Short communication

Hydrogen releasing reaction between $Mg(NH_2)_2$ and CaH_2

Jianjiang Hu [a], Zhitao Xiong [a], Guotao Wu [a], Ping Chen [a,*], Kenji Murata [b], Ko Sakata [b]

[a] *Department of Physics, National University of Singapore, Singapore 117542, Singapore*
[b] *The Institute of Applied Energy, Tokyo, Japan*

Available online 19 May 2006

Abstract

A two-stage hydrogen release of 4.9 wt.% was observed on a mixture of $Mg(NH_2)_2$ and CaH_2 at 1:2 molar ratio. The H_2 desorption in the temperature range from room temperature to 260 °C was recyclable, which was observed by temperature-programmed-desorption (TPD), volumetric measurement and Fourier transform infrared (FT-IR). At high temperature, a ternary nitride $CaMg_2N_2$ and a solid solution of $CaNH/Ca_2NH$, characterized by X-ray diffractometry (XRD), were formed.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrogen desorption; Magnesium amide; Calcium hydride; Ternary nitride

1. Introduction

In pursuit of alternative energy sources for the traditional fossil fuel, hydrogen presents to be a kind of clean energy that can eliminate the evolution of greenhouse gas. Although there are a variety of industrial processes for hydrogen production, the storage of hydrogen gas proves to be a key issue in the application as on-board power source. Compared to the physical approaches like compression and cryogenic method, chemical hydrogen storage in solid state has among others the merits in high volumetric and gravimetric hydrogen density.

Starting from metal nitride [1], investigations on the hydrogen storage media extend to metal amides and imides. The concept of affinitive combination of proton $H^{\delta+}$ and protide $H^{\delta-}$ was put forth for the destabilization of hydrides [2]. Amides of alkali and alkali earth metals possess proton $H^{\delta+}$ in the molecules in this respect. Thus, appropriate metal amide–hydride pairs provide possibility for effective H_2 release. Interesting systems such as $Mg(NH_2)_2$–LiH, $LiNH_2$–MgH_2, and $Mg(NH_2)_2$–NaH have been reported [3–5].

Magnesium amide $Mg(NH_2)_2$ is a light-weighted amide candidate which was synthesized and characterized a few decades ago [6,7]. It has recently become interesting as a hydrogen storage precursor [3,8]. CaH_2 itself can release hydrogen only at temperatures higher than 700 °C. But its mixture with Ca_3N_2 could reversibly deliver H_2 at relatively low temperature [9]. $Mg(NH_2)_2$ and CaH_2 represent a low-cost amide–hydride combination which may be of interest as a practical hydrogen storage material.

2. Experimental

2.1. Materials

CaH_2 was purchased from Alfa Aesar and used as received. $Mg(NH_2)_2$ was prepared in the laboratory by reacting Mg powder (Alfa Aesar) with ammonia.

2.2. Sample preparation

$Mg(NH_2)_2$ and CaH_2 with a molar ratio of 1:2 were loaded in a cylindrical jar in a glovebox (MBraun, Germany) and ball-milled for 24 h by using Spex 8000. About 18 psi H_2 was released during ball milling of 3.16 g mixture, which is equivalent to 0.6 wt.%.

2.3. Methods

Temperature-programmed-desorption (TPD, dehydriding) and soak were carried out on a home-built apparatus which has been described in detail elsewhere [10]. Heating rates of 2 and 1 °C min^{-1} were used for TPD and soak, respectively. XRD was conducted on a Brucker X-ray diffractometer equipped with an in situ cell. Pellets of powdery samples were made

---

by a pellet press and placed in the in situ cell which was subsequently evacuated to avoid moisture and oxygen from air. Volumetric measurements were performed on a Sieverts' apparatus from Advanced-Material Corporation (USA). About 500 mg sample was used for each experiment. Differential scanning calorimetry measurements (DSC) were performed on Netsch DSC 204 HP at a heating rate of $2\,^\circ C\,min^{-1}$ with Ar as purging gas at 30 ml min^{-1} flowrate.

