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Composite Materials composed of Light Elements for Hydrogen Storage

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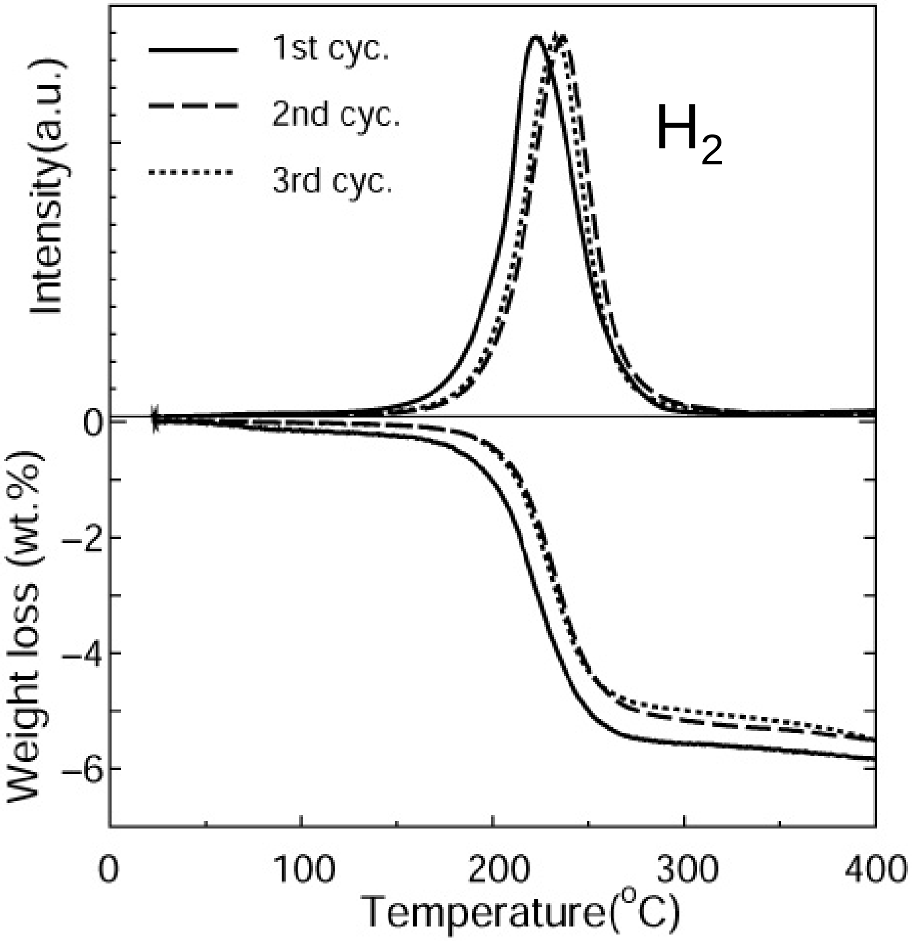
1. Research Directions to High-performance H-storage Materials in Hiroshima university

- 1. Chemical Hydride Materials
- 2. Specific Nano-structured Carbon Materials
- 3. Mg-based Nano-composite Materials

1. Chemical Hydride Materials

M – N – H Systems



$LiNH_2 + LiH \Leftrightarrow Li_2NH + H_2$

$TiCl_3$ is doped as catalyst

~ 5.5 wt% hydrogen desorbs at lower than 250 ℃
(ΔH = - 44.5 kJ/mole)

P_H = 0.1 MPa at 250 °C

Still too high temperature for an on-board use

T. Ichikawa et al, JAC **365**, 271 (2004).

Clarification of Reaction Mechanism

$$LiNH_2 + LiH \Rightarrow Li_2NH + H_2$$

$\Delta H^0 = 45$(kJ/mol H_2) Endothermic

・The second reaction was demonstrated by milling LiH under a NH_3 gas at room temperature.

・The ammonia mediated 2-elemental reaction model was proved by Isotopic exchange experiment from H to D.

Elemental reactions mediated by ammonia gas

① $2LiNH_2 \rightarrow Li_2NH + NH_3$

$\Delta H^0 = 42$(kJ/mol) Endothermic

② $LiH + NH_3 \rightarrow LiNH_2 + H_2$

$\Delta H^0 = -40$(kJ/mol H_2) Exothermic

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

Development of synthesizing metal amides

$$MH_x + xNH_3 \rightarrow M(NH_2)_x + xH_2$$

(M = Li, Na, Mg and Ca)

(**Exothermic**)

+Metal amides was synthesized by ball milling metal hydrides at room temperature under an ammonia atmosphere.

