

Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

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Project ID: STP 2

This presentation does not contain any proprietary or confidential information

Overview

Timeline:

- Project start date: December 2004
- Project end date: December 2008
- Percent complete: 30%

Budget:

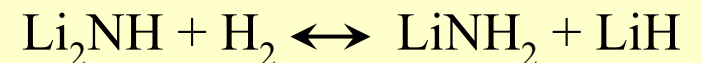
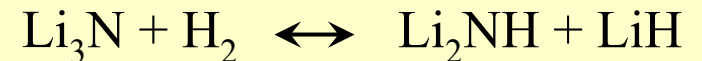
- Total project funding
 - DOE share: \$1.6 mil
 - Contractor share: \$0.4 mil
- Funding received in FY05: \$168,000
- Funding received in FY06: \$240,000

Partners:

- Sandia National Laboratory
- Pacific Northwest National Laboratory
- Universidad de Extremadura, Badajoz, Spain

Barriers

Sorption/desorption temperatures are too high for the following two reactions:



Need to reduce these sorption/desorption temperatures to near ambient.

Objectives

Overall Objective in 4 Years:

- Investigate, model and develop a novel, mechanically activated, nanoscale Li_3N -based material that is able to store and release ~ 10 wt% hydrogen at temperatures below 100°C with a plateau hydrogen pressure of less than 10 bar

Objective in FY 05:

- Mechanical activation on LiNH_2 to Li_2NH transition
- Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH_2 and LiH mixture

Objective in FY 06:

- Mechanical activation on hydrogen sorption/desorption kinetics of the LiNH_2 and LiH mixture (cont. from FY 05)
- Stability of LiH in different environments
- Dehydrogenation behavior of the MgH_2 and LiNH_2 mixture
- Advanced catalysts for the LiNH_2 and LiH mixture

Approaches

- **Mechanical Activation** to reduce hydrogen sorption/desorption temperatures and increase the hydrogen storage capacity.
- **Chemical Modification** of lithium amide/imide to destabilize the compounds thermodynamically and thus further reduce hydrogen sorption/desorption temperatures.
- **Advanced Catalysts** to catalyze the reactions and thus further enhance hydrogen sorption/desorption processes.
- **Quantum-Chemical Modeling** to identify advanced catalysts and to develop fundamental understanding and guide the efforts of mechanical activation and chemical modification.

Technical Accomplishments, Progress and Results

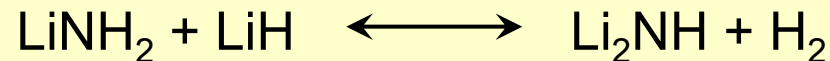
(May 22, 2005 – May 15, 2006)

- I. Enhancement of LiNH_2 to Li_2NH Transition via Mechanical Activation*
- II. Enhancement of Hydrogen Sorption/Desorption of the $\text{LiNH}_2 + \text{LiH}$ System via Mechanical Activation*
- III. Studies of the Stability of LiH in Different Environments*
- IV. Dehydrogenation Behavior of the $\text{LiNH}_2 + \text{MgH}_2$ Systems*
- V. Initiation of the Investigation of Catalysts for the $\text{LiNH}_2 + \text{LiH}$ Systems*

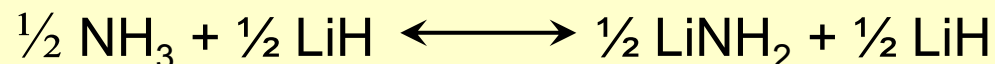
I. Enhancement of LiNH₂ to Li₂NH Transition via Mechanical Activation



- Enhancement of LiNH₂ to Li₂NH transition is necessary because this is the first step for the following dehydrogenation reaction:

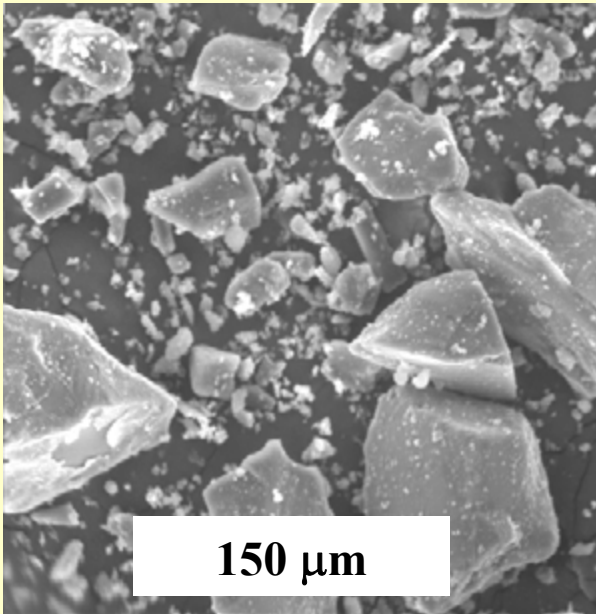


- NH₃ generated from the decomposition of LiNH₂ will react with LiH to form LiNH₂ and H₂:

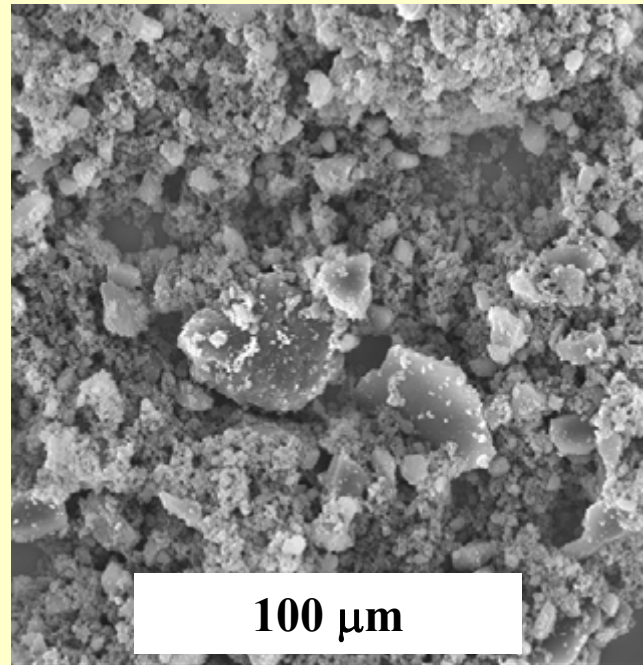


- Complete decomposition of LiNH₂ results in the formation of 37 wt% NH₃. It is important to capture all of these NH₃.

SEM Images of LiNH_2 Powder with and without Ball Milling

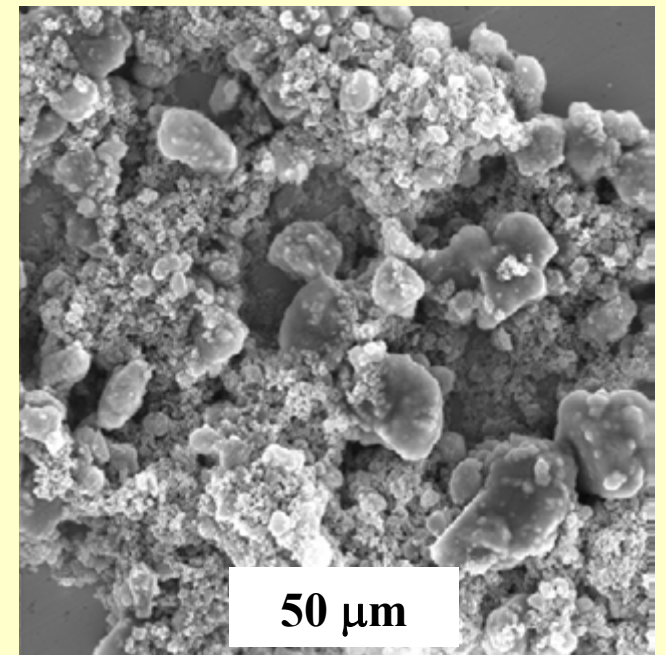


Before milling



Milled for 45 min
at RT

Milled for 180 min
at RT



Specific Surface Area (SSA) and Crystallite Size as a Function of Mechanical Activation

Composition	Milling time (min)	SSA (m ² /g)	Crystallite Size (nm)	Equivalent Particle size (μm)**
LiNH ₂	0	3.72	> 100	1.37
LiNH ₂	45	40.71	5.9	0.13
LiNH ₂	180	46.65	5.5	0.11