3. Results

3.1. Temperature-programmed-desorption results

The hydrogen release temperature of calcium hydride lies above $700\,^\circ C$ (Fig. 1a). NH$_3$ was starting to release during the thermal decomposition of pure Mg(NH$_2$)$_2$ at temperature around $260\,^\circ C$. TPD experiment of magnesium amide showed a peak temperature at $384\,^\circ C$ (not shown) which is attributed to the decomposition of magnesium amide with evolution of NH$_3$. This is similar to the observation in literature [11]. The TPD curve of the freshly ball-milled mixture (Fig. 1b) shows distinct features in the H$_2$ desorption behaviors other than their individual component CaH$_2$ or Mg(NH$_2$)$_2$. The TPD curve consists of two stages: a relatively sharp peak in the lower temperature range and a broad one in the higher temperature range. It can be seen that the hydrogen release starts at a temperature as low as about $60\,^\circ C$ for the freshly ball-milled sample and peaks at $201\,^\circ C$. No ammonia gas was detected throughout the tested temperature range (20–$520\,^\circ C$).

The H$_2$ release in the lower temperature range is of interest for use in hydrogen storage. So the temperature range from 20 to $260\,^\circ C$ was used for the reversibility study of hydrogen desorption/uptake. The sample was at first heated at $2\,^\circ C\,min^{-1}$ to $260\,^\circ C$, and kept at $260\,^\circ C$ for 5 h for completion of H$_2$ release. The post-TPD sample then underwent a H$_2$ soak treatment at 100 atm at $1\,^\circ C\,min^{-1}$ from 20 to $200\,^\circ C$ and maintained at $200\,^\circ C$ for 5 h. Afterwards, second TPD testing was carried out (Fig. 1c). The TPD features in the high temperature range was

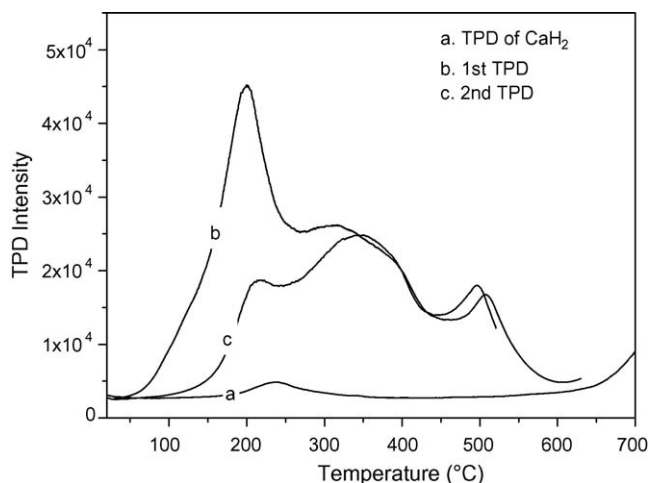reproduced, indicating that the first cycle of desorption/uptake did not affect the TPD characteristics beyond the treatment temperature. Compared to the first TPD, hydrogen release started at about $100\,^\circ C$ and the peak temperature shifted from 201 to $216\,^\circ C$. The fact that hydrogen could be released from the recycled sample indicates that hydrogen was recharged to the post-TPD sample by the H$_2$ soak treatment. Despite the decrease in intensity of the first peak, a partial recyclability of hydrogen in this sample is manifest.

3.2. Volumetric measurements

The volumetric release test was carried out using the same temperature program as for the TPD treatment. Thus, hydrogen desorption was conducted at $2\,^\circ C\,min^{-1}$ till $260\,^\circ C$. The temperature was kept at $260\,^\circ C$ for 5 h. 2.0 wt% of H$_2$ was released from the as-prepared sample (Fig. 2a). Subsequently, hydrogen soak was performed at 100 atm H$_2$ with the same temperature program like for H$_2$ soak experiment (20–$200\,^\circ C$ at $1\,^\circ C\,min^{-1}$, $200\,^\circ C$ for 5 h). Consistent with the results in the second TPD, only about 1.0 wt.% H$_2$ could be desorbed in the second release experiment (Fig. 2b). Like the TPD experiment, the H$_2$ release shifted to higher temperature in the second release, compared to the first release from the as-prepared sample.

When temperature was raised to $510\,^\circ C$, about 3.8 wt.% H$_2$ was released from the as-prepared sample (Fig. 2c). Along with the H$_2$ release during ball milling (0.6%), the H$_2$ amount released was 4.4 wt.%. Taking account of the purity of the starting materials, the amount of hydrogen release till $510\,^\circ C$ can be estimated to 4.9 wt.%. However, no hydrogen could be absorbed by the sample after the high temperature release, and no hydrogen release was observed accordingly.

