



Mechanism of hydrogenation reaction of Li-Mg-N-H
system composed of 8LiH and $3\text{Mg}(\text{NH}_2)_2$

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New H-storage group --- Metal-N-H

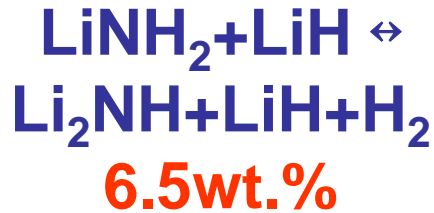
Chen, et al., Nature, 420, 302 (2002)



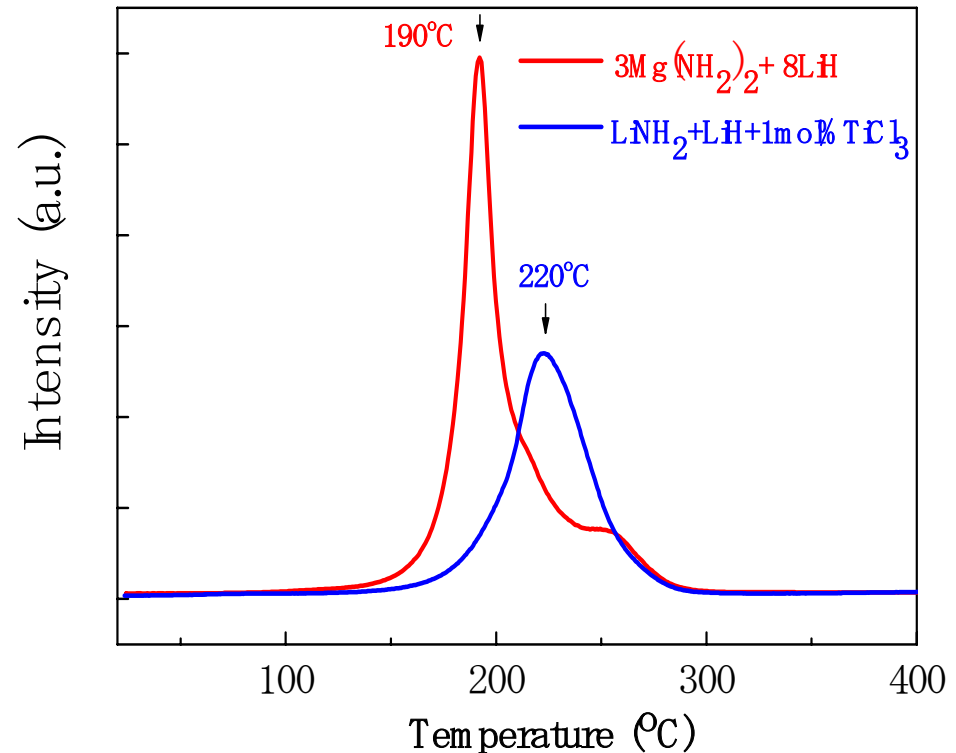
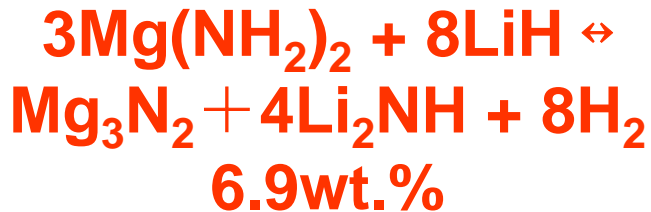
$\Delta H_1: 148 \text{ KJ/mole H}_2$

$\Delta H_2: 45 \text{ KJ/mole H}_2$

Ichikawa, et al., J. Alloys Comp., 365,271(2004)