$LiNH_2$, $NaNH_2$, $Mg(NH_2)_2$, $Ca(NH_2)_2$

react with metal hydrides LiH, NaH, MgH_2, CaH_2

H-storage reactions are designed as follows

$$M(NH_2)_x + xMH_x \rightarrow MN_{x/2}H_{x/2} + (x/2)NH_3 + xMH_x$$

$$\rightarrow M_2N_{x/2}H_{x/2} + (1/2)M(NH_2)_x + (x/2)H_2 + (x/2)MH_x$$

$$\rightarrow \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot$$

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

Materials designing of New M-N-H systems

No.	Reversible Chemical reaction for H-storage	Theoretical H-capacity (wt.%)
1	$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2NH + MgNH + 2H_2$	5.58
2	$3Mg(NH_2)_2 + 8LiH \leftrightarrow 4Li_2NH + Mg_3N_2 + 8H_2$	6.93
3	$Mg(NH_2)_2 + MgH_2 \leftrightarrow 2MgNH + 2H_2$	4.88
4	$Mg(NH_2)_2 + 2MgH_2 \leftrightarrow Mg_3N_2 + 4H_2$	7.40
5	$4LiNH_2 + 3MgH_2 \leftrightarrow Mg_3N_2 + 2Li_2NH + 6H_2$	7.08
6	$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$	6.32
7	$LiNH_2 + 2LiH \leftrightarrow Li_3N + 2H_2$	10.37
8	$3Mg(NH_2)_2 + 12LiH \leftrightarrow 4Li_3N + Mg_3N_2 + 12H_2$	9.15
9	$2LiH + Ca(NH_2)_2 \leftrightarrow Li_2NH + CaNH + 2H_2$	4.58
10	$8LiH + 3Ca(NH_2)_2 \leftrightarrow 4Li_2NH + Ca_3N_2 + 8H_2$	5.76
11	$Ca(NH_2)_2 + 2CaH_2 \leftrightarrow Ca_3N_2 + 4H_2$	5.16
12	$4LiNH_2 + 3CaH_2 \leftrightarrow Ca_3N_2 + 2Li_2NH + 6H_2$	5.54

New Li-Mg-N-H system for H-storage

Development of New M-N-H system for H-storage

$8LiH + 3Mg(NH_2)_2 \leftrightarrow$

$Mg_3N_2 + 4Li_2NH + 8H_2$

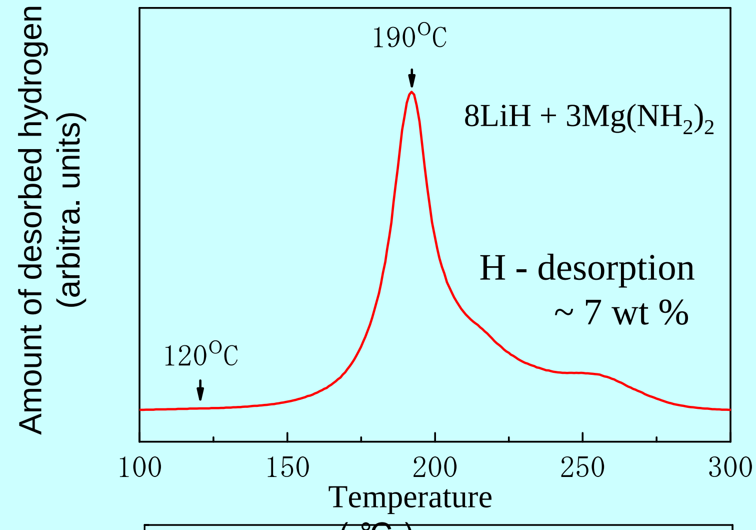
H-storage mechanism:

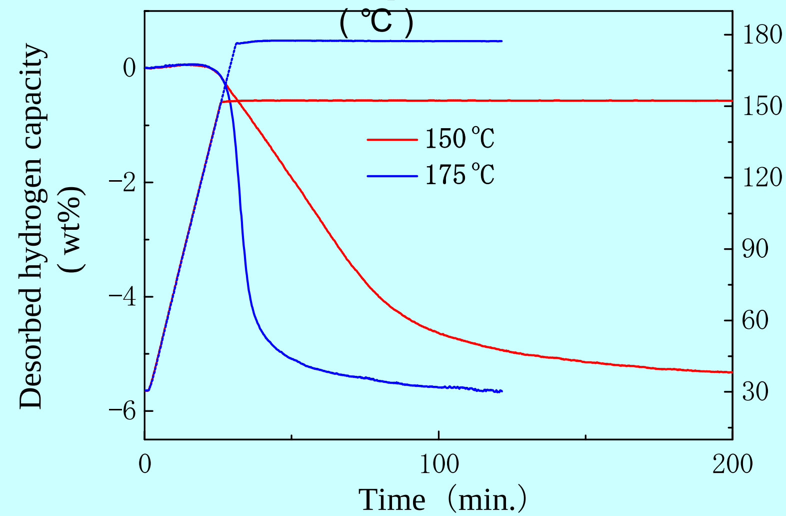
3elemental reactions mediated by NH_3

1) $3Mg(NH_2)_2 \leftrightarrow Mg_3N_2 + 4NH_3$
2) $4NH_3 + 4LiH \leftrightarrow 4LiNH_2 + 4H_2$
3) $4LiNH_2 + 4LiH \leftrightarrow 4Li_2NH + 4H_2$

The sample was prepared by ball milling 8LiH and $3Mg(NH_2)_2$ at RT under 1 MPa hydrogen atmosphere for 2 h.