3.3. FT-IR measurements

FT-IR spectra of samples subjected to different treatments are shown in Fig. 3. Fig. 3a is the spectrum of Mg(NH$_2$)$_2$
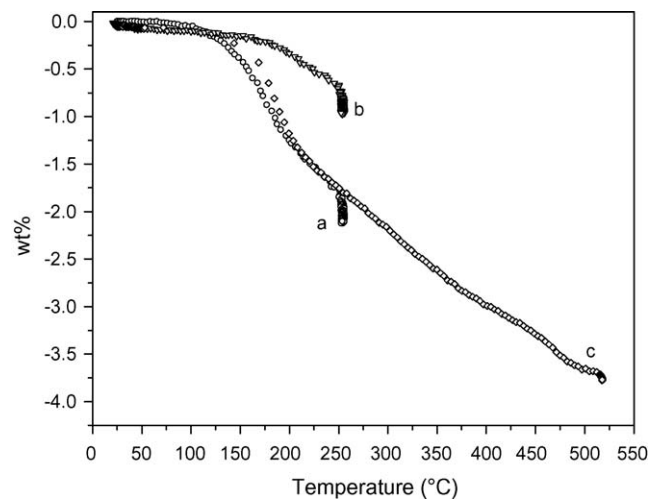

Fig. 1. TPD curves at heating rate of $2\,^\circ C\,min^{-1}$: (a) TPD of CaH$_2$; (b) TPD of as-prepared sample; (c) second TPD of H$_2$ soaked post-TPD sample.

Fig. 2. Volumetric release: (a) release of as-prepared sample to $260\,^\circ C$; (b) second release to $260\,^\circ C$ after soak at $200\,^\circ C$; (c) release of as-prepared sample to $510\,^\circ C$.
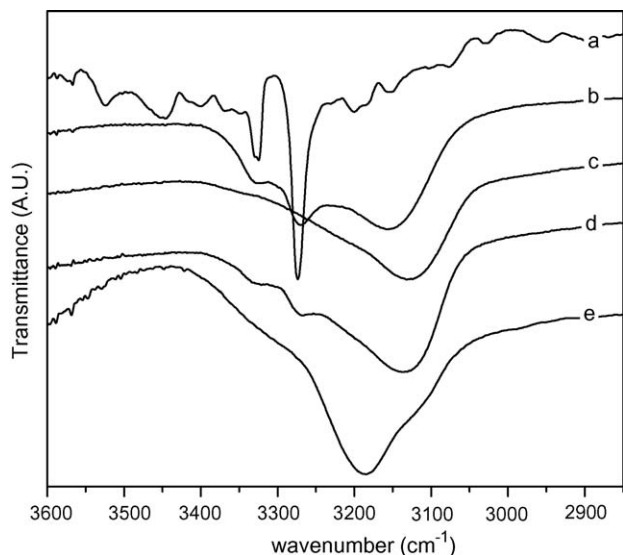
Fig. 3. FT-IR spectra: (a) Mg(NH$_2$)$_2$ as reference; (b) as-prepared sample; (c) after TPD till 260 °C and further 5 h at 260 °C; (d) after rehydrogenation of post-TPD sample; (e) after TPD to 700 °C.

as reference which shows the typical stretching vibration of amide group (–NH$_2$) [6] at 3273/3324 cm^{-1}. In the spectrum from the as-prepared sample (Fig. 3b), the vibration of amide group can still be seen, but with lower intensity. In addition, a new broad absorbance at about 3155 cm^{-1} appeared. The absorbance of amide group disappeared completely after the sample was subjected to TPD treatment to 260 °C (Fig. 3c). On the other hand, the broad absorbance at 3155 cm^{-1} became the only absorbance in this region. Although the origin of the absorbance at 3155 cm^{-1} is unclear to us at the present state, it falls in the region of N–H bonding in imide. So the absorbance may be related to a kind of ternary imide of Ca and Mg. Interestingly, the absorbance of the amide groups at 3273/3324 cm^{-1} re-appeared after H$_2$ soak treatment to 200 °C of the post-TPD sample (Fig. 3d), indicating the formation or recovery of amide groups through hydrogenation. The absorbance shifted to higher wavenumber for the sample subjected to TPD at 700 °C (Fig. 3e), indicating further changes in structure.

