of Mg(NH₂)₂ (a) after heat treatment at 300°C under ammonia atmosphere for 1 h; (b) after thermal desorption under a helium flow at 320°C for 2 h (c) after thermal desorption under a helium flow up to 500°C at a heating rate of 5°C/min. The broad peak around 20° is due to grease using for fixing the powder on the sample holder.

hydrogen.

Next, we examined the reversibility of the reaction (12) by following procedure. First, the milled mixture of 3Mg(NH₂)₂ and 8LiH is dehydrogenated in vacuum at 170°C for 8 h. Secondly, the mixture is hydrogenated by slow cooling in the furnace after keeping it at 200°C under a H₂ pressure of 3 MPa for 8 h. As shown in Fig. 8(b), the profile indicates that the dehydrogenating reaction from 3Mg(NH₂)₂ and 8LiH to Mg₃N₂ and 4Li₂NH proceeds even at 170°C in vacuum. After the re-hydrogenating treatment, the product is again transformed into the original mixture of 3Mg(NH₂)₂ and 8LiH (see Fig. 8(c)). Thus, we conclude that the chemical reaction (12) is completely reversible.

Similar to the progress of the HD reaction between LiNH₂ and LiH,⁴⁷⁾ the dehydrogenation reaction from the mixture of 3Mg(NH₂)₂ and 8LiH should proceed by the following three

kinds of elementary reactions: (i) The first one is that 3Mg(NH₂)₂ decomposes to 3MgNH and 3NH₃, and then 3MgNH continues to decompose to Mg₃N₂ and NH₃ at relatively higher temperatures; (ii) the second one is that the emitting 4NH₃ reacts with 4LiH and transforms into 4LiNH₂ and 4H₂; (iii) the third one is that 4LiNH₂ decomposes to 2Li₂NH and 2NH₃. Continuously, 2NH₃ again reacts with remaining 2LiH, transforming into 2LiNH₂ and 2H₂ and then 2LiNH₂ decomposes to Li₂NH and NH₃, and such successive steps continue until 4LiNH₂ and 4LiH completely transform into 4Li₂NH and 4H₂. It seems that these successive reactions might proceed even at lower temperature through the close contact between Mg(NH₂)₂ and LiH in a nano-scale by milling treatment.

On the other hand, the hydrogenation reaction process in the reaction (12) can not be simply understood. This is because that pure Li₂NH is hydrogenated into LiH and LiNH₂,^{46,47)} and similarly Mg₃N₂ can be hydrogenated into 2MgH₂ and Mg(NH₂)₂.⁴⁹⁾ If these reactions proceed as well, the phases of MgH₂ and/or LiNH₂ might appear in addition with the phases of LiH and Mg(NH₂)₂ after the hydrogenation has been performed. However the above reactions do not proceed in this work. Therefore, if there are some elementary solid-gas reactions mediated by ammonia even in the hydrogenation reaction, the hydrogenation reaction can be understood as well. Currently, the mechanism of hydrogenation for this system is under investigation. In addition, preliminary results indicated that the H₂ release pressure in the HD reaction is higher than 5 MPa at 200°C.

In conclusion, the above experimental results indicate that the novel metal-N-H system composed of 3Mg(NH₂)₂ and 8LiH prepared by ball milling is one of the promising candidates for H-storage.⁴⁸⁾

3. Hydrogen Storage Properties of Graphite Based Materials

Generally, hydrogen is adsorbed in carbon based materials on chemisorption and physisorption. Chemisorbed hydrogen is strongly bound with large adsorption heat of 2~3 eV and requires high temperatures more than 300°C to be released, while physisorbed hydrogen is more weakly bound with small adsorption heat of ~0.1 eV, which has been considered to be suitable for H-storage at room temperature.