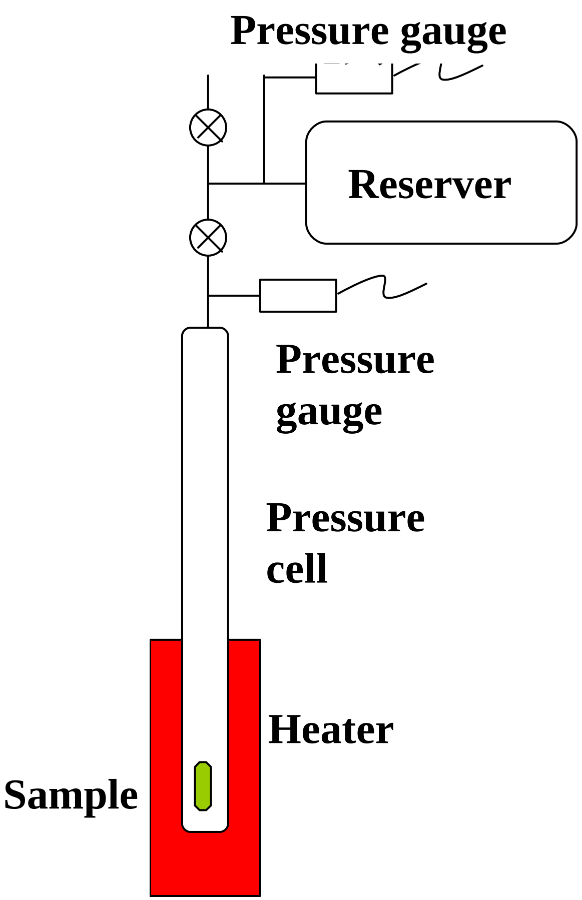
- **Target：H-storage capacity > 5 wt% at T < 100 ºC and P_H > 0.1 MPa**





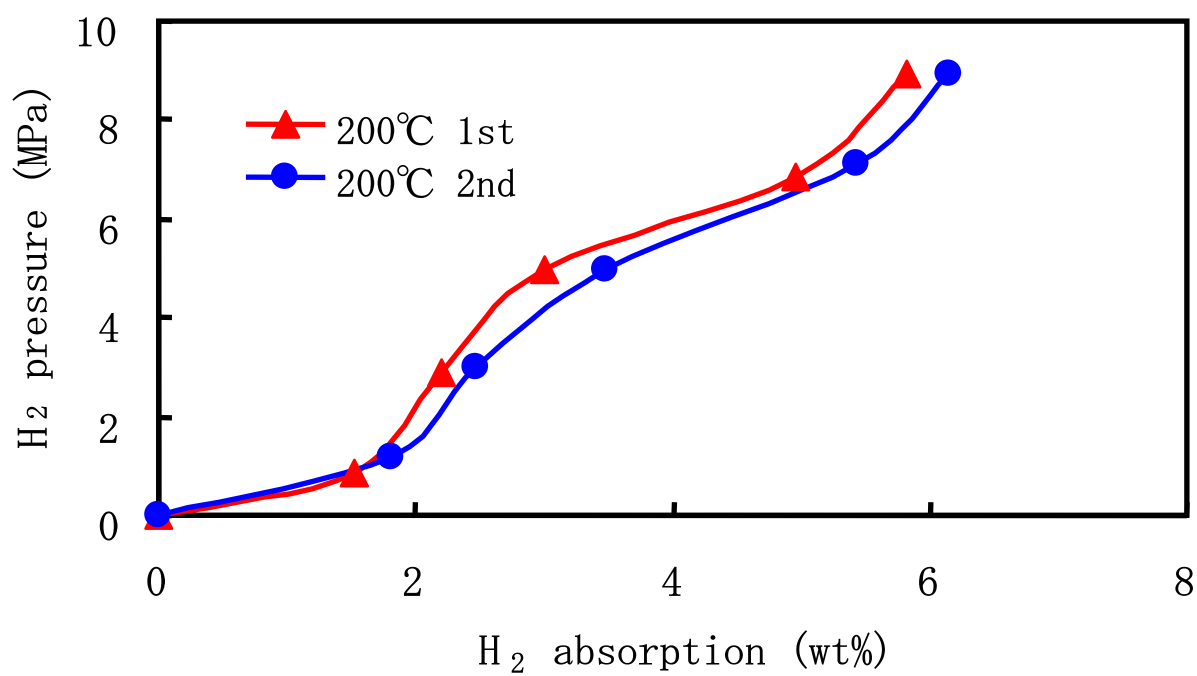
Thermodynamical Properties

H-absorption in Li-Mg-N-Hsystem



PCT – measurement equipment

After 10 H-absorbed/desorbed cycles,
PCT profile was measured at 200 ºC.