Based on the FT-IR analysis, we would describe the hydrogen desorption/uptake process as follows: hydrogen is released with the consumption of the amide, leading to a structure similar to imide which gives rise to the broad absorbance at 3155 cm^{-1}. This structure can be converted to amide upon hydrogenation. In this regard, a reversible hydrogen desorption/uptake is feasible at temperature below 260 °C.

3.4. DSC measurement

Fig. 4 is the DSC curve of the as-prepared sample. The first endothermic peak lies at 203 °C, which is in consistence with the TPD result. Using the peak fitting method along with the H$_2$ amount released till 260 °C, the enthalpy of desorption was estimated to 21.4 kJ mol^{-1} H$_2$. According to the thermodynamic principle, an exothermic hydrogenation is a prerequisite for a reversible H$_2$ uptake/release system, and the hydriding
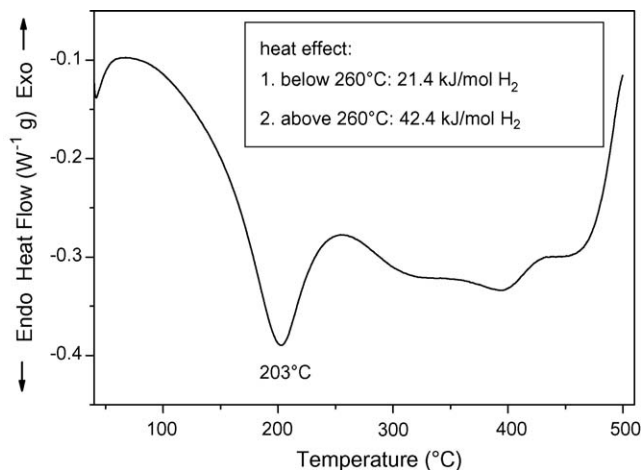

Fig. 4. DSC curve of as-prepared sample.

enthalpy at 298 K lies in the range of −29 to −46 kJ mol^{-1} H$_2$, given the H$_2$ pressure of metal hydride for practical hydrogen storage purpose of 0.1–10 bar [12]. The endothermic dehydrogenation in our experiment would predict an exothermic hydrogenation reaction, i.e., a thermodynamically reversible H$_2$ uptake/release process at low temperatures in this system. However, the enthalpy range of hydriding was deduced from the entropy change of metals with an approximated value of −125 J mol^{-1} K^{-1} which may be not the case for the studied system. As shown in the above sections, a partial reversible H$_2$ uptake/release was realized, but with higher temperature and pressure for hydrogenation than those predicted by the available thermodynamics.

The amount of H$_2$ that can be released at higher temperature was 3.0 wt.% or 4.2 H atoms per Mg(NH$_2$)$_2$–2CaH$_2$ with an endothermic effect of 42.4 kJ mol^{-1} H$_2$ which is still in the range for a thermodynamic reversible dehydrogenation. However, the rehydrogenation was not successful under the experimental conditions available. Investigations should be done to find out if kinetics plays a role in the rehydrogenation.

3.5. X-ray diffraction measurements

In the XRD profile (Fig. 5a) of the as-prepared sample, only CaH$_2$ phase was identified. Mg(NH$_2$)$_2$ readily becomes amorphous during ball milling and cannot be detected by XRD [5]. The CaH$_2$ phase retained but with lower intensity after the H$_2$ desorption to 260 °C (Fig. 5b). Additional diffraction patterns appeared at 35.5, 51.5, 60.9, 63.9, which may be assigned to imides, when in connection with the FT-IR absorbance at 3155 cm^{-1}. The further hydrogenation treatment of the post-desorped sample added little change to the diffraction patterns (Fig. 5c). Nonetheless, characteristic patterns of calcium magnesium nitride (CaMg$_2$N$_2$) and a solid solution of CaNH and Ca$_2$NH became discernable as the desorption temperature was raised to 510 °C (not shown). At 700 °C, the diffraction patterns at 32.6, 41.2, 44.4, 54.0, 62.4, 68.4, 70.5 and 85.1 and at 30.6, 35.5, 51.5, 60.9, 63.9 and 86.2 confirmed the formation of CaMg$_2$N$_2$ and CaNH/Ca$_2$NH, respectively (Fig. 5d). The forma-
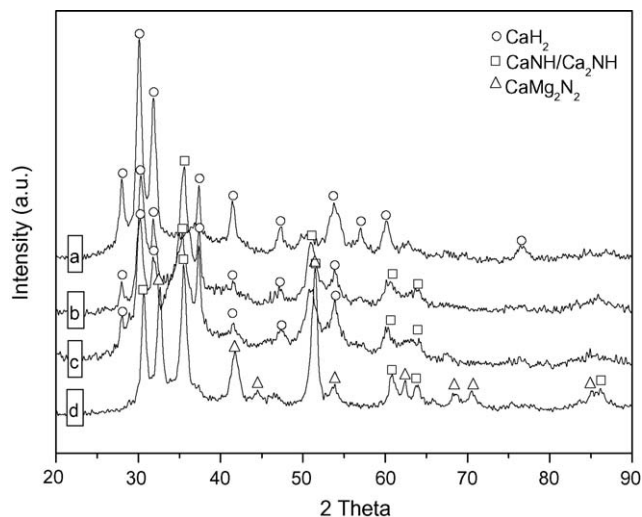
Fig. 5. XRD patterns of samples with different treatments: (a) as-prepared sample; (b) TPD till 260 °C; (c) H$_2$ soak of post-TPD 260 °C; (d) TPD till 700 °C.