Since the discovery of new carbon materials such as carbon nanotubes, fullerenes, nanofibers and so on, much attention has been paid on hydrogen adsorption on/in new carbon systems for H-storage.⁵⁰⁻⁶⁴⁾ In 1997, Dillon *et al.* reported that single walled carbon nanotube (SWNT)⁵⁰⁾ could store up to 5~10 mass% of hydrogen by physisorption under a H₂ gas pressure of 0.05 MPa and at room temperature by opening the caps of SWNT. After that, many researchers have performed similar experiments on SWNT, but their data on H-storage capacity at room temperature have widely scattered from 0 to 7 mass%. Therefore, how much hydrogen absorbs in SWNT is still an unsettled issue till now. In 1998, Chambers *et al.* claimed that the Herringbone-type carbon nanofiber could adsorb up to 67 mass% of hydrogen by physisorption at room temperature and reversibly adsorbed/desorbed ~70% of the adsorbed hydrogen at room temper-

ature.⁵¹⁾ These data have not been reproduced yet as well. So, it is impossible to draw definitive conclusions on the prospects for H-storage on new carbon materials at present. The usage of carbon materials for H-storage seems to be significant potential, but the path to reach the goal still requires a considerable amount of research works.

Motivated by the above reports, our group have studied the H-storage properties of nonstructural graphite prepared by ball milling for 1~80 h under hydrogen atmosphere of 1 MPa using Cr steel pot and balls so far.^{52–56)} The results obtained are summarized as follows: A large amount of hydrogen is chemisorbed up to 7.4 mass% after milling for 80 h. The chemisorbed hydrogen seems to occupy two different types of the atomic sites, which has been clarified by the neutron diffraction experiments⁵⁵⁾ and H^1 NMR measurements.⁵⁴⁾ One is the C-D(H) covalent bonding site located at the edges of the graphite sheets and the other is the defective sites located in between the graphite layers.⁵⁵⁾ The two H_2 -desorption peaks are observed at 450 and 720°C in the TDMS profile as shown in Fig. 9; the former is due to the desorbed hydrogen from the defective sites, and the later is from the covalent bonding sites. The XRD profiles from the ball milled graphite before and after heating up to 900°C are shown in Fig. 9. We notice that nano-structured graphite is formed by ball milling for 80 h under H_2 gas atmosphere of 1 MPa (confirmed by neutron diffraction studies), while the (002) peak grows up after heating up to 900°C, indicating recovery of a long-range crystallization of graphite interlayer along the c-axis, and the peaks indexed by Fe_3C grow up after heating up to 900°C, indicating 1~2 at% of Fe contamination from the Cr steel pot and balls after milling for 80 h.

Fig. 9 TDS profiles of nanostructural graphite prepared by mechanically milling in Cr steel pot and balls without any extra catalysts under hydrogen atmosphere for 80 h and XRD (after milling and after heating) profiles of corresponding nanostructural graphite before and after heat treatment up to 900°C, and the indexations are given for Fe_3C .

Fig. 10 XRD (after milling and after heating) and TDS profiles (H_2 , CH_3 , CH_4 , and C_2H_4 traces) of the samples A~E after milling for 32 hours.

3.1 Catalytic effect of 3d-transition metals on hydrogen storage properties

To clarify whether the contaminated iron acts as a catalyst for H-storage in ball milled graphite, we studied the doping effects of 3d-transition metals on H-storage properties.^{65,66)} Nano-particle metals Fe, Co, Ni and Cu were used as dopants in this work. In Fig. 10, the TDMS profiles of some graphite catalyzed by Fe^{nano} , Co^{nano} , Ni^{nano} and Cu^{nano} are shown together with the XRD profiles before and after heating at 900°C, where these samples were prepared by ball milling the mixture of graphite and a small amount (1 at%) of Fe, Co, Ni and Cu with several ten nanometer sizes for 32 h under a H_2 gas pressure of 1 MPa, respectively, using Cr steel pot and balls. It is to be noted that 32 h milling led to very few Fe contamination from the Cr steel pot and balls. The sample E in Fig. 10 was prepared by mechanical milling with ZrO_2 balls in ZrO_2 pot, in which graphite is hardly contaminated with iron.