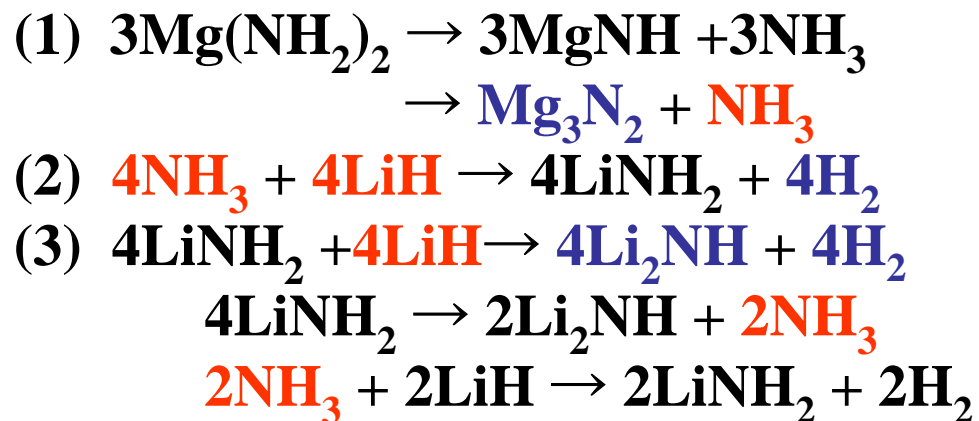
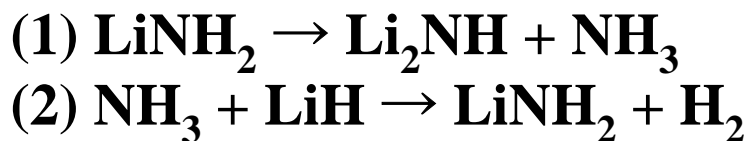
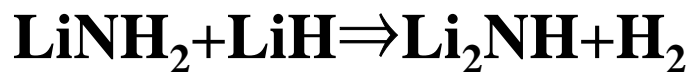


Leng, et al., J. Phys. Chem. B, 108, 8763(2004)



Mechanism of H-Desorption

Ichikawa, et al., J. Phys. Chem. B, 108, 7887(2004)



Mechanism of **hydrogen absorption** of system composed $3\text{Mg}(\text{NH}_2)_2$ and 8LiH



Experiment methods

➤ Sample preparation

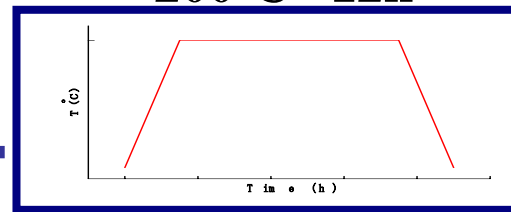
Samples were made by ball milling.



➤ Hydrogenation Process

5MPa H₂

+



➤ Analysis methods:

To identify the changes of phases:

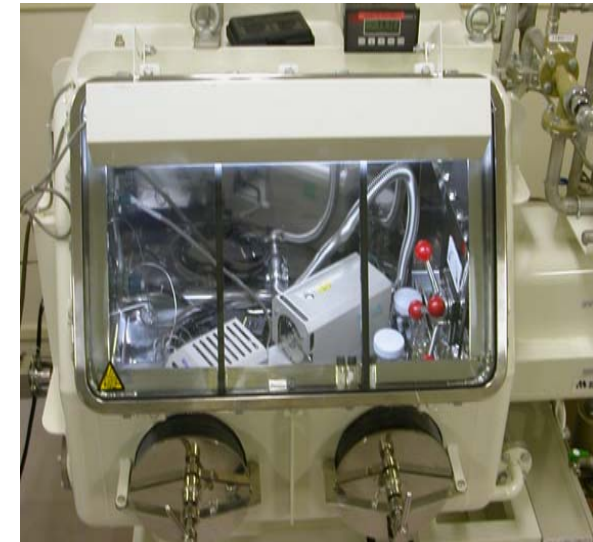
X-ray Diffraction (**XRD**)