tion of calcium magnesium nitride (CaMg$_2$N$_2$) was previously reported as the first ternary nitride of alkali-earth metal synthesized at 1050 °C by reacting Mg$_3$N$_2$ with Ca$_3$N$_2$ under N$_2$ [13]. However, the mixture of CaMg$_2$N$_2$ and CaNH/Ca$_2$NH lost its ability to re-absorb H$_2$ under the experimental conditions.

From the XRD results, the hydrogen releasing reaction between Mg(NH$_2$)$_2$ and CaH$_2$ may be accounted for with the following reaction equation:

$$2Mg(NH_2)_2 + 4CaH_2 = CaMg_2N_2 + Ca_2NH + CaNH + 7H_2$$
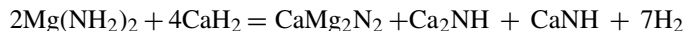
with a theoretical H$_2$ capacity of 5.0 wt.%, close the experimental value (4.9 wt.%).

4. Conclusion

The amide–hydride reaction between Mg(NH$_2$)$_2$ and CaH$_2$ at 1:2 molar ratio yielded a mixture of an alkali-earth metal nitride and calcium imides with about 4.9 wt.% hydrogen release at temperature of 510 °C. A partially reversible hydrogen desorption/uptake was observed in the low temperature range. High temperature resulted in a mixture of ternary nitride of alkali-earth metal and calcium imides, which showed no interaction with H$_2$.

References

[1] P. Chen, Z.T. Xiong, J.Z. Luo, J.Y. Lin, K.L. Tan, Nature 420 (2002) 302–304.
[2] W. Grochala, P.P. Edwards, Chem. Rev. 104 (2004) 1283–1315.
[3] Z.T. Xiong, G.T. Wu, J.J. Hu, P. Chen, Adv. Mater. 16 (2004) 1522–1525.
[4] W.F. Luo, J. Alloy Comp. 381 (2004) 284–287.
[5] Z.T. Xiong, J.J. Hu, G.T. Wu, P. Chen, J. Alloy Comp. 395 (2005) 209–212.
[6] G. Linde, R. Juza, Z. Anorg. Allg. Chem. 409 (1974) 191–198.
[7] G. Linde, R. Juza, Z. Anorg. Allg. Chem. 409 (1974) 199–214.
[8] H.Y. Leng, T. Ichikawa, S. Hino, N. Hanada, S. Isobe, H. Fujii, J. Phys. Chem. B 108 (2004) 8763–8765.
[9] Z.T. Xiong, P. Chen, G.T. Wu, J.Y. Lin, K.L. Tan, J. Mater. Chem. 13 (2003) 1676–1680.
[10] P. Chen, Z.T. Xiong, J.Z. Luo, J.Y. Lin, K.L. Tan, J. Phys. Chem. B 107 (2003) 10967–10970.
[11] Y. Nakamori, G. Kitahara, S. Orimo, J. Power Sources 138 (2004) 309–312.
[12] Libowitz, G. George, The Solid-State Chemistry of Binary Metal Hydrides, W.A. Benjamin Inc., New York, 1965 (the physical inorganic chemistry series).
[13] V. Schultz-Coulon, W. Schnick, Z. Naturforsch. B 50 (1995) 619–622.