As is evident from Fig. 10, the Fe-doped sample revealed the most superior H-storage properties among all the doped samples: The TDMS profile indicates that the desorption has two peaks around 450 and 720°C, the onset for hydrogen release is $\sim 330^\circ C$, and the amount of desorbed hydrogen reaches up to ~ 4 mass% for 32 h milling. It is to be noted that the TDMS profile is similar to that obtained in the Fe contaminated graphite during milling for 80 h (Fig. 8). On the other hand, the TDMS profile of the Co-doped graphite shows that the absorbed hydrogen concentration reaches up to ~ 2 mass% by mechanical milling for 32 h, and the

desorption takes only a broad peak around 820°C, but the onset lowers down to 230°C. The TDMS profiles of Ni and Cu doped graphite are no peak structure, being similar to that of no Fe doping graphite (sample E). This indicates that the Ni and Cu doping do not show any improvement for H-storage. These results suggest that the catalytic effect of iron on H-storage properties correlates with the strongest affinity of iron with carbon (graphite) among the other 3d-transition metals.

Despite of the same milling time (32 h), the XRD profiles shows different features dependent on the doped samples as shown in the right hand side of Fig. 10. The (002) diffraction peak of hexagonal graphite corresponding to graphitic lamellar structure disappears in the Fe-doped graphite after milling for 32 h similar to the case in the Fe contaminated graphite, while the (002) peak remains even after milling in the other Co, Ni, Cu-doping and no doping graphite. This indicates that Fe contamination during milling brings a lot of defective sites between the graphene sheets and covalent bonding sites, leading to structure-less (nano-structured) broad profile in the XRD pattern, where a large amount of hydrogen is adsorbed.

From the above results, we conclude that nano-particle iron uniformly dispersed on graphite (confirmed by TEM observation) acts as the most superior catalyst for H-storage, where hydrogen is absorbed up to ~7 mass% for 80 h milling under a H₂ atmosphere of 1 MPa and the H₂ desorption forms a characteristic two-peak structure around 450 and 720°C. However, the desorption temperature of chemisorbed hydrogen in nano-structured graphite is still too high for H-storage. Therefore, some break-through is necessary for developing graphite as one of the carbon based H-storage materials.

3.2 Milling H₂-gas pressure effect on hydrogen storage properties

In the above experiment, we noticed that the inner pressure of hydrogen gas in milling pot lowered down to 0.05 MPa from 1 MPa after milling for 80 h in the closed system because of the hydrogen adsorption in graphite. Then, we studied H-storage properties of mechanically milled graphite under some hydrogen pressures up to 6 MPa in order to know whether the intrinsic H-storage properties of graphite are improved or not by increasing the milling hydrogen pressure up to 6 MPa.^{66,67)}

In Fig. 11, the TDMS profiles of hydrogen are shown for mechanically milled graphite at a frequency of 10 Hz for 80 h under various H₂-gas pressures by a vibrating ball mill equipment, together with that for graphite milled at 400 rpm for 80 h under a H₂-gas pressure of 1 MPa by a planetary ball mill method as well. We can see a common two-peak structure in all kinds of the Fe contaminated graphite. As already described above, the low temperature peak is assigned to the desorption of hydrogen trapped at some defective sites, while the high-temperature one to that of those trapped at the edges of graphene sheets. As is evident from Fig. 11, the intensity of low temperature peak for nano-structured graphite milled by a vibrating mill method is weaker than that milled by a planetary mill one. On the other hand, the high temperature peak due to hydrogen desorption unexpectedly shifts to higher temperature side with increas-

Fig. 11 TDMS profiles of mass number 2 (H₂-gas) for the nanostructural graphite prepared by vibrating milling for 80 h under various hydrogen pressures; 0.3, 1.0, 3.0, 6.0 MPa and by planetary milling for 80 h under 1.0 MPa.

ing the milling pressure. However, at the same initial pressure, the position of high temperature peak due to the rotating mill process is almost the same as in the vibrating process, irrespective of the milling type. The structural properties were examined by the XRD measurements. Figure 12 shows the XRD profiles of graphite milled for 2 h under various hydrogen gas pressures. The intensity of the main (002) peak increases with increasing the milling pressure, indicating that it is hard to make the defects in graphite by milling under higher hydrogen pressure. Actually, we obtained the result that the hydrogen absorption capacity determined by the oxygen combustion hydrogen analysis (OCHA) decreased with increasing the milling pressure. Those unusual results indicate that higher milling pressure of hydrogen leads to further decrease in the chemisorbed hydrogen content and further stability on the occupied sites, which are strongly related with the number of defective sites in the nano-structured graphite.