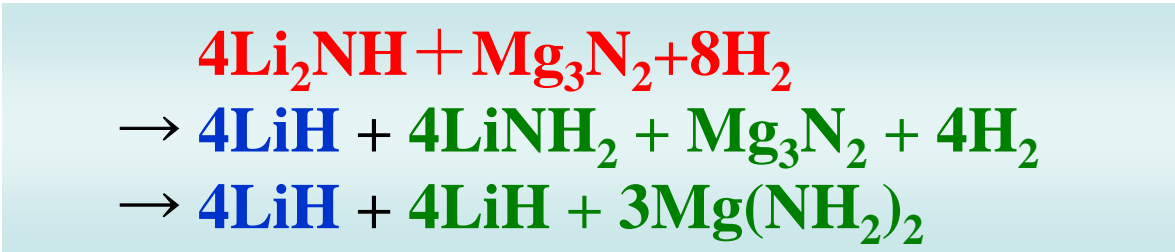
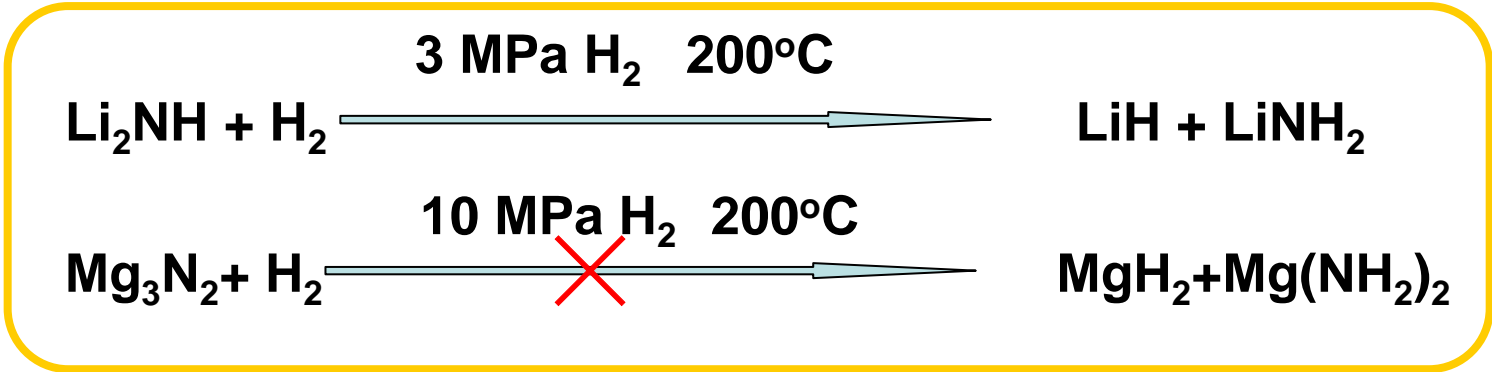
To analyze the gas desorption of samples :

Thermogravimetry (**TG**)

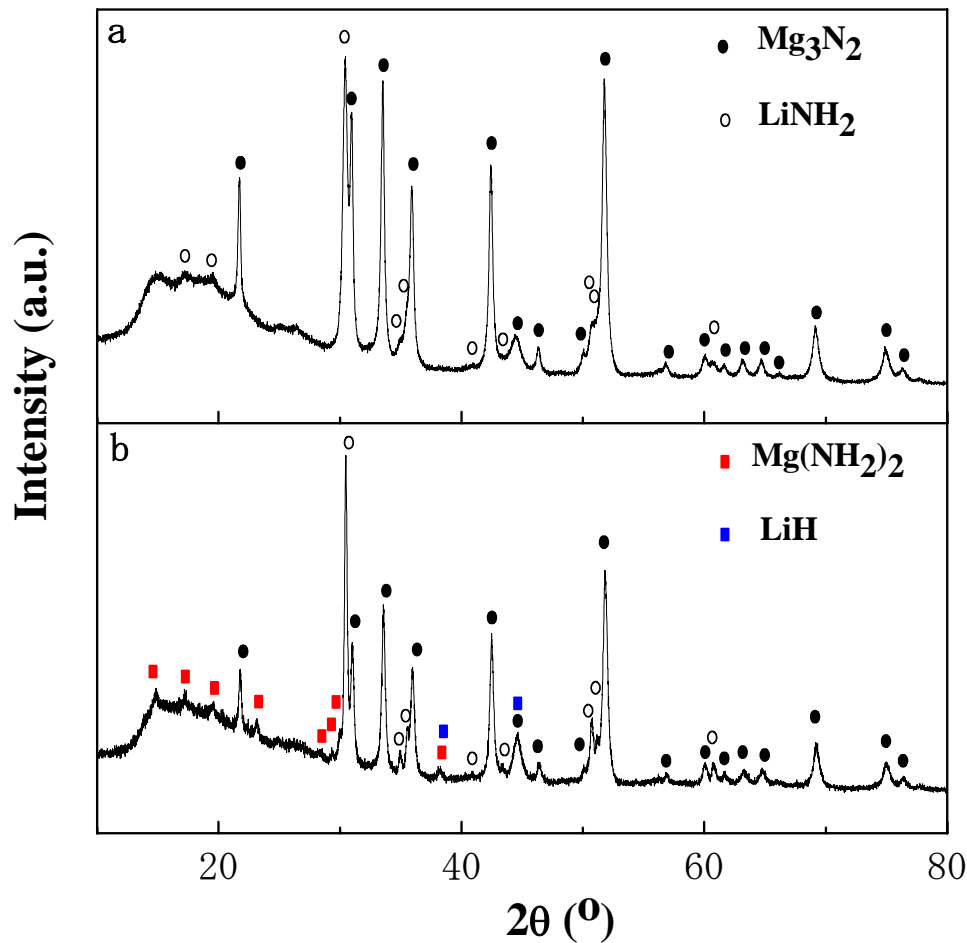
Thermal Desorption Mass Spectroscopy (**TDMS**)