H-absorption equilibrium pressure is ~ 6 MPa at 200 ºC.
H content reaches up to ~6 wt % at 9 MPa.

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Summary

- **The new system composed of $Mg(NH_2)_2$ and LiH is promising for hydrogen storage, which can desorb/absorb ~ 7 wt% hydrogen at moderate temperature (<200°C) and pressure (<10MPa).**
- **This new system has high equilibrium pressure of hydrogen absorption/desorption.**

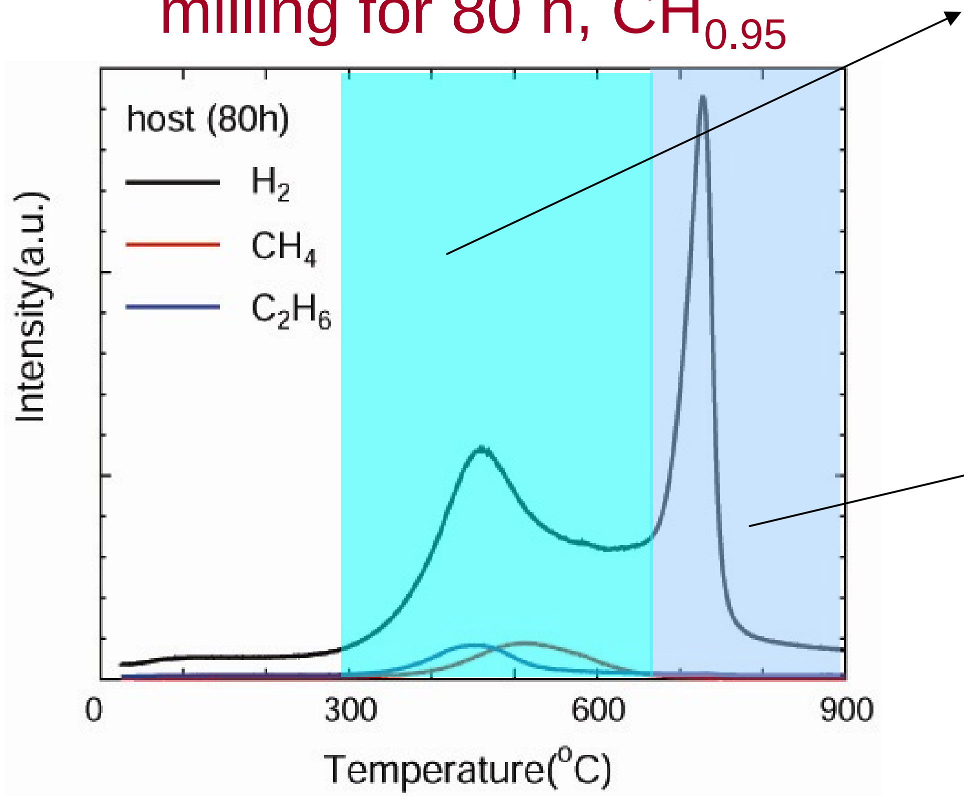
At 200°C, P_{eq}> 5.5 MPa. (ΔH ~ 34 kJ/mol/H_2)

Therefore, this system is one of the most promising materials for H-storage .

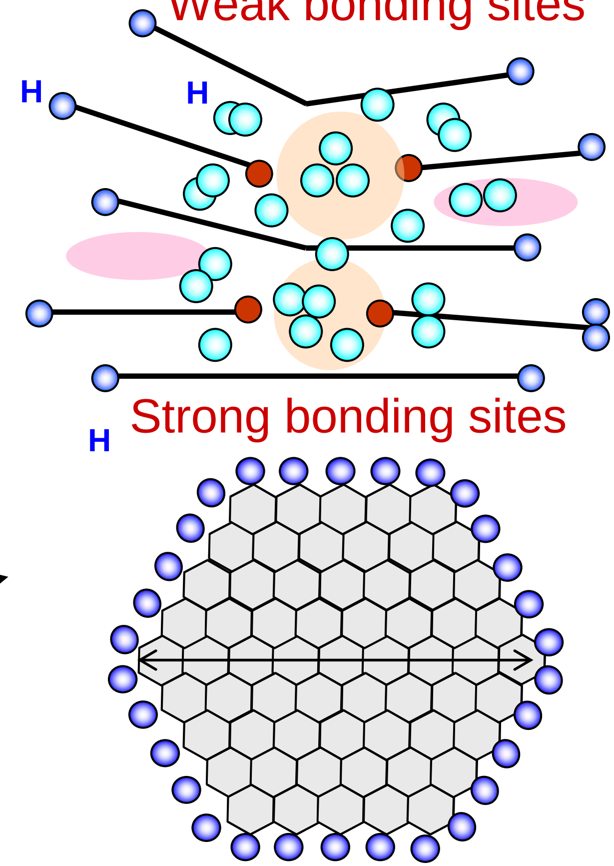
2. Specific Nanostructured Carbon Materials