3.3 Appearance of physisorption-like hydrogen in graphite milled under high H₂-gas pressures

Hydrogen concentrations determined by a volumetric method and by an OCHA method are compared in Table 1 for the ball milled graphite under various hydrogen gas pressures for 80 h. As is well known, total amount of both chemisorbed and physisorbed hydrogen were estimated from the pressure change in milling pot before and after milling by a volumetric method, while only the chemisorbed hydrogen could be determined by the OCHA method. Therefore, the difference between both of them gives the physisorbed

Fig. 12 XRD profiles of the nanostructural graphite milled for 2 h by vibrating type mill equipment under various hydrogen pressure atmosphere.

Table 1 List of estimated H_2 concentration on each H_2 pressure by volumetric and OCHA methods.

H_2 Pressure	H_2 Concentration (volumetric method)	H_2 Concentration (OCHA method)
6.0 MPa	6.1 mass%	6.1 mass%
3.0 MPa	5.9 mass%	5.7 mass%
1.0 MPa	5.7 mass%	4.5 mass%
0.3 MPa	5.1 mass%	4.1 mass%

hydrogen capacity in high-pressure milled graphite. As is seen in the Table 1, we notice that the difference *i.e.*, physisorbed hydrogen concentration, increases with increasing the milling pressure. To clarify how much hydrogen is absorbed in graphite during milling under high pressures of hydrogen gas, the following experiments were performed. (i) Hydrogen gas of 6 MPa was exactly filled in the milling pot with graphite before and after milling and kept at $25.0 \pm 0.1^\circ\text{C}$. (ii) Then, the valve connecting the milling pot and the reservoir cell was closed, and only the reservoir was degassed below 3×10^{-4} Pa. (iii) Finally, after the valve was opened, the equilibrium pressures in the system were determined for graphite milled under H_2 -gas pressures of 0.3, 1.0, 3.0 and 6.0 MPa. The results obtained are given in Table 2. Here, the physisorption-like hydrogen capacity was evaluated from the difference between the equilibrium pressures before and after milling under various H_2 gas pressures. We notice that a considerable physisorbed hydrogen of 0.5~1.0 mass% is only observed in graphite after milling under higher pressures than 3 MPa of H_2 -gas.

Table 2 List of pressure value, the gas kind during milling process by vibrating mill, equilibrium hydrogen pressure and estimated unstable H_2 concentration.

Pressure	Atmospheric Gas	Equilibrium H_2 pressure	Concentration (unstable H_2)
Milling sample (after milling for 80 h)			
6.0 MPa	H_2	0.882 MPa	>0.5 mass%
6.0 MPa	Ar	0.870 MPa	0.0 mass%
3.0 MPa	H_2	0.882 MPa	~0.5 mass%
1.0 MPa	H_2	0.868 MPa	0.0 mass%
0.3 MPa	H_2	0.868 MPa	0.0 mass%
Host (before milling)			
		0.870 MPa	0.0 mass%

From the above results, we conclude that the amount of chemisorbed hydrogen decreased with increasing the milling pressure, while physisorption-like hydrogen appeared the milling pressure above 3 MPa, the amount of which increased with increasing the milling pressure. On the other hand, the higher milling pressure gave suppression of the fracture rate of graphite structure more effectively, suggesting that the hydrogen atoms trapped at the edges of the graphene sheets and between the graphene sheets near the surface are responsible for preserving the lamellar structure of nanometer scale, which may be the host for H-storage on physisorption.^{66,67)}

4. Hydrogen Storage Properties of Magnesium Based Materials

Magnesium hydride (MgH_2) is one of the attractive H-storage materials because it is directly formed from the reaction of bulk Mg with gaseous hydrogen and reaches up to high hydrogen capacity (7.6 mass%). However, the reaction is too slow for practical use and needs higher temperature than 300°C for progressing the HD reaction.^{68–70)}