** Estimated according to the SSA.

Decomposition of LiNH_2 at Ambient Temperature

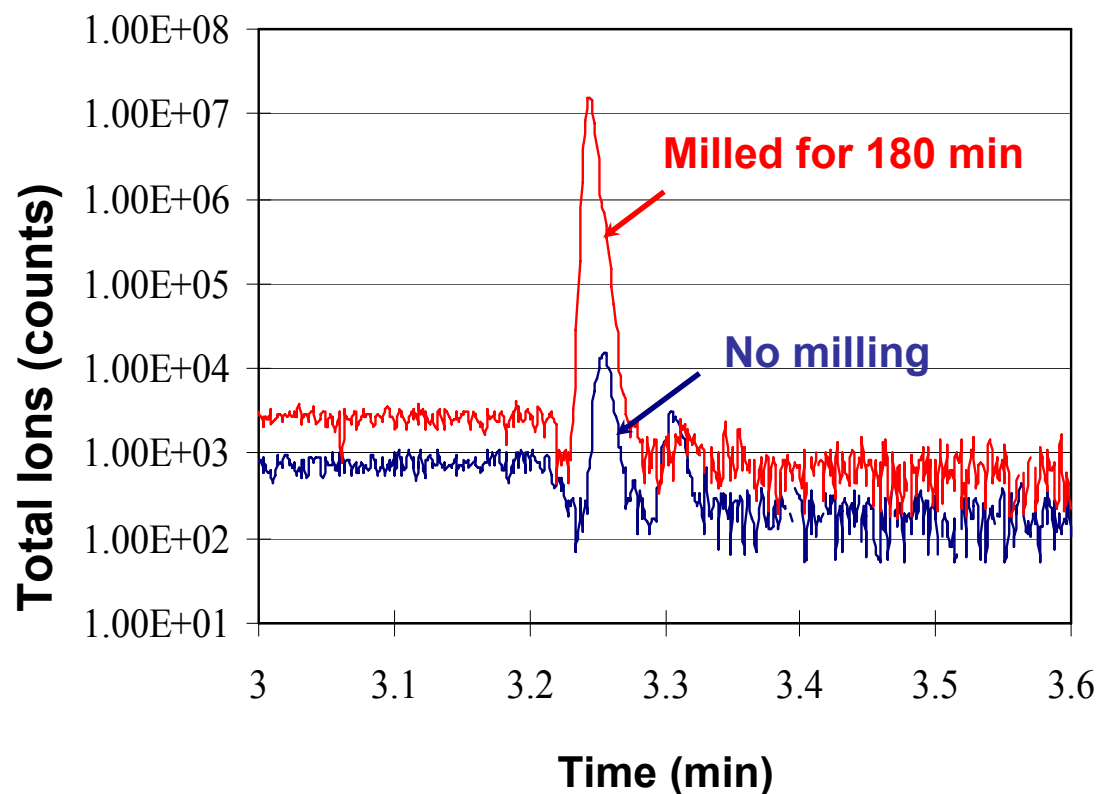
➤ LiNH_2 can decompose to NH_3 and Li_2NH according to the following reaction



➤ Ball milling has decreased the decomposition temperature dramatically.

➤ The gas chromatograph (GC)/mass spectrometry (MS) analysis shows that NH_3 released by the ball milled LiNH_2 at 50°C is 820 times higher than that from the LiNH_2 without milling.

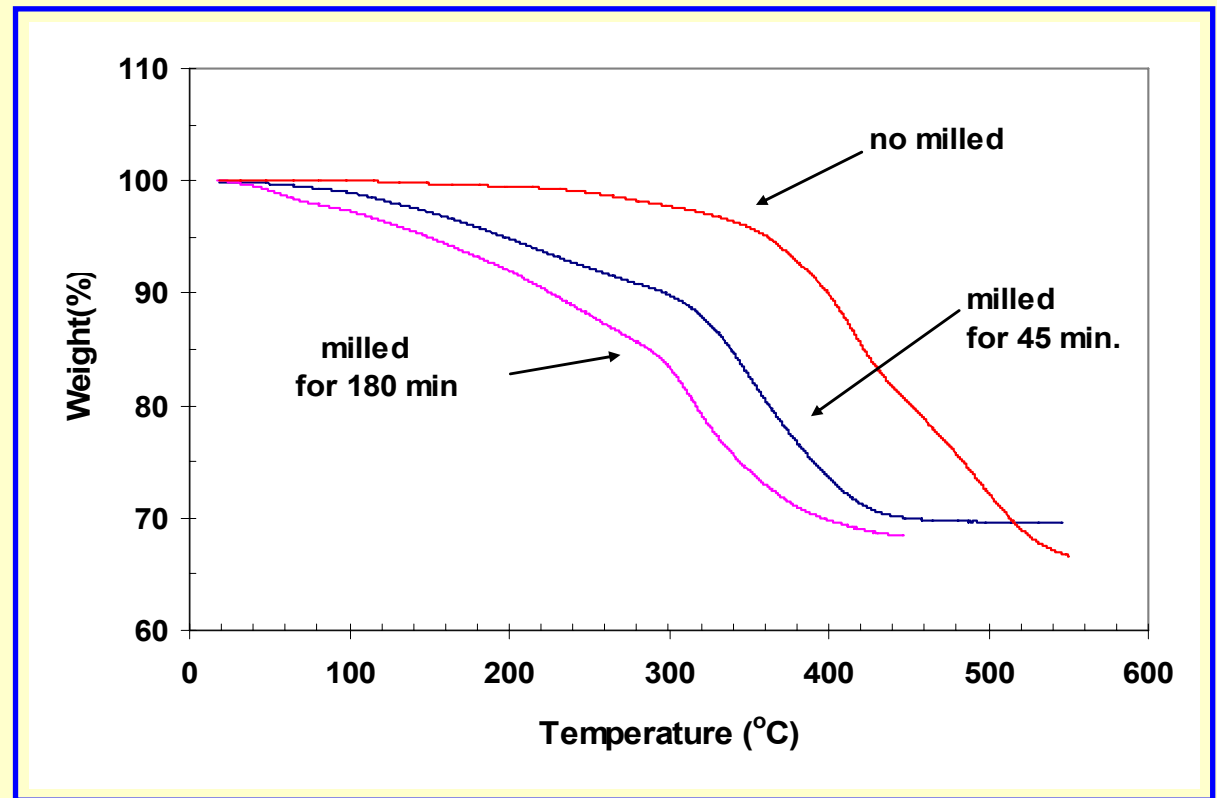
GC/MS Analysis of NH_3



TGA Analysis of LiNH_2 with and without Mechanical Activation

TGA Results

- The onset temperature for weight loss of the LiNH_2 without milling is 120°C , whereas the corresponding value for the LiNH_2 with ball milling is room temperature.
- The transition rate from LiNH_2 to Li_2NH and NH_3 increases with the ball milling time, i.e., the more mechanical activation, the higher the transition rate.

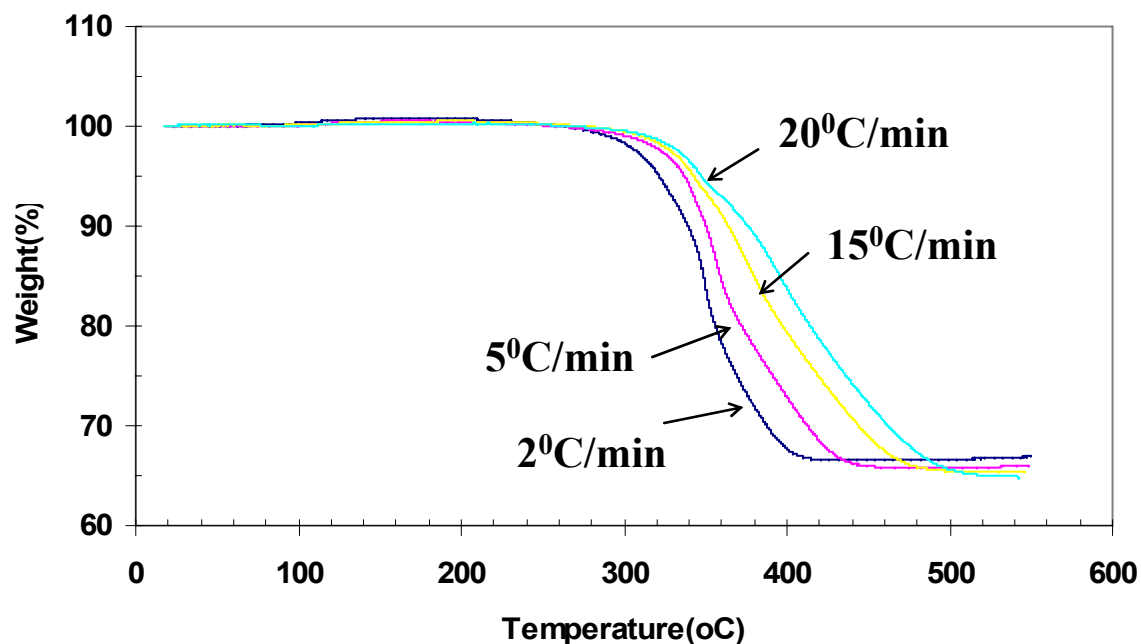


Calculation of the Activation Energy for LiNH_2 Decomposition via the Flynn-Wall Method

Flynn-Wall-Ozawa Equation:

$$\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2.315 - \frac{0.457E_a}{RT}$$