TDS profile

milling for 80 h, $CH_{0.95}$



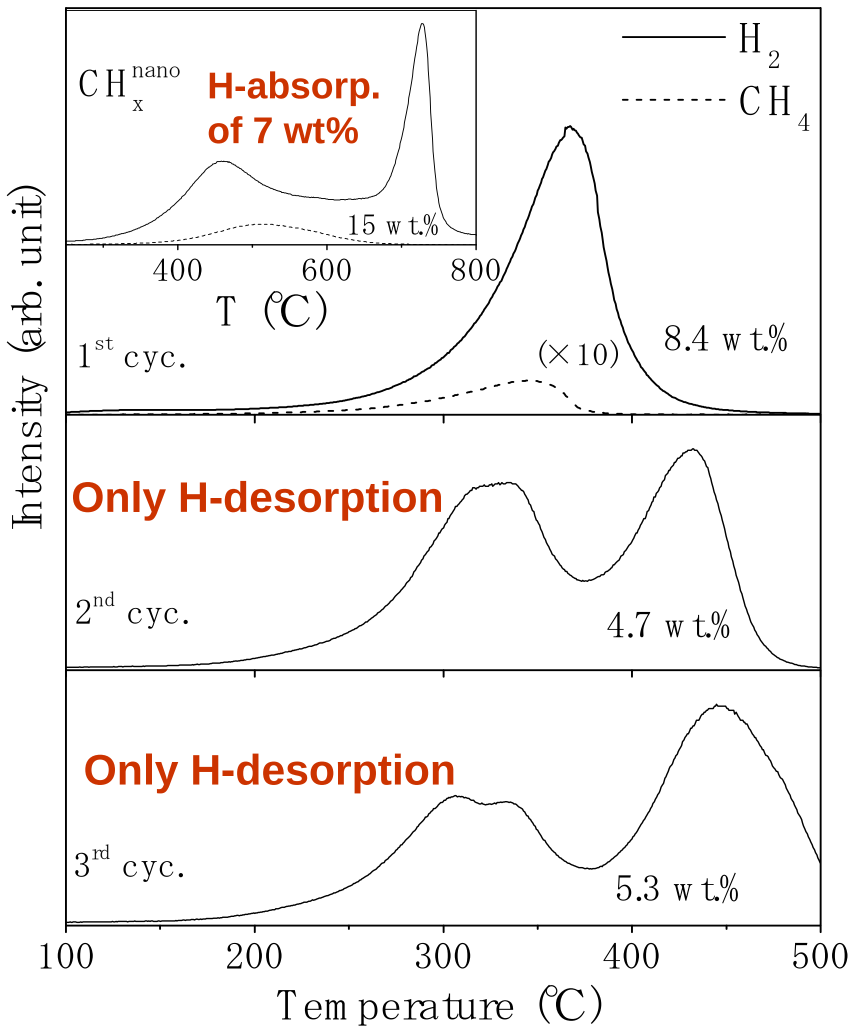
d=~1.8 nm, $CH_{0.5}$



d=~1.1 nm, $CH_{0.5}$

H-desorption temperature was higher than 300 °C, and it was impossible to reversibly absorb/desorb hydrogen in nanocrystalline graphite.

Mixing effect of Li hydride into nanocrystalline G



Quite recently, we succeeded destabilization of C-H bonding by the mixing

Optimization of milling conditions

Target : H-storage of 5.5 wt% at T<100 °C

Li-C-N system

A New Category for H-storage

Li-B-H, Li-Al-H, Li-N-H

Ichikawa et al., (Hiroshima Univ.) Appl. Phys. Lett. 86 (2005) 1

3. Mg-based Nano-composite Materials for improving kinetics

7.6 wt% at 360 ℃ with no catalyst

2000 Huot et. al., (Res. Insti. Hydro-Quebec, Canada)

A. V and Ti doped Mg Nano-composites

Abs. 5~6 wt% H at 100ºC , Des. Temp. 200~250ºC

2002 Higuchi et. al., (Hiroshima Pref.Lab. Japan)

B. Nano-composite Pd/Mg Thin Films

Abs./Des. 4~5 wt% H at T<100oC under Vac.