Recently, the nano-structured Mg or MgH_2 prepared by a mechanical milling method has been studied to improve the reaction kinetics without reducing its high hydrogen capacity.^{71–73)} Furthermore, the H-storage properties of some catalyzed Mg or MgH_2 by a small amount of transition metals Ti, V, Mn, Fe, Co, Ni, Cu and Pd or transition metal oxides has been studied so far.^{73–83)} Liang *et al.* have reported some good H-storage properties of ball milled MgH_2 with 5 at% transition metals (Ti, V, Mn, Fe and Ni).^{74–78)} Zaluska *et al.* have studied H-storage properties of Mg composites prepared by ball milling with 1 mass% transition metals (Pd and Fe), in which ~5 mass% of hydrogen was absorbed at 300°C within ten minutes under a H_2 -gas pressure of 1 MPa.⁷³⁾ They observed that the catalyst was uniformly distributed on the magnesium surface in the form of nanoparticles. This indicates that when very small (of the size of several tens nanometers) particles of the catalyst is uniformly distributed on the metal surface, a small amount of catalysts is sufficient for improving the reaction kinetics. Recently, Kanoya *et al.* have investigated H-storage properties of some ball milled Mg with a small amount of nano-sized metals (Ni and Fe) as a catalyst.⁷⁹⁾ Their results indicated that Mg-

0.33Ni-0.17Fe (at.%) absorbed 7.49 mass% of hydrogen at 300°C by ball milling for only 15 min. Oelerich *et al.* have reported some good catalytic effect of the transition metal oxide for MgH_2 .^{80–83)} The composites prepared by ball milling for 100 h with 0.2 mol% Nb_2O_5 absorbed 7 mass% of hydrogen within 60 s and desorbed within 130 s at 300°C.⁸³⁾

In our group, it has been reported that Pd-coated nano-structured Mg films prepared by a RF sputtering method absorb ~ 5 mass% at 100°C under hydrogen atmosphere of 0.1 MPa and completely desorb below 100°C in vacuum. This confirms that MgH_2 is applicable for practical use if we can modify bulk MgH_2 into suitable nano-structure.^{84,85)} Prior to the studies of catalytic effect on H-storage properties of MgH_2 , we examined the correlation between H-storage properties and structural characteristics in mechanically milled magnesium hydride MgH_2 itself.⁸⁶⁾ The results indicated that at the early stage within 2 h milling, the amount of desorbed hydrogen decreases $\sim 16\%$ from 7.3 to 6.1 mass% and the onset temperature of dehydrogenation decreases by 70°C from 400°C, while both the powder size and the crystallite size in powder decrease with increasing the milling time down to 1 μm and 15 nm, respectively, and the lattice strain of 0.3% is rapidly introduced as well.

At the next step of systematic studies of improving H-storage properties in Mg systems, we studied the catalytic effect of 3d-transition metals Fe, Co, Ni, and Cu and oxide Nb_2O_5 on H-storage in MgH_2 without exposing to air the products in all the preparing and measuring processes.

4.1 Catalytic effect of 3d-transition metals on H_2 -storage properties in milled MgH_2

We examined the doping effect of nanometer-sized 3d-transition metals, Fe, Co, Ni, and Cu on H-storage properties in MgH_2 prepared by mechanically milling method.

Figure 13 shows the TDMS profiles of the H_2 gas for pure MgH_2 and some catalyzed MgH_2 with 1 mol% Fe, Co, Ni and Cu nanoparticle metals prepared by ball milling for 2 h under a H_2 gas atmosphere of 1 MPa. We can see that all the composites with nanoparticle metals as catalyst exhibit better HD properties than the pure milled MgH_2 : The HD temperature is lowered and a larger amount of hydrogen (~ 7 mass%) are desorbed by introducing a small amount (1 mol%) of catalysts. It should be noted that all the catalyzed MgH_2 indicated a larger desorbed hydrogen capacity than non-catalyzed MgH_2 . This may be due to release of excess hydrogen absorbed during milling MgH_2 with catalysts under H_2 -gas atmosphere. The Ni-doped composite shows the best HD properties among all the catalyzed MgH_2 composites and the peak temperature (260°C) is about 100°C lower than that of the pure milled MgH_2 . In addition, it seems likely that these HD properties depend on the states of 3d-electrons because the peak temperature of hydrogen desorption decreases with increasing a number of occupied 3d-electrons on those transition metals except for Cu, which is known as one of non-catalytic materials from the fact that the 3d-electron shell of Cu metal is fully occupied.⁸⁷⁾

Next, we examined how the HD properties in the Ni-doped system are improved by changing the milling time, the milling revolution speed and the amount of Ni catalyst to optimize the milling conditions for H-storage.