(With a heating rate of 5°C/min)





LiNH₂ was observed in the hydrogenation process of 4Li₂NH and Mg₃N₂ by in situ XRD

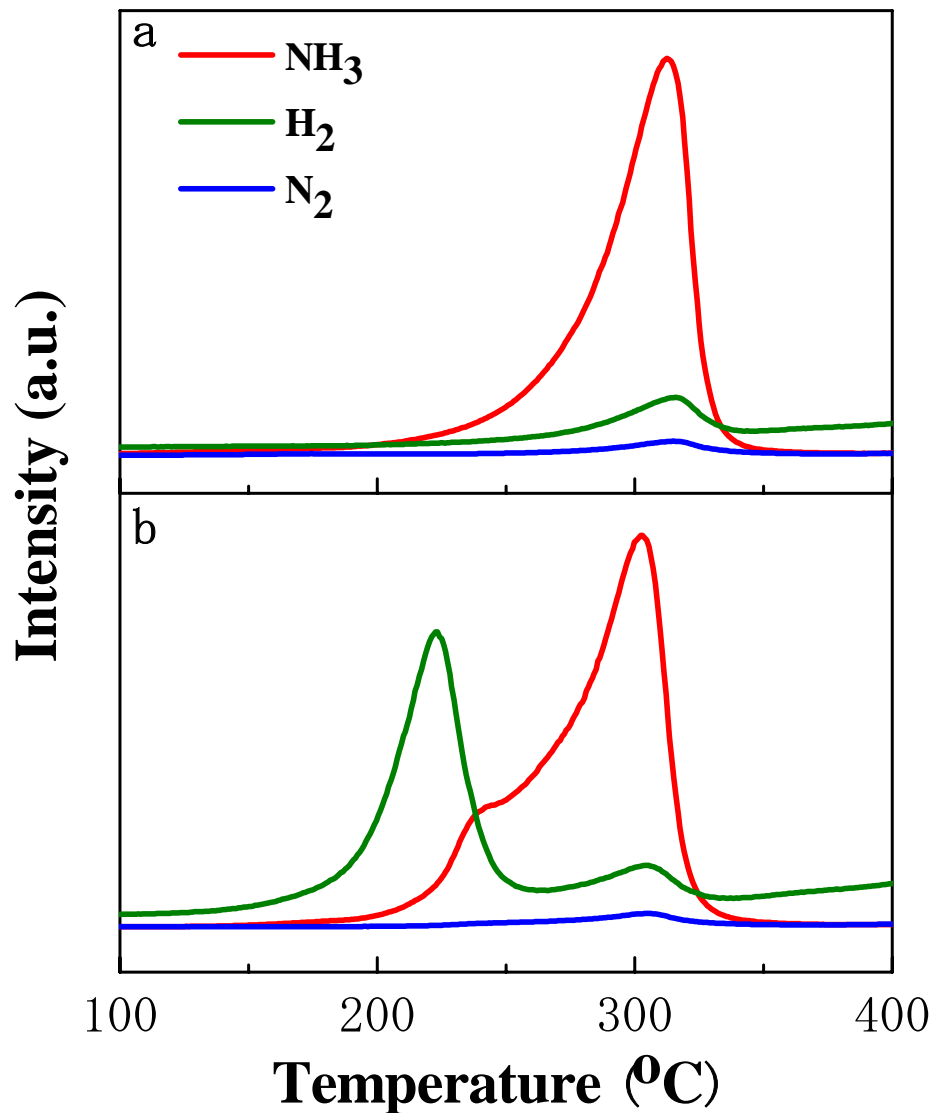


(a) Before hydrogenation

LiNH_2 and Mg_3N_2

(b) After hydrogenation
at 5MPa H_2 and 200°C

LiH and $\text{Mg}(\text{NH}_2)_2$ appear!