2003 Barkhordarian et al., (Insti.Mat.Res.Germany)

C. Nb_2O_5 and Cr_2O_3 doped Mg Nano-composites

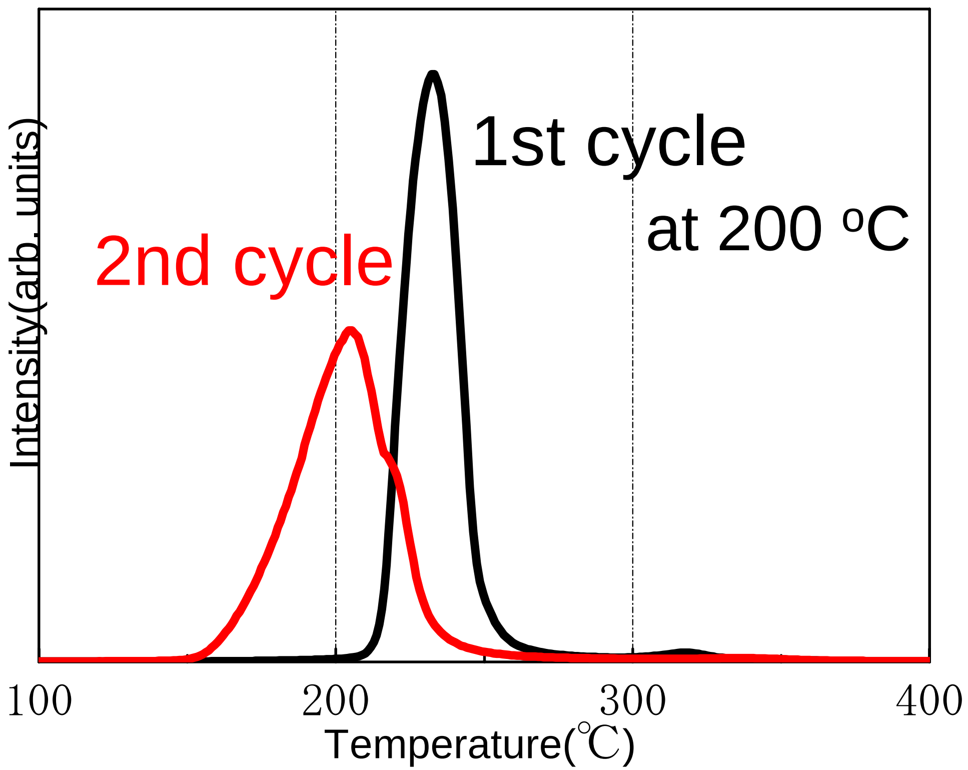
~7 wt% H des. within 140 s at 250ºC

Focus on Nb_2O_5 Catalyst Effect in this work

Significant Improvement of Reaction Kinetics

MgH_2+1mol% Nb_2O_5 prepared by ball milling for 20 h.

TDMS profile for H-desorption



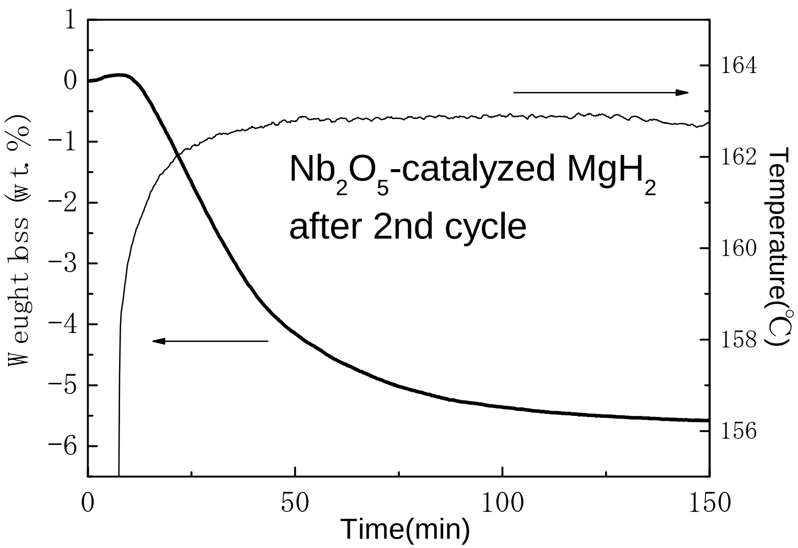
~ 6 wt% hydrogen is desorbed at lower temperature than 230 °C under a He flow.