Fig. 13 Thermal desorption mass spectra (TDMS) of hydrogen for pure MgH_2 and catalyzed MgH_2 by adding a small amount (1 mol%) of Cu, Fe Co and Ni nanoparticle metals milled for 2 h.

(1) At the first step, we changed the milling time from 15 min to 2 h at 400 rpm for 1 mol% Ni-doped MgH_2 composite, and examined the TDMS profiles. The results are shown in Fig. 14. We notice that the composite milled for 15 min leads to the onset temperature of HD reaction about at $\sim 150^\circ\text{C}$ and the decrease in the peak temperature to 210 from 260°C. So, we conclude that the shorter of the milling time brings the better HD properties. However, the HD spectra composed of two broad peaks and distribute in wide temperature range of 150–300°C.

(2) At the second step, we changed the milling revolution speed from 400 rpm to 200 rpm under the short milling time of 15 min, and performed the TDMS measurements. In Figs. 15(a) and (b), the TDMS profiles are shown for the 1 mol% Ni-doped MgH_2 composite milled at 400 rpm and 200 rpm, respectively. You can see that the profile of the composite milled at 200 rpm consists in a single HD peak, but the temperature range is still wide from 150 to 300°C.

(3) Finally, we changed the amount of Ni nanoparticle catalyst from 1 mol% to 2 mol% under the same conditions of the short milling time for 15 min and the slow milling revolution speed at 200 rpm, and we performed the TDMS measurements. As is shown in Fig. 15(c), the MgH_2 composite with 2 mol% Ni shows the most superior HD profile in the TDMS curves in all the composites examined in this work.

Thus, we found that the 2 mol% Ni-doped MgH_2 prepared by ball milling under the short milling time for 15 min and slow milling revolution speed at 200 rpm desorbs a large amount of hydrogen (~ 6.5 mass%) in the temperature from 150 to 250°C at the heating rate of 5°C/min. From these results, we conclude that the short milling time and slow

Fig. 14 TDMS profiles of hydrogen from the MgH_2 composite catalyzed by 1 mol% Ni in the milling conditions for 15 min, 1 h, and 2 h at 200 rpm under a H_2 gas atmosphere of 1 MPa.

Fig. 15 TDMS profiles of hydrogen for the products milled MgH_2 for 15 min (a) at 400 rpm with 1 mol% Ni, (b) at 200 rpm with 1 mol% Ni, and (c) at 200 rpm with 2 mol% Ni, respectively.

milling revolution speed brings the better HD properties for the $\text{MgH}_2 + 2 \text{ mol\% Ni}$ composite. To clarify the reason why the HD properties for MgH_2 are so improved by a small amount of Ni catalyst, we examined the observation of morphology of the 2 mol% Ni-doped MgH_2 composite. In Fig. 16, the EDX micrographs corresponding to the Mg and Ni element distribution are shown for $\text{MgH}_2 + 2 \text{ mol\% Ni}$ composite milled for 15 min at 200 rpm. We can see that the nanoparticle Ni uniformly disperses on the surface of the MgH_2 particles by ball milling for such a short time and under such a slow milling revolution speed. When the micron meter sized Ni was used as a catalyst in MgH_2 in the milling

Fig. 16 EDX micrographs of (a) Mg and (b) Ni elements in the catalyzed MgH_2 composite by 2 mol% Ni prepared by milling for 15 min at 200 rpm.

process, we could not find out such superior H-storage properties.