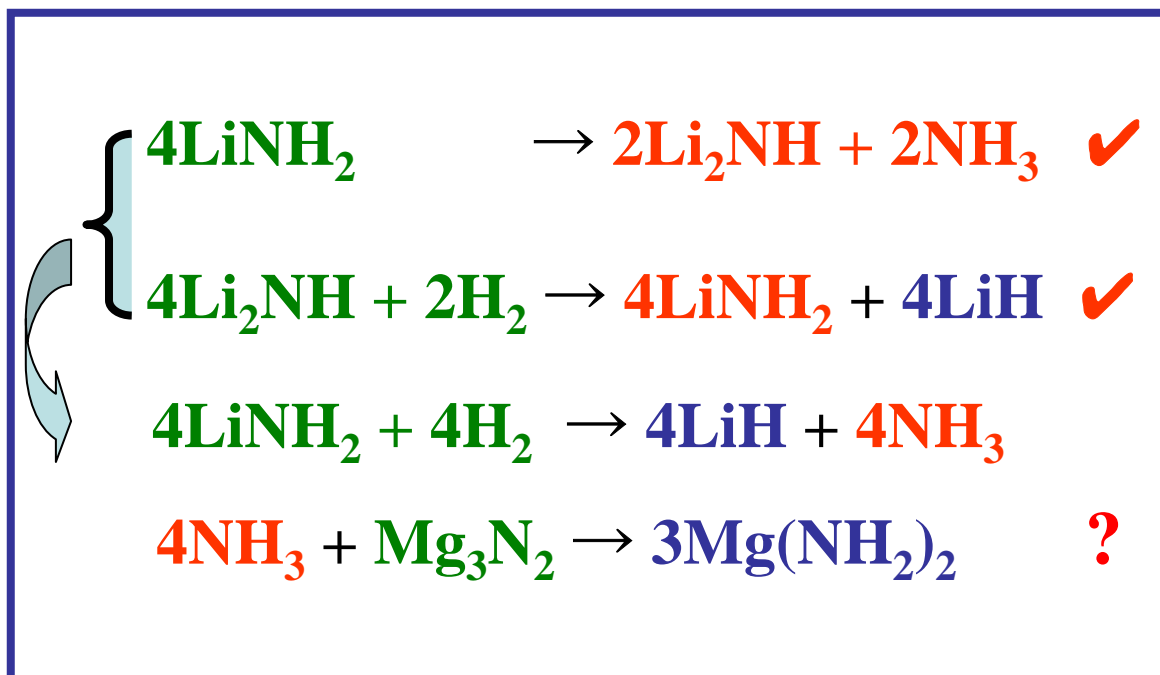
(a) Before hydrogenation

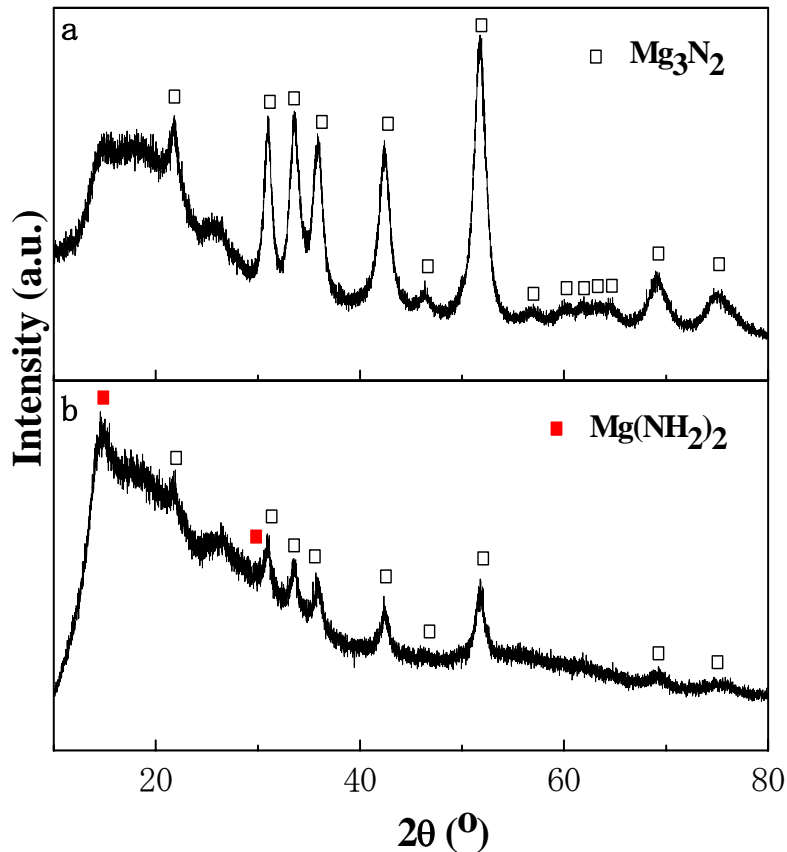
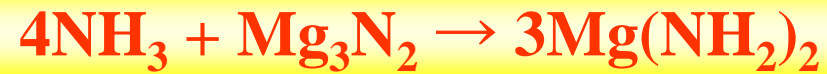
NH₃ desorbed from the sample of LiNH₂ and Mg₃N₂ phases, synchronizing to small amount H₂ and N₂ desorbed due to the decomposition of NH₃