TGA Curves vs Heating Rate



where

β = heating rate

E_a = activation energy

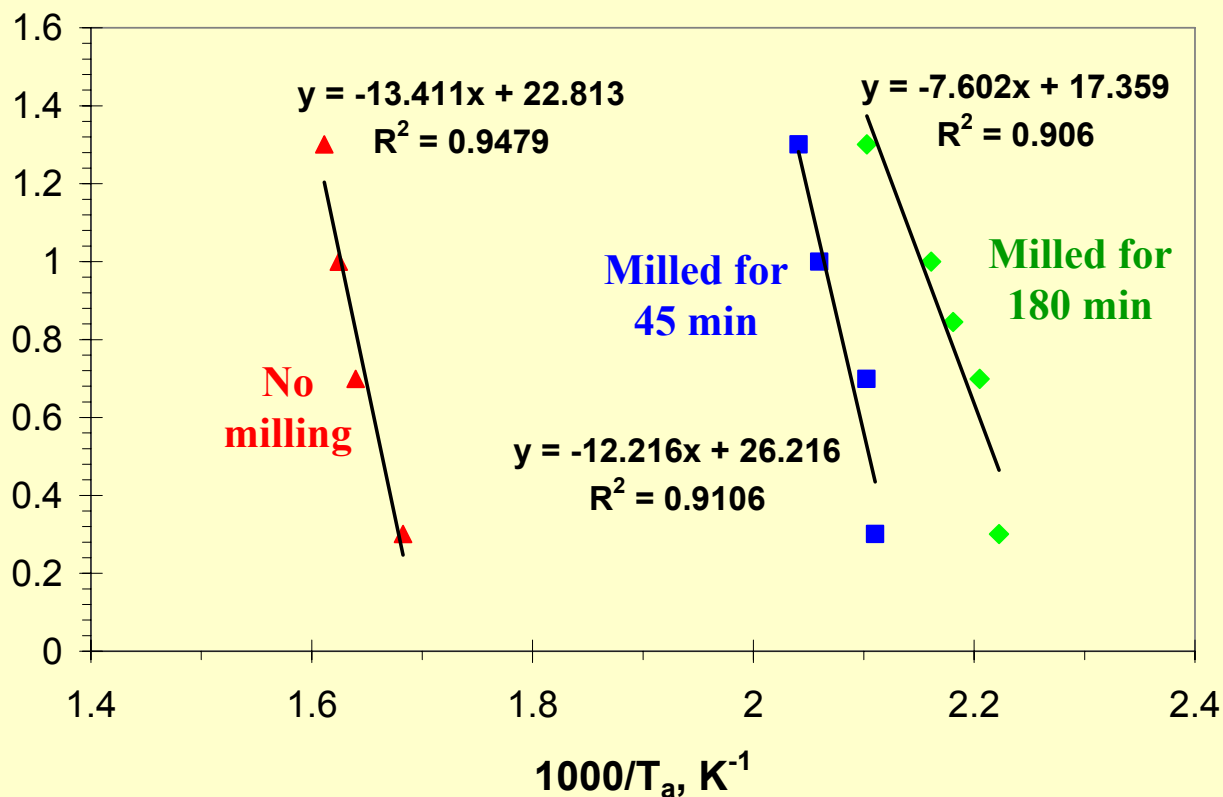
α = fraction of transformation

$g(\alpha)$ = the kinetic function

A = the pre-exponential factor of the Arrhenius equation

Activation Energy for LiNH_2 Decomposition via the Flynn-Wall Method

Flynn-Wall Plot



Calculated
Activation Energy

Un-milled LiNH_2 :

$$E_a = 243.9 \text{ kJ/mol}$$

LiNH_2 milled for 45 min:

$$E_a = 222.2 \text{ kJ/mol}$$

LiNH_2 milled for 180 min:

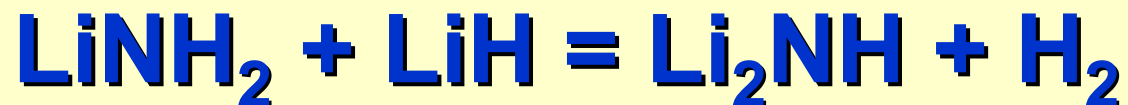
$$E_a = 138.0 \text{ kJ/mol}$$

The activation energy decreases as the ball milling time increases!

Summary for Enhancement of LiNH_2 to Li_2NH and NH_3 Transition

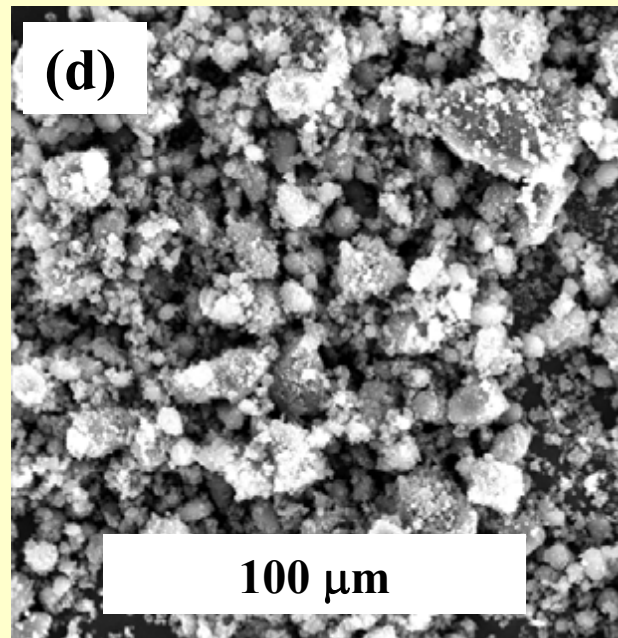
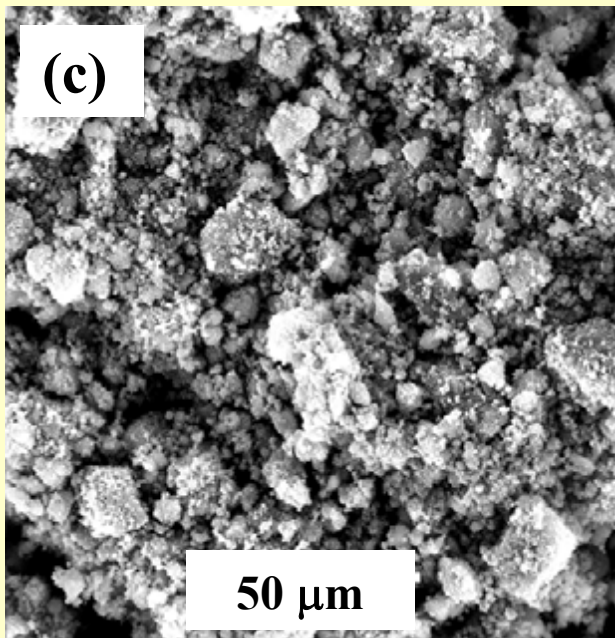
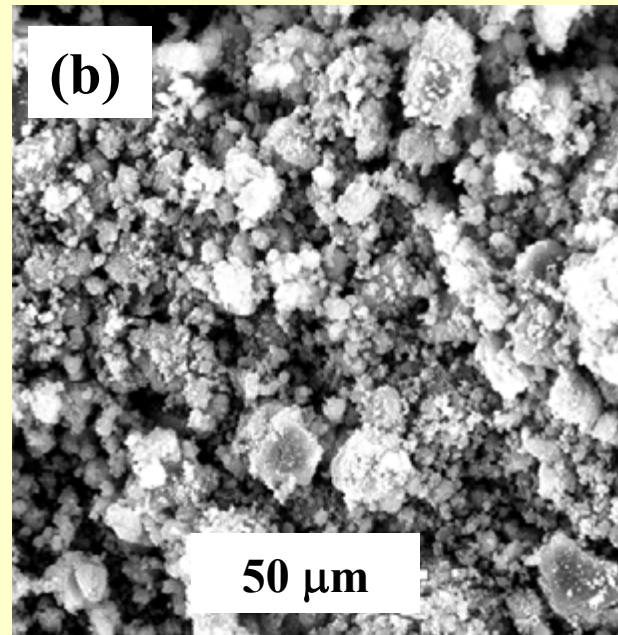
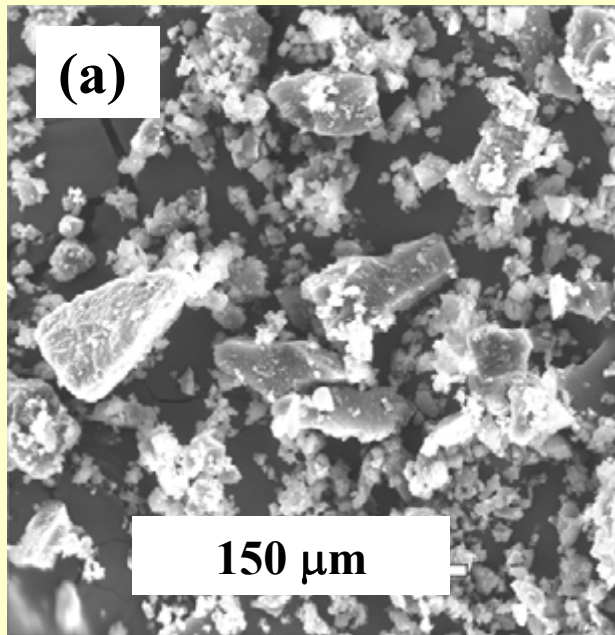
1. Ball milling reduces particle size, increases specific surface area, and introduces nanograins as well as a large amount of defects to LiNH_2 crystals.
2. All of these enhance the transition of LiNH_2 to Li_2NH and NH_3 . The activation energy for the transition decreases as the ball milling time increases.
3. The onset temperature for the decomposition of LiNH_2 without ball milling is 120°C , while the corresponding value for the LiNH_2 with ball milling is room temperature.
4. The transition rate from LiNH_2 to Li_2NH and NH_3 increases with the ball milling time, i.e., the more mechanical activation, the higher the transition rate.
5. The decomposition of LiNH_2 without ball milling does not complete even above 550°C , while this temperature is reduced to 450°C for LiNH_2 with ball milling.

II. Enhancement of Hydrogen Sorption/Desorption of the LiNH₂ plus LiH Systems



- The key to the success of this system is to reduce its hydrogen sorption/desorption temperatures to near ambient
- Complete dehydriding of the LiNH₂ + LiH mixture releases 6.5 wt% H₂

SEM Images of $\text{LiNH}_2 + \text{LiH}$ Powders



- (a) Before milling
- (b) Milled for 90 min
- (c) Milled for 180 min
- (d) Milled for 1,440 min

- Particle sizes decrease with increasing the milling time.
- The reduction rate of particle sizes becomes smaller as the milling time becomes larger.

Specific Surface Area (SSA) and Crystallite Size as a Function of Mechanical Activation

Composition	Milling time (min)	SSA* (m ² /g)	Crystallite Size LiNH ₂ / LiH (nm)	Equivalent Particle size (μm)**
LiNH ₂ +LiH	0	4.65	> 100 / > 100	-
LiNH ₂ +LiH	90	47.36	7.2 / 13.6	0.120
LiNH ₂ +LiH	180	51.32	4.1 / 32.4	0.111
LiNH ₂ +LiH	1,440	62.35	-	0.091

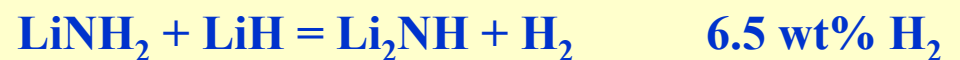
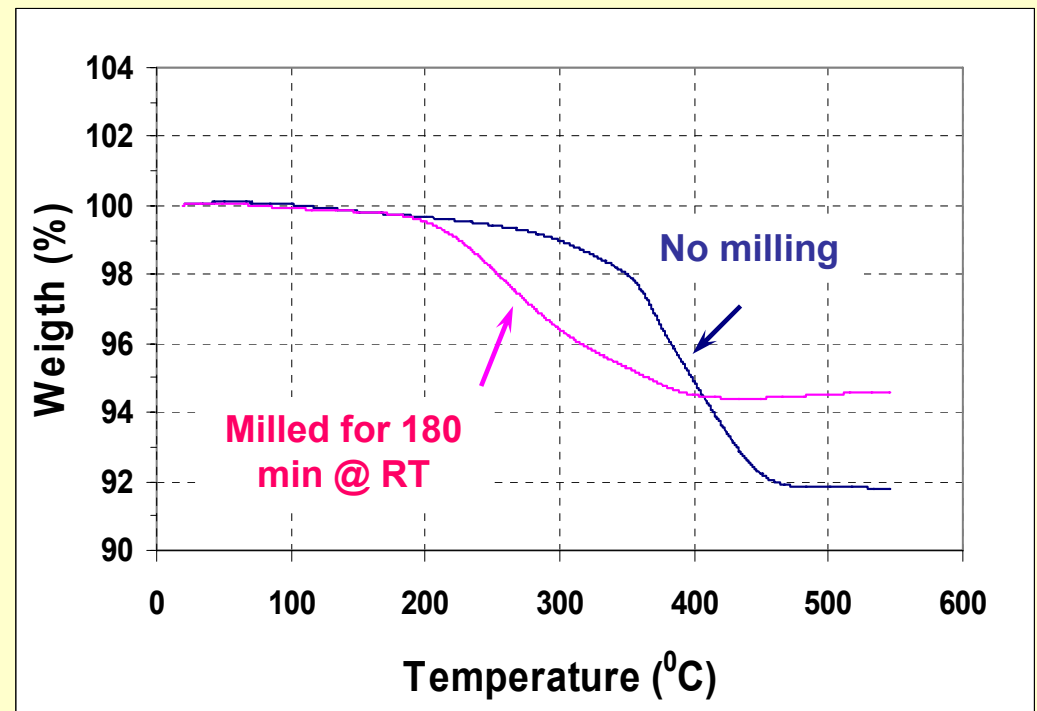
* Based on the SSA using the average density (1.05 g/cm³) of the mixture.

** Estimated from the SSA.

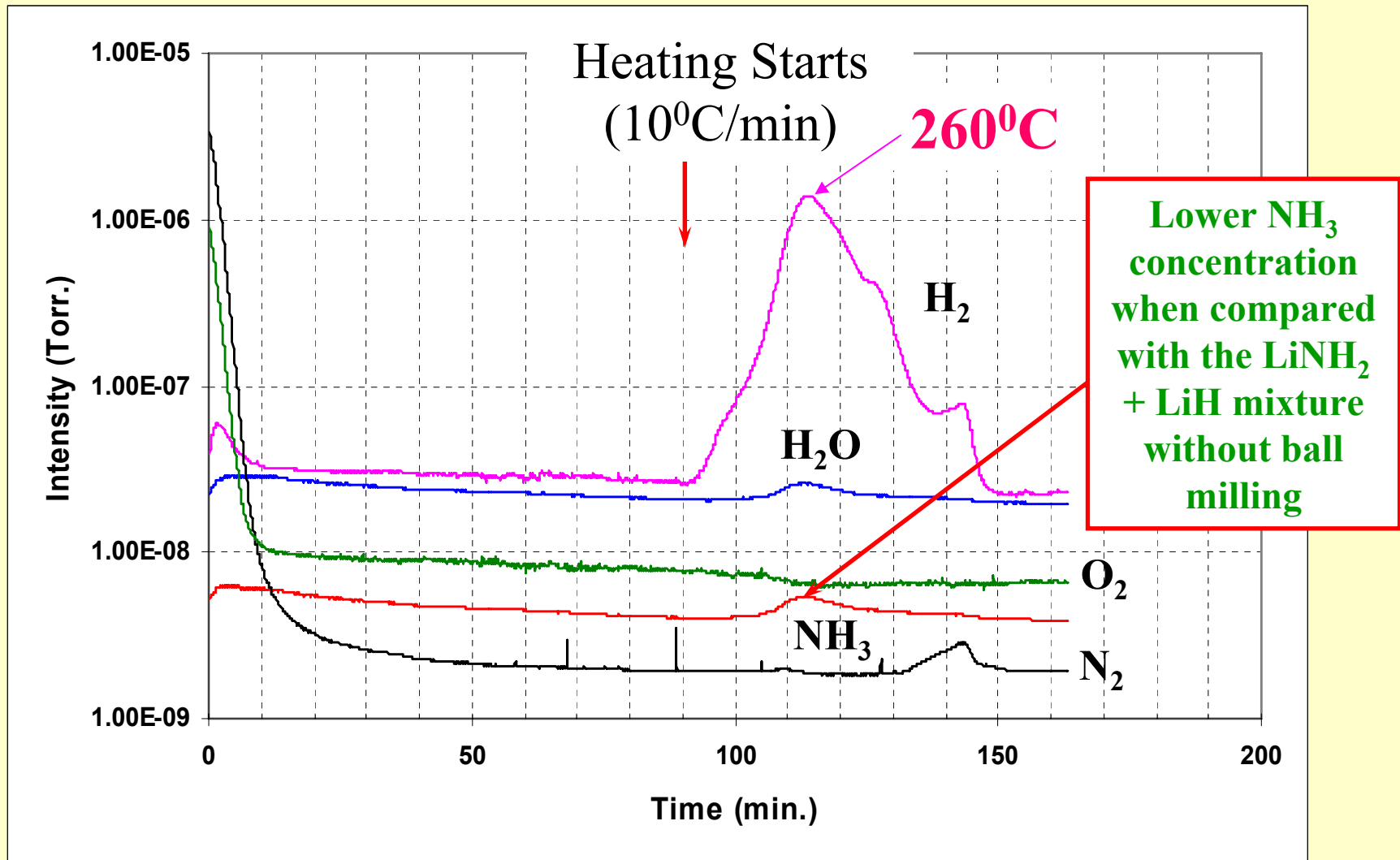
TGA Curves of LiNH₂ + LiH Mixtures with and without Mechanical Activation

- The onset temperatures for hydrogen release from the LiNH₂ + LiH mixtures with and without ball milling are 25 and 50°C, respectively.
- The temperature for release of a large amount of H₂ (e.g., 2 wt%) is decreased from about 350°C to 255°C after ball milling.
- The weight loss for the milled sample is about 5.5% which is slightly smaller than 6.5% if the mixture were 100% LiNH₂ + LiH.
- The weight loss for the sample without milling is substantially larger than 6.5% because of the NH₃ escape due to the incomplete reaction between ammonia and lithium hydride.

TGA Results

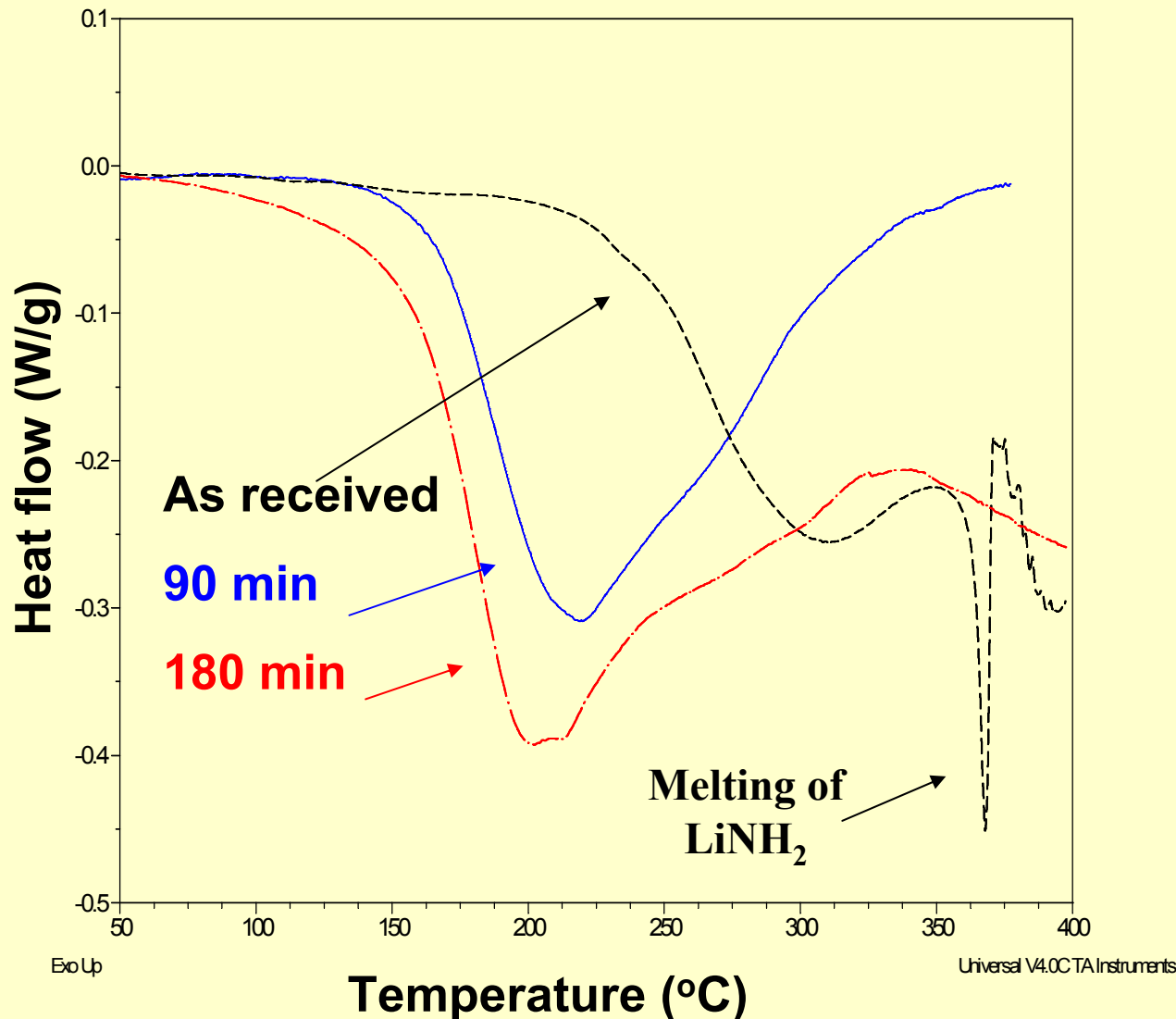


Composition Analysis of the Effluent Gas from $\text{LiNH}_2 + \text{LiH}$ Mixture with Mechanical Activation (90 min ball milling at RT)



DSC Curves of $\text{LiNH}_2 + \text{LiH}$ Mixtures with Different Degrees of Mechanical Activation

(heating rate = $1^\circ\text{C}/\text{min}$)



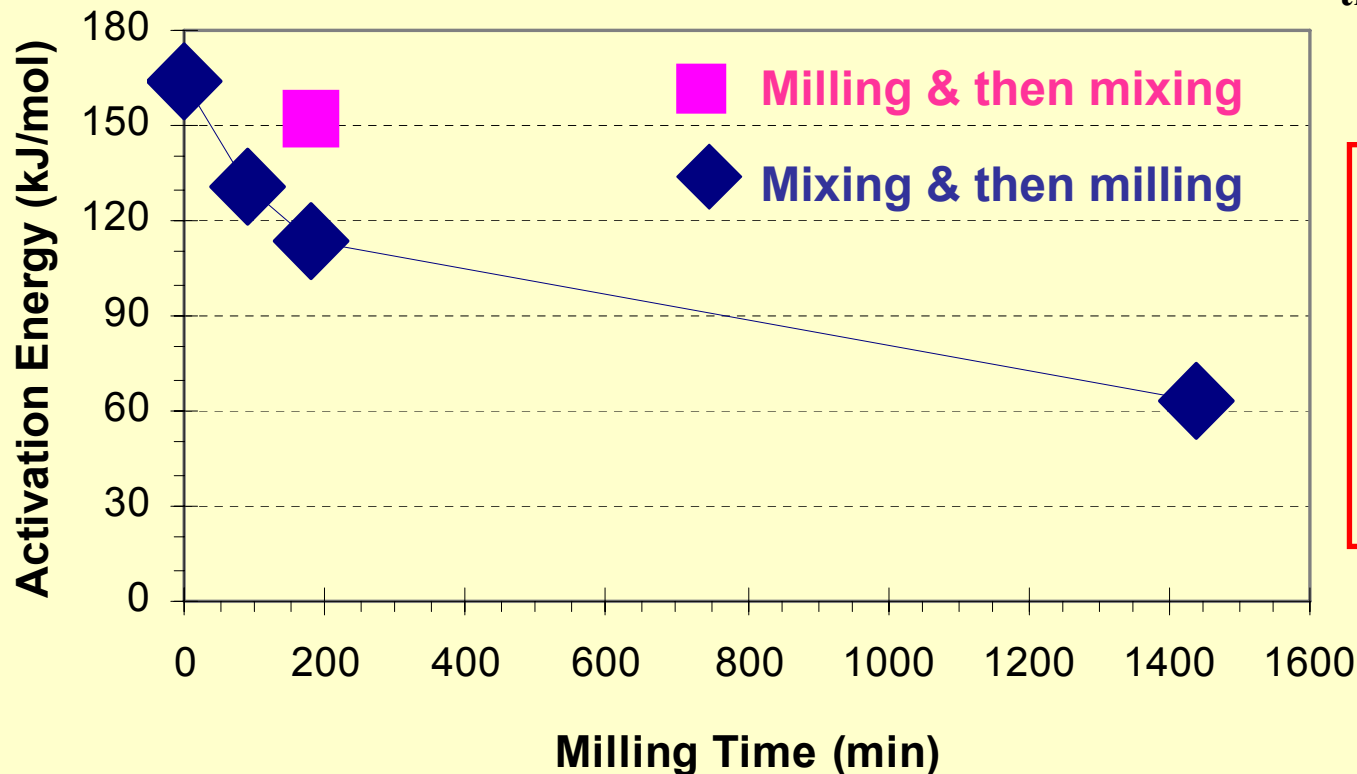
- The dehydrogenation rate of $\text{LiNH}_2 + \text{LiH}$ mixture increases with the ball milling time.
- Dehydrogenation occurs at ambient temperature when the ball milling time is 180 min.
- The mixture without ball milling exhibits melting of LiNH_2 at $\sim 360^\circ\text{C}$ because of the slow reaction rate at low temperatures.

Calculation of the Activation Energy for Dehydrating Reaction via the Kissinger Method

- Reaction: $\text{LiNH}_2 + \text{LiH} = \text{Li}_2\text{NH} + \text{H}_2$

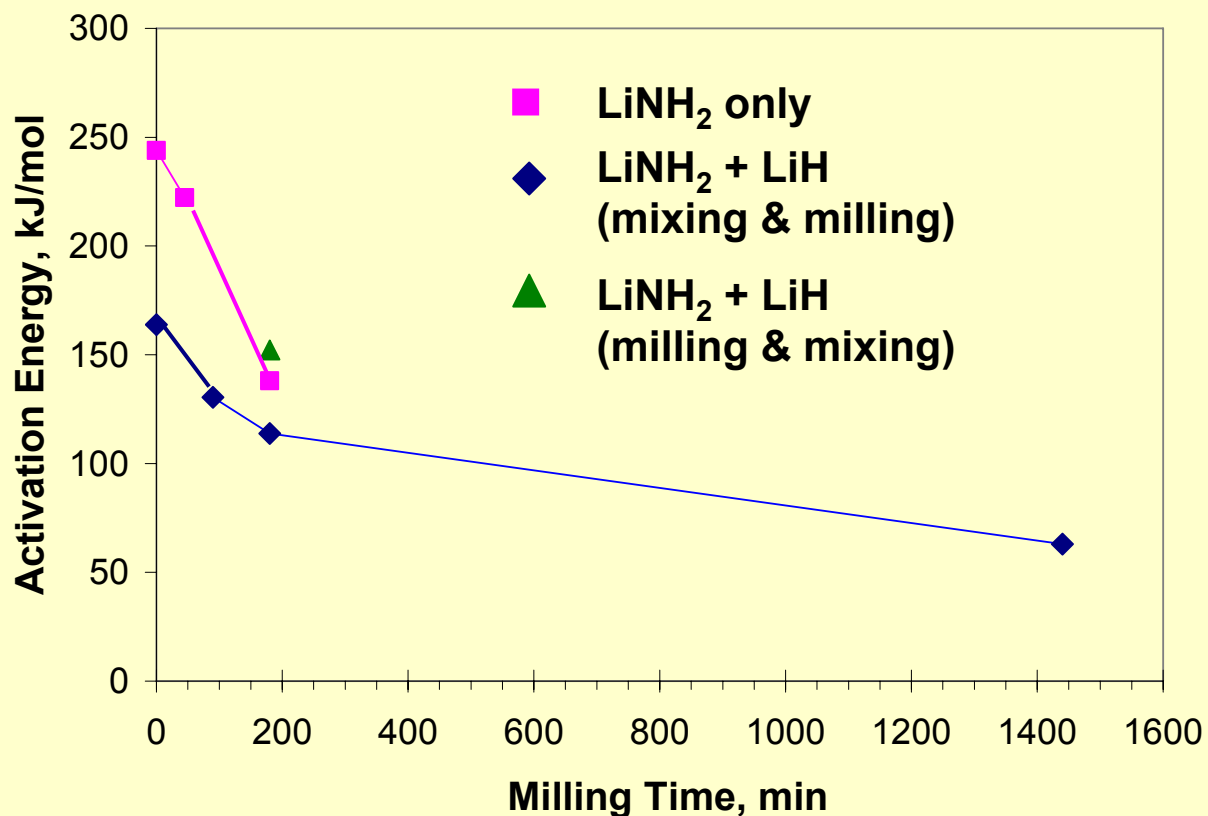
- Kissinger Method:
$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + F_{KAS}(\alpha)$$

where T_p is the endothermic peak temperature measured for the heating rate, β , during DSC. $F_{KAS}(\alpha)$ is a parameter that is a function of the fraction of transformation, α .



- The activation energy decreases with increasing the milling time.
- The activation energy is affected by the milling and mixing sequence.

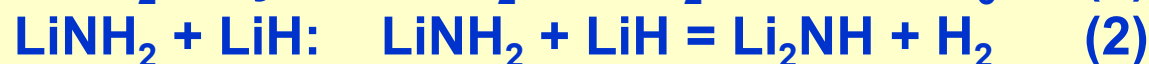
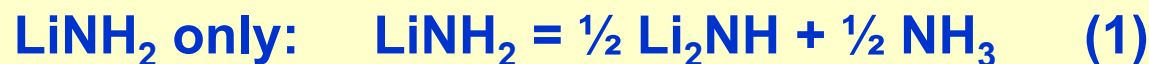
Comparisons of the Activation Energies



- The activation energy decreases with increasing of the milling time for all reactions.

- Reaction 1 is the first step of Reaction 2. However, the “apparent” activation energy of Reaction 2 is lower than that of Reaction 1, suggesting that the presence of LiH can reduce the activation energy of Reaction 1.

- The activation energy is also affected by the milling and mixing sequence, supporting the notion that LiH does have the catalytic effect on Reaction 1.



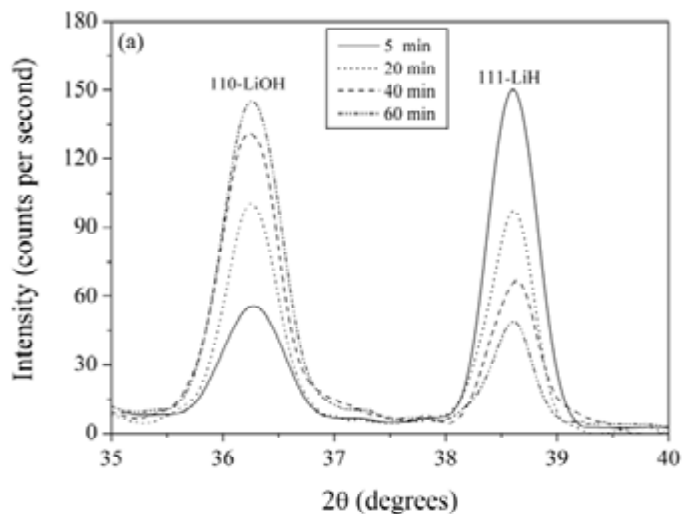
Summary for Enhancement of Hydrogen Sorption/Desorption of $\text{LiNH}_2 + \text{LiH}$ Systems

1. Mechanical activation through ball milling reduces particle size, increases specific surface area, and introduces nanograins as well as a large amount of defects to LiNH_2 and LiH crystals.
2. All of these changes induced by ball milling enhance the hydrogen sorption/desorption of $\text{LiNH}_2 + \text{LiH}$ systems. The activation energy decreases as the ball milling time increases.
3. LiH has a catalytic effect on the transition of LiNH_2 to Li_2NH and NH_3 . This is manifested in that (a) the activation energy for the reaction between LiNH_2 and LiH is lower than that for the transition of LiNH_2 to Li_2NH and NH_3 , and (b) the activation energy for the reaction between LiNH_2 and LiH depends on the mixing and milling sequence.
4. Although the onset temperature for dehydrogenation of the mechanically activated $\text{LiNH}_2 + \text{LiH}$ system is improved to ambient, the peak temperature for releasing the largest amount of H_2 is still very high (260°C). Other approaches (e.g., advanced catalysts and modification of the composition) are needed to reduce the peak temperature to near ambient.

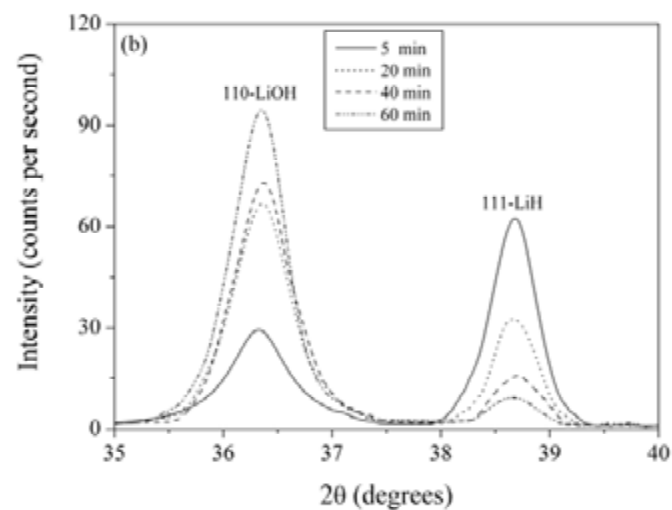
III. Stabilities of LiH in Different Environments

- The cyclic stability of $\text{LiNH}_2 + \text{LiH}$ systems in hydrogen uptake and release cycles depends on the sensitivity of these lithium hydrides, amides, and imides to impurities in the hydrogen source. This is an especially important issue if impurities enter the hydrogen storage tank with each refueling.
- The present study investigates the stability of LiH under (i) a high purity argon atmosphere, (ii) an argon atmosphere with some O_2 and H_2O impurities, and (iii) ambient air at both room and high temperatures.

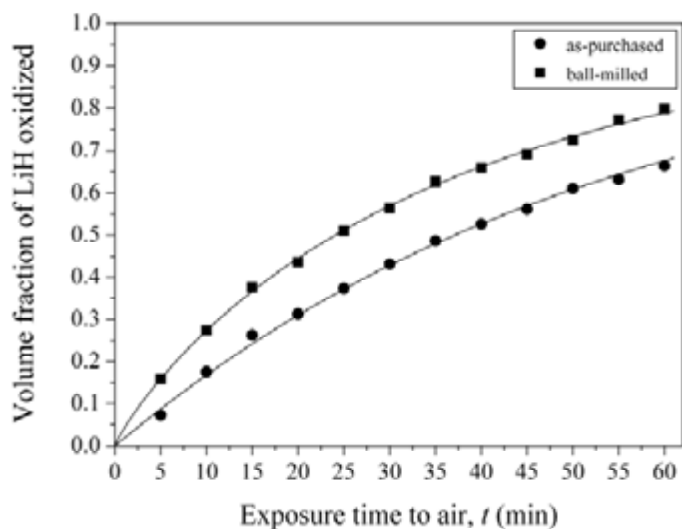
XRD Patterns of LiH Exposing to Ambient Air as a Function of Time



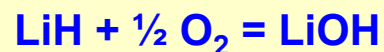
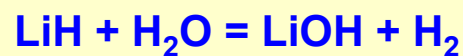
LiH without milling



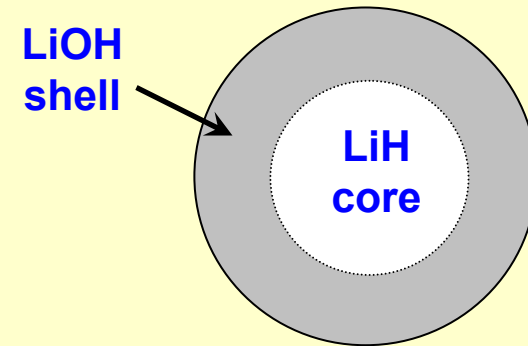
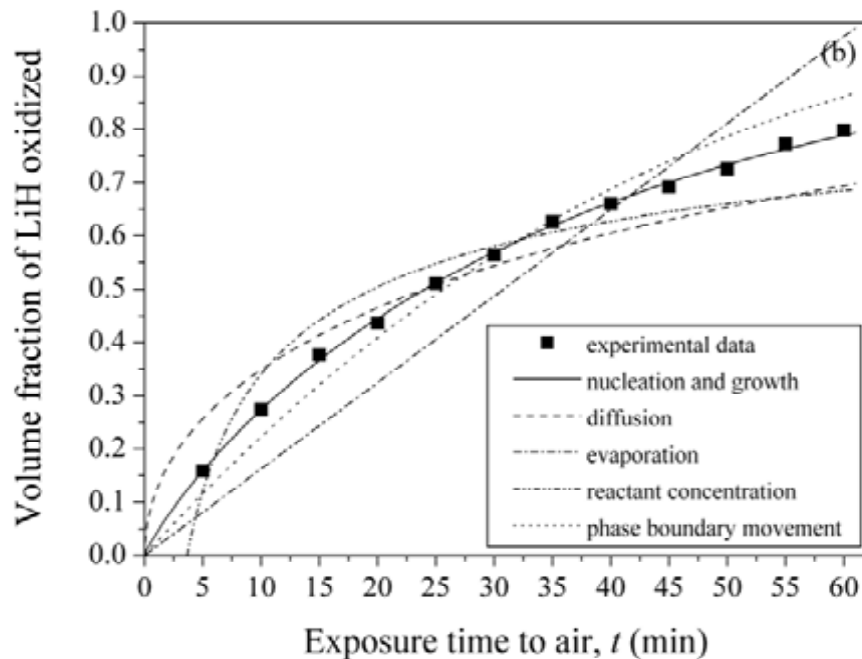
LiH with milling for 3 h



- The oxidation product of LiH in ambient air is LiOH.
- The oxidation rate of the milled LiH is faster than that of the un-milled LiH.
- The oxidation of LiH in ambient air proceeds with the following two reactions:



Rate-Controlling Mechanisms for Oxidation of LiH in Ambient Air



The oxidation rate of LiH in ambient air is controlled by the nucleation and growth of the LiOH shell, and can be described by Johnson-Mehl-Avrami (JMA) equation.

JMA Equation for LiH with milling:

$$f = 1 - \exp(-0.028t^{1.01})$$

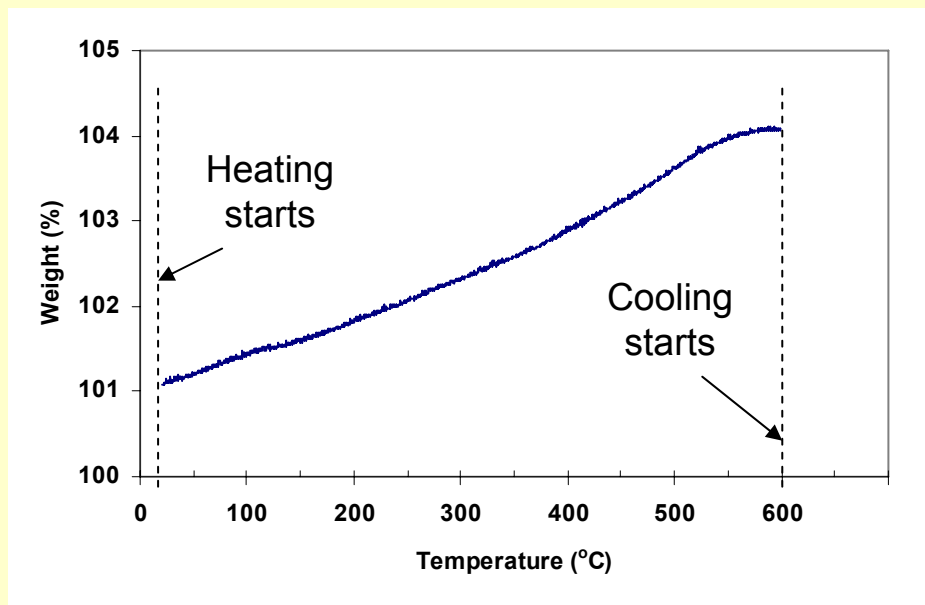
JMA Equation for LiH without milling:

$$f = 1 - \exp(-0.018t^{1.01})$$

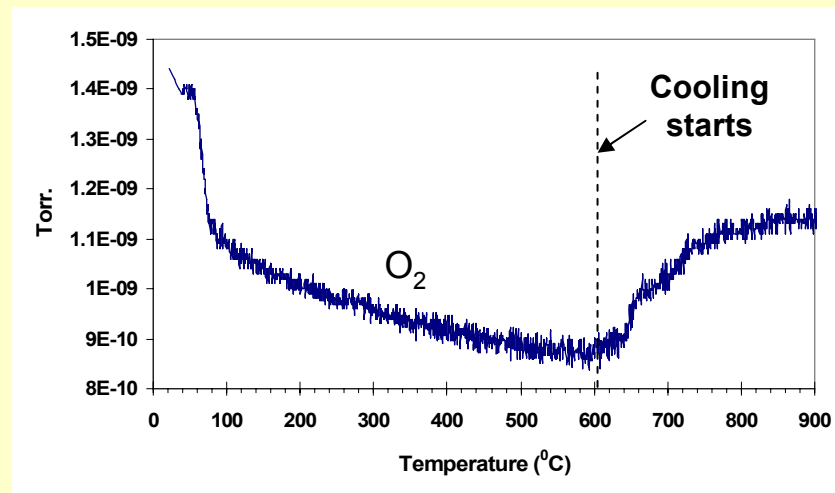
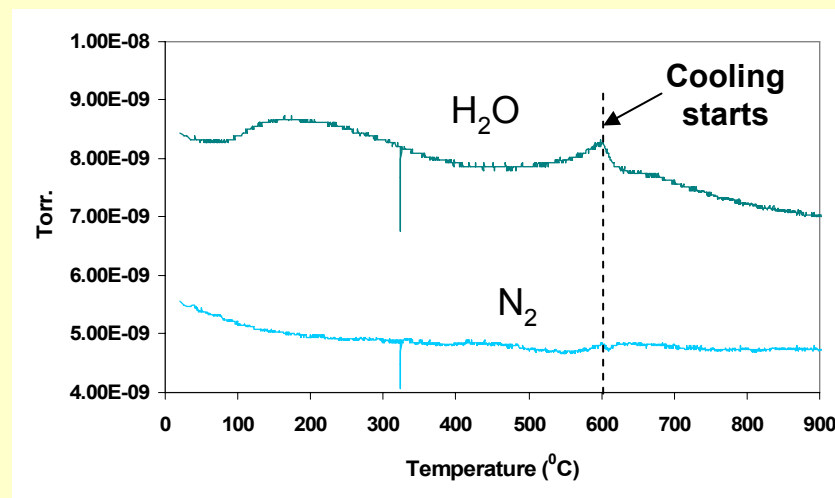
Ball milling increases the oxidation rate of LiH in ambient air.

Oxidation of LiH in Argon with O₂ and H₂O Impurities during TGA Analysis

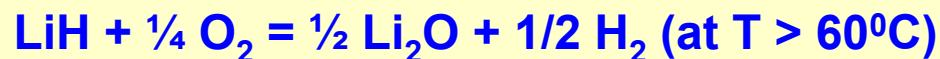
TGA Curve



Composition Analysis of Effluent Gases



With 515 ppm O₂ and 5,692 ppm H₂ in argon, the oxidation of LiH proceeds with the following reactions:



Summary for Stabilities of LiH in Different Environments

1. No oxidation of LiH occurs under an argon atmosphere of 99.999% purity with $\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 1$ ppm, $\text{H}_2 < 3$ ppm, $\text{N}_2 < 5$ ppm, and THC < 0.5 ppm.
2. The oxidation product of LiH in ambient air with a relative humidity of 27% at room temperature is LiOH.
3. The oxidation kinetics of LiH in ambient air at room temperature can be described very well by the Johnson-Mehl-Avrami equation.
4. Oxidation of LiH occurs under an argon atmosphere containing 5,692 ppm H_2O , 515 ppm O_2 , 585 ppm H_2 , 88 ppm N_2 , and 1.3 ppm NH_3 . At temperatures ranging from ~ 55 to 600°C , oxidation of LiH proceeds via the equation of $\text{LiH} + \frac{1}{4} \text{O}_2 = \frac{1}{2} \text{Li}_2\text{O} + \frac{1}{2} \text{H}_2$.
5. At room temperature, oxidation of LiH in ambient air and in an argon atmosphere containing 5,692 ppm H_2O , 515 ppm O_2 , 585 ppm H_2 , 88 ppm N_2 , and 1.3 ppm NH_3 is due to two reactions: $\text{LiH} + \text{H}_2\text{O} = \text{LiOH} + \text{H}_2$ and $\text{LiH} + \frac{1}{2} \text{O}_2 = \text{LiOH}$.

IV. Dehydrogenation Behavior of the **LiNH₂ + MgH₂ Systems**

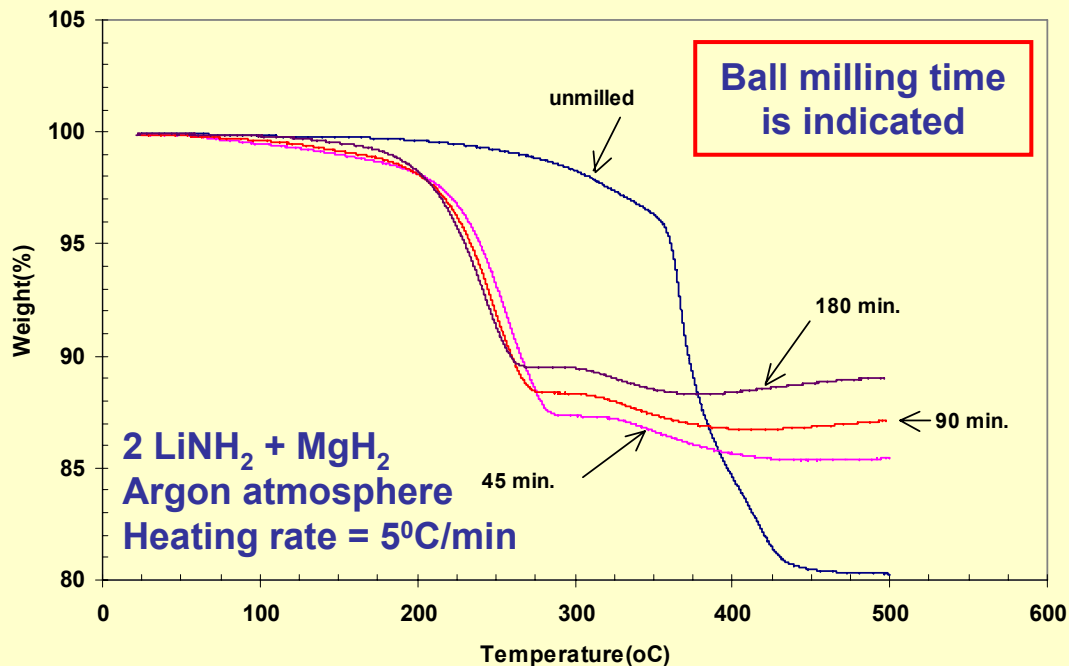
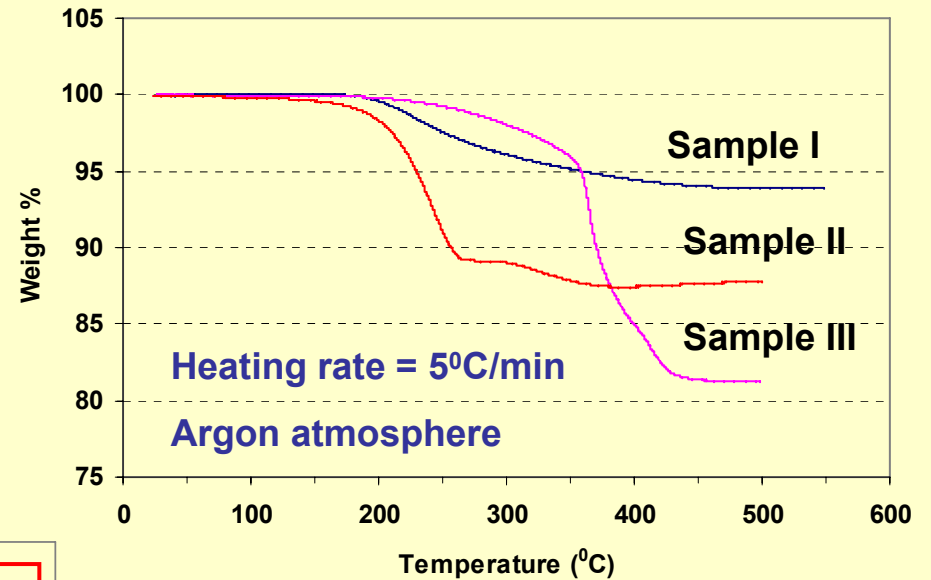
- Partial substitution of Li by Mg in LiNH₂ can destabilize the compound and thus reduce the hydrogenation and dehydrogenation temperatures.
- The present study investigates dehydrogenation behavior of the LiNH₂ plus MgH₂ system and compares this behavior to that of the LiNH₂ plus LiH system with particular attention to the reaction kinetics.

TGA Analysis of LiNH_2 and MgH_2 Mixtures

(In a 2-to-1.1 ratio)

Sample I = $\text{LiNH}_2 + \text{LiH}$ (3hr milling)
 Sample II = $2\text{LiNH}_2 + \text{MgH}_2$ (3hr milling)
 Sample III = $2\text{LiNH}_2 + \text{MgH}_2$ (no milling)

- Ball milling reduces the dehydrating temperature.
- The MgH_2 -containing system exhibits lower dehydrating temperatures than the LiH -containing system when both systems are ball milled.
- The weight loss of the MgH_2 -containing systems with and without ball milling is substantially larger than the theoretical prediction.

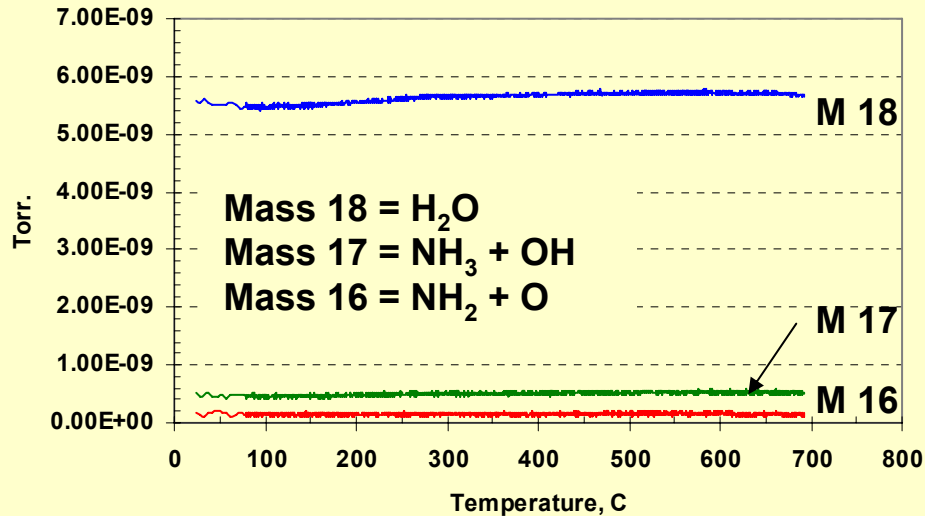


- The weight loss decreases as the ball milling time increases.
- However, after 3-hr of ball milling the weight loss is still larger than the theoretical prediction based on the following reaction:

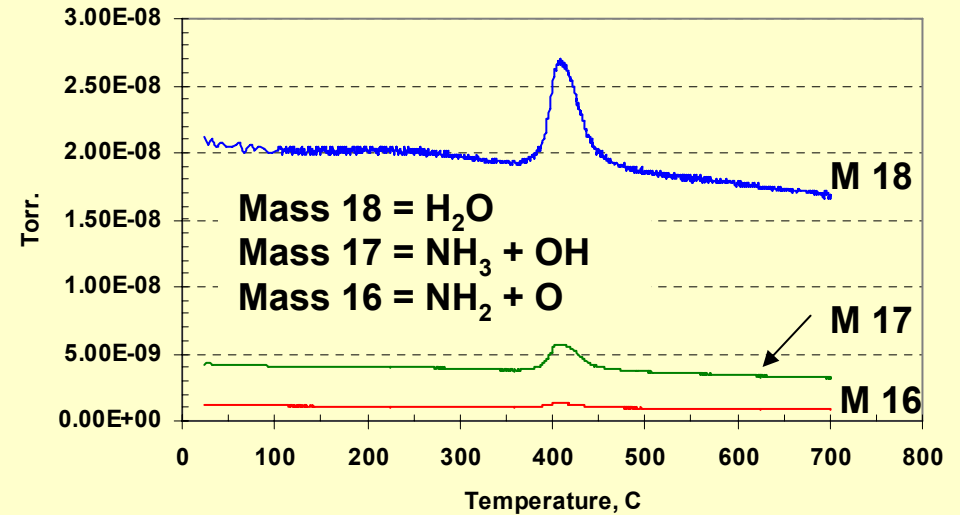
$$2 \text{LiNH}_2 + \text{MgH}_2 = \text{Li}_2\text{MgN}_2\text{H}_2 + 2 \text{H}_2$$
- The large weight loss results from the NH_3 escape owing to the slow reaction between MgH_2 and NH_3 , as confirmed by the composition analysis of the effluent gases.

Analysis of NH₃ Concentration in the Effluent Gases using Residual Gas Analyzer

Blank Sample in TGA



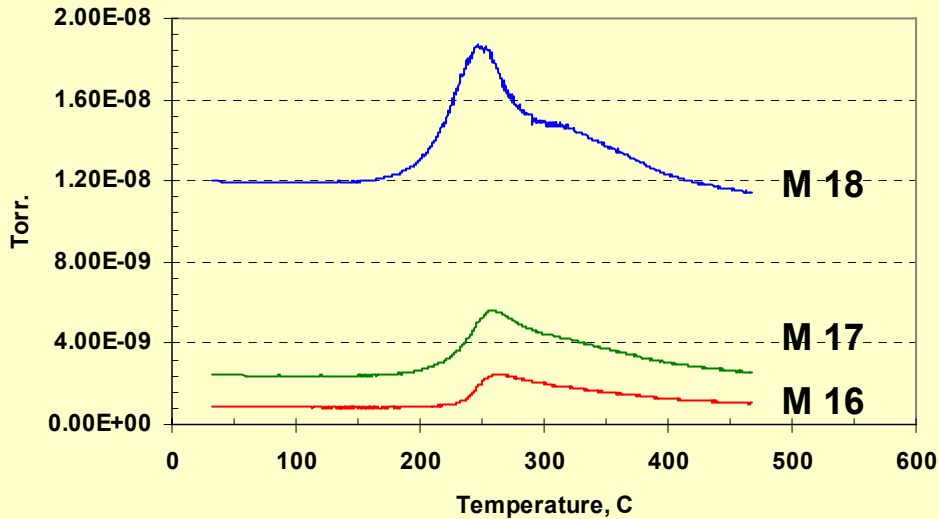
MgH₂ only in TGA



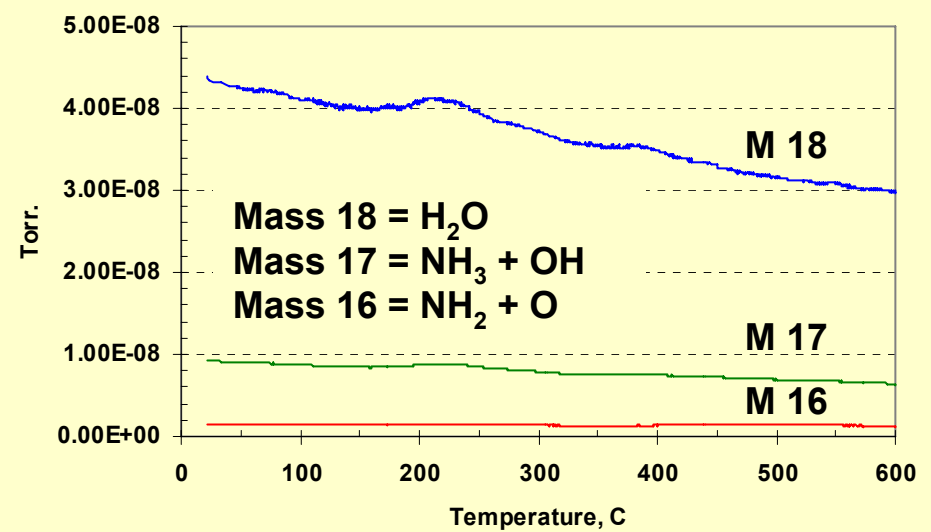
- Detection of NH₃ in the outlet gas during TGA analysis using a quadrupole residual gas analyzer (RGA) is difficult because NH₃ signal is interfered by OH species which also has a mass of 17.
- Monitoring the signal of Mass 16, however, provides a satisfactory result for semi-quantification of the