Next, we examined the reversible properties of hydriding/dehydriding reactions for the sample of $\text{MgH}_2 + 2 \text{ mol\% Ni}$ prepared by milling for 15 min at 200 rpm under H_2 gas atmosphere of 1 MPa. The reversibility was tested by the following cyclic processes: the dehydrogenation was performed by holding the sample at 150°C (corresponding to the onset temperature for dehydrogenation) and at 200°C (corresponding to the peak temperature for dehydrogenation) for 12 h under high vacuum, and then the hydrogenation was performed under pure hydrogen gas up to 3 MPa at 150 and 200°C for 12 h, respectively. After completing those hydrogen absorbing/desorbing cycles, we examined the HD properties by the TGA and TDMS measurement. The results obtained are shown in Fig. 17. The dehydrogenation properties after 2nd cycle at 150°C is better than that after 2nd cycle at 200°C , but is slightly worse than that after 1st cycle after

Fig. 17 TDMS profiles of hydrogen for the 2 mol% Ni catalyzed MgH_2 composite prepared by milling for 15 min at 200 rpm. The solid, dashed and dotted lines are corresponding to the product after milling for 15 min at 200 rpm, the sample after the 2nd hydriding/dehydriding cycle at 150°C and the sample after 2nd cycle at 200°C , respectively.

Fig. 18 X-ray diffraction profiles for the 2 mol%Ni-catalyzed MgH_2 composite prepared after milling for 15 min at 200 rpm, the product after dehydrogenation at 150°C and the sample after dehydrogenation at 200°C.

milling. As is seen in Fig. 18, the X-ray diffraction profiles indicate that both of the products after milling and after its dehydrogenating at 150°C have a small peak corresponding to only Ni-metal phase in addition to the main peaks for MgH_2 . But, in the sample after dehydriding at 200°C, there are the peaks corresponding to not only metal Ni-metal phase but also Mg_2Ni phase. Since the catalytic effect of Mg_2Ni is weaker than Ni-metal for improving the H-storage properties, the formation of Mg_2Ni in the MgH_2 +Ni composite would lead to the worse H-storage properties. This is also the reason why the short milling time and slow milling revolution speed brings the better HD properties for the MgH_2 +2 mol%Ni composite. Because the milling for a long time at high revolution speed easily leads to the Mg_2Ni phase at the phase boundaries between the nanoparticle Ni and main Mg phases due to the strong affinity between Mg and Ni atoms.

4.2 Catalytic effect of metal oxide Nb_2O_5 on hydrogen storage properties

Figure 19 shows the TDMS profiles of H_2 for the MgH_2 composite with 1 mol% Nb_2O_5 prepared by ball milling for 15 min, 2 h, and 20 h at 400 rpm under a H_2 gas atmosphere of 1 MPa. The composite milled for 15 min has two HD peaks around 230°C and 270°C, which are much lower than that for pure MgH_2 milled for 15 min (370°C). This indicates that Nb_2O_5 is one of the good catalysts for improving the HD properties in MgH_2 . To optimize the milling condition for improving the HD properties, we increased the milling time up to 20 h from 15 min for the Nb_2O_5 -doped composite. After 2 h milling, the HD peak at high temperature becomes much weaker as is shown in Fig. 19. Furthermore, the milling for 20 h leads to single HD peak around 230°C, possessing a large amount of hydrogen (~ 6.0 mass%). This result indicates that the HD properties of the Nb_2O_5 -doped composite are much improved with increasing the milling time in contrast to the case of the Ni-catalyzed composite.

As is evident from Fig. 20(a), the composite of MgH_2 and 1 mol% Nb_2O_5 milled for 20 h shows the existence of $\beta\text{-MgH}_2$ and a small amount of MgO in the XRD profiles, but there is no trace corresponding to the niobium oxide Nb_2O_5 . This indicates that Nb_2O_5 disperses on the surface of MgH_2

Fig. 19 TDMS profiles of hydrogen from the MgH_2 composite with 1 mol% Nb_2O_5 prepared by milling for 15 min, 2 h, and 20 h at 400 rpm under a H_2 gas atmosphere of 1 MPa.