(b) After hydrogenation at 5MPa H₂ and 200°C

H₂ desorbed from Mg(NH₂)₂ and LiH in the hydrogenated sample

Hydrogenation reaction model between LiNH_2 and Mg_3N_2



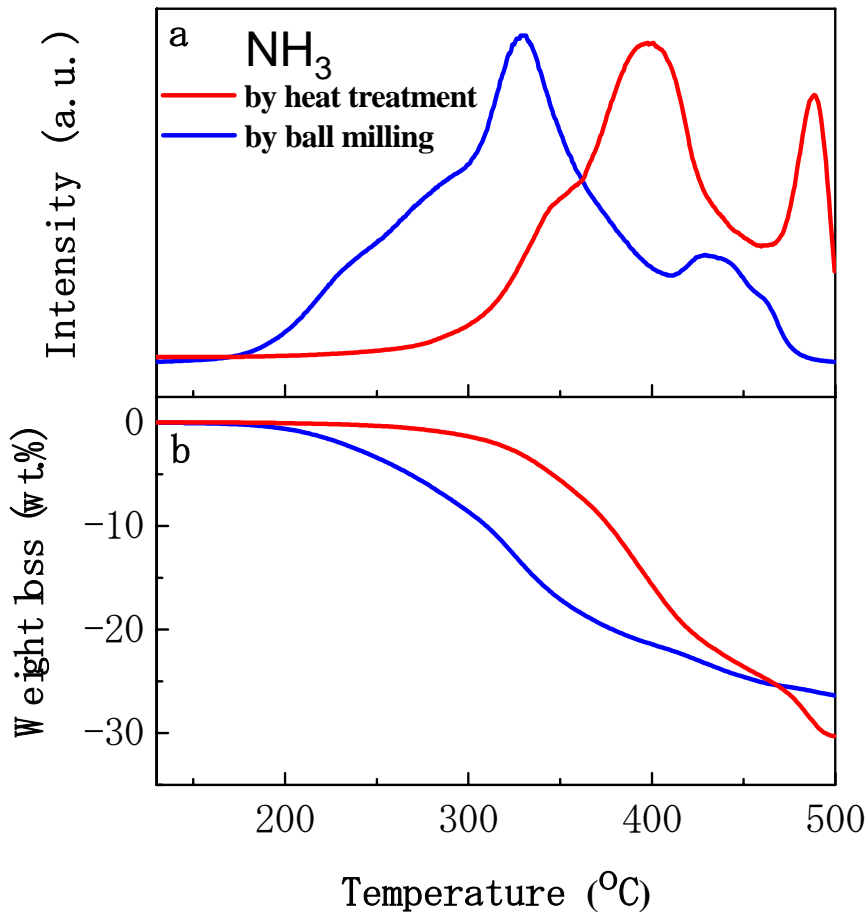
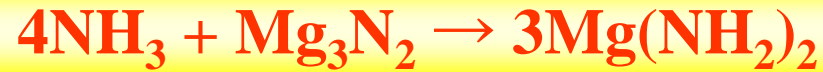