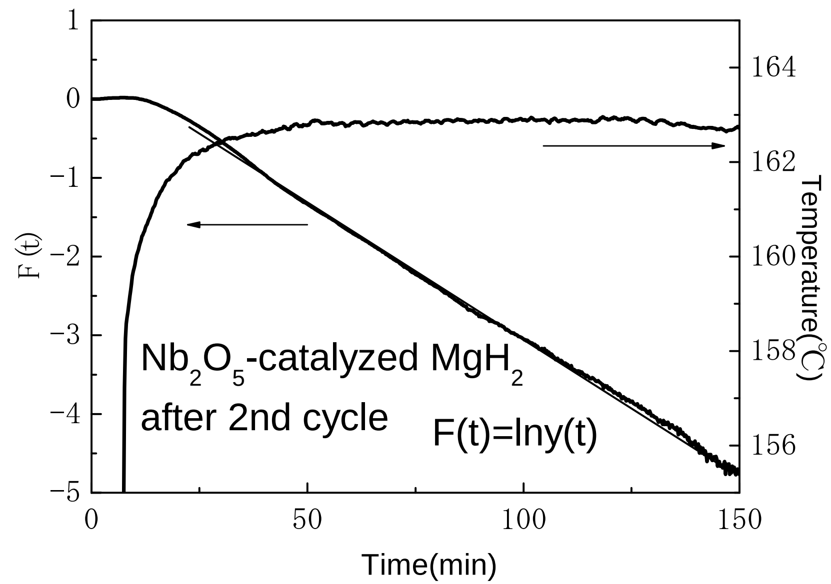
Hanada et al., JALCOM in press.

H-desorption properties after 2nd cycyle is better than after1st cycle.
indicating a good durability.

H-desorption reaction process

MgH_2+1mol% Nb_2O_5 prepared by ball milling for 20 h





~5 wt% hydrogen is desorbed within 60 min
at 163 °C under a He-gas flow.