Fig. 20 X-ray diffraction profiles for (a) the 1 mol% Nb_2O_5 -catalyzed MgH_2 composite prepared by milling for 20 h, (b) the composite after heat treatment up to 450°C, (c) the pure MgH_2 by milling for 20 h after heat treatment up to 470°C.

in the nanometer scale by ball milling and acts as a good catalyst. The XRD profile after heat treatment up to 450°C in Fig. 20(b) indicates the existence of Mg and MgO . In details, the intensity corresponding to the MgO peak is larger than that in pure MgH_2 milled for 20 h in Fig. 20(c). Therefore, it seems likely that Nb_2O_5 dispersed in nanometer scale is reduced by Mg to form metal Nb and MgO during ball milling or heat treatment as follows

Since the standard enthalpy change of this reaction is negative and large, this reduction reaction should be possible to proceed during ball milling or heat treatment. Consequently, the metallic Nb dispersed in nanometer scale could act as an excellent catalyst on hydrogen desorption from MgH_2 .

Next, we examined the reversible properties of hydriding/dehydriding reactions at 200°C for the composite of MgH_2 and 1 mol% Nb_2O_5 milled for 20 h according to the same cyclic processes as the MgH_2 composite with Ni nanoparticle. As is shown in Fig. 21, the dehydrogenation property after 2nd cycle at 200°C is better than that after 1st cycle. This suggests that Nb_2O_5 is reduced by Mg to form metallic Nb during dehydriding/hydriding cycle at 200°C , leading to the hydrogen desorption of $\sim 6\text{ mass\%}$ in the temperature range from 150 to 250°C . This result indicates that Nb is the best catalyst we have studied so far. Thus, it seems that some magnesium composites catalyzed by 3d-transition metals nano-particles is acceptable for practical application as a H_2 tank for off-board H-storage.

5. Prospective

In this paper, we have presented our recent results of H-storage properties on lithium, graphite and magnesium based materials prepared by some mechanical milling methods. There were some progress on basic materials properties in lithium-N-H and catalyzed magnesium nano-composite systems for H-storage.

Especially, the kinetic properties of the H-storage reactions in Mg metal were significantly improved by doping a small amount of Ni metals with several ten nanometers in diameter or Nb oxides, reaching a level of practical use as a H-storage tank for off-board storage.

In some Li-N-H systems, we found that a large amount of hydrogen (more than 6 mass%) were reversibly stored in the temperature range from 140 to 200°C , the temperature of which is still higher than the target of NEDO project or COE

target. However, recent quick developments make imagine us that the NEDO target will be cleared in near future in lithium based systems.

On the contrary, we found that the ball milled graphite could make a large amount of hydrogen (more than 7 mass%) absorbed. However, not only the desorption temperature was not only still too high for H-storage, but also the H-storage reaction was not reversible. Many efforts have been paid on improving H-storage properties in nano-structured graphite prepared by ball milling under hydrogen gas atmosphere, but the properties were still too far from the NEDO target. Therefore, in graphite system, some break-through is necessary to clear the NEDO target. Before proceeding further improving studies, it is important to know whether there is a new, hitherto unknown interaction between carbon and hydrogen whose interaction energy falls between physisorption and chemisorption or not. We believe that the basic studies such as neutron scattering experiments should give us an answer to above question whereby we can solve the carbon controversy concerning how much hydrogen is stored in carbon single wall nano-tube.

As we have mentioned above, currently, in the hydrogen research laboratories all over the world, new approach using non-traditional and nano-technological techniques have been applied to design high-performance H-storage materials. Thus, we believe that, due to this kind of research works, better H-storage materials which absorb and desorb at least 6 mass% hydrogen at temperatures lower than 150°C , will be discovered and developed for practical use on board hydrogen tank in near future.

Acknowledgements

This work was supported by the NEDO project “Development for Safe Utilization and Infrastructure of Hydrogen Industrial Technology” in Japan and the Grant-in-Aid for COE Research (No. 13CE2002) of the Ministry of Education, Culture, Sports, Sciences and Technology of Japan. The authors gratefully acknowledge Miss E. Gomibuchi, Mr. K. Nabeta, Mr. K. Kimura, Mr. S. Hino and Mr. T. Nakagawa for their help in our laboratory.

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Fig. 21 TDMS profiles of hydrogen for the 1 mol% Nb_2O_5 -catalyzed MgH_2 composite prepared by milling for 20 h (1st cycle) and the sample after 2nd dehydriding/hydriding cycle at 200°C (2nd cycle).

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