(a) Mg_3N_2 milled for 20 hrs in Ar

Mg_3N_2

(b) Mg_3N_2 heated treatment in NH_3 atmosphere for 8 hrs at 200°C

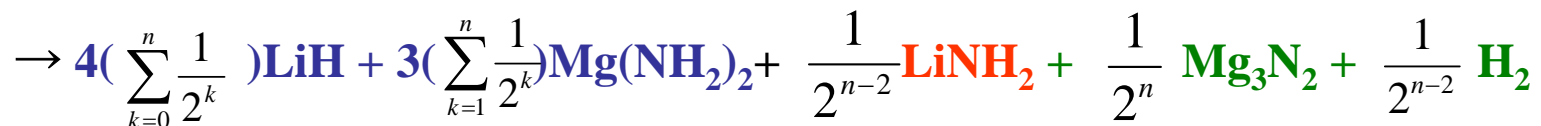
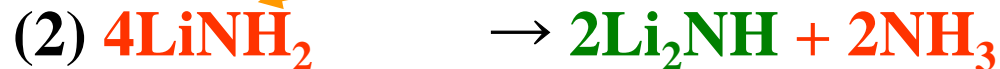
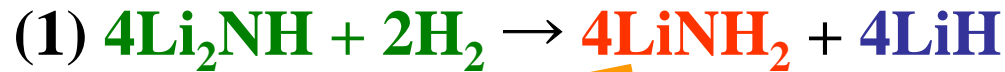
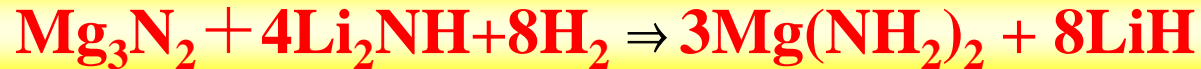
$\text{Mg}(\text{NH}_2)_2$ phase appears!



Products of the reaction between Mg_3N_2 and NH_3 by heat treatment (—) and by ball milling (—)
 (a) TDMS (b) TG

- NH_3 desorbed from $\text{Mg}(\text{NH}_2)_2$ in the sample of Mg_3N_2 heated in NH_3 and the sample of Mg_3N_2 milled in NH_3
- $\text{Mg}(\text{NH}_2)_2$ made by ball milling decomposed at lower temperature than that produced by heat treatment!

Mechanism of H-absorption



➤ Mechanism of hydrogenation reaction from Li_2NH and Mg_3N_2 to LiH and $\text{Mg}(\text{NH}_2)_2$ was proposed:

Li_2NH was first hydrogenated to LiH and LiNH_2 .

Further, the LiNH_2 and Mg_3N_2 interacted by NH_3 mediated reaction and were hydrogenated to LiH and $\text{Mg}(\text{NH}_2)_2$.