This solid-gas reaction
is of first order *:*

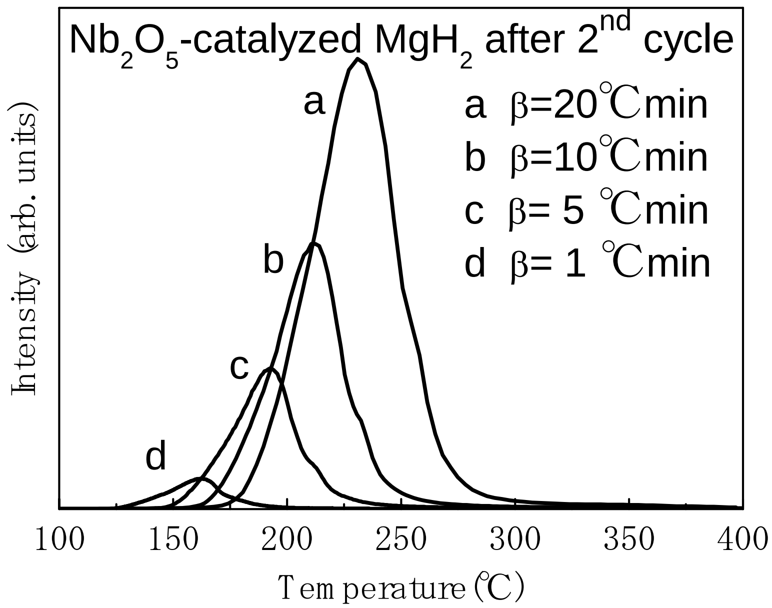
$$\frac{dy}{dt} = -k\,y$$

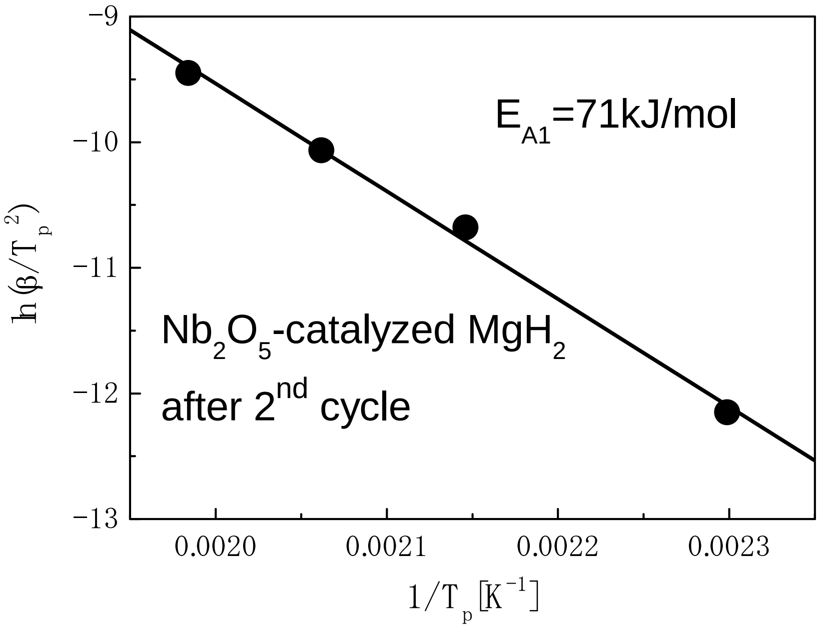
← *lny(t) vs t is linear*

Activation energy for H-desorption

MgH_2+1mol% Nb_2O_5 prepared by ball milling for 20 h

Kissinger plot



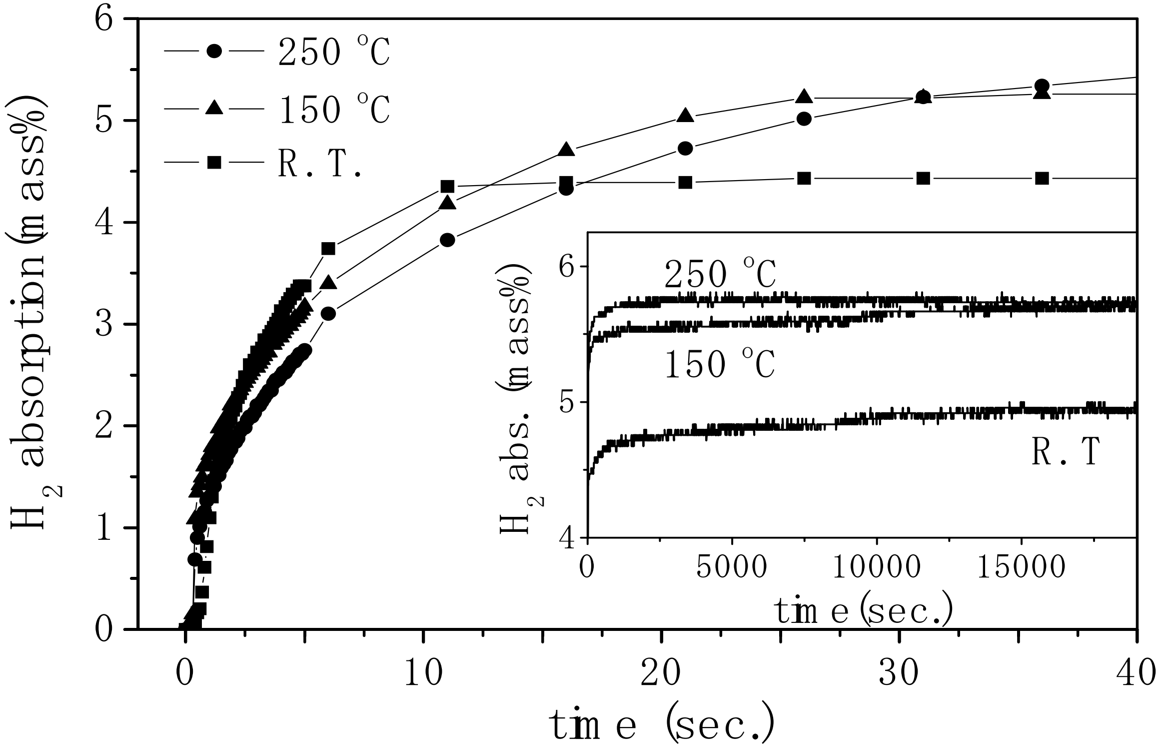


Activation energy of **71** kJ/mol in Nb_2O_5-catalyzed MgH_2 is the smallest among all the metal and oxide catalysts we studied so far.

Significant improvement of H-desoption reaction

H-absorption kinetics

MgH_2+1mol% Nb_2O_5 prepared by ball milling for 20 h



Hydrogen is absorbed ~ 4.5 wt% at room temperature within 15 s under 1 MPa, suggesting that Nb_2O_5-doped MgH_2 is quite suitable for stationary H-storage.

Fully Activated Mg Hydride

Summary

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1. The Nb_2O_5-catalyzed MgH_2 prepared by ball milling for 20h showed superior H-storage properties: ~ 4.5 wt.% hydrogen was absorbed within 15 s under 1 MPa at 25 ^oC, while the hydrogen was desorbed at 160 ^oC within 60 min under a He gas flow.

2. The Nb_2O_5 catalyst was reduced to metallic Nb by MgH_2 and homogeneously dispersed on the surface of MgH_2 during mechanical milling.

3. The metallic Nb dispersed in nanometer scale could act as an excellent catalyst for hydrogen absorption and desorption in MgH_2.

At present, this system is one of the most promising materials for stationary H-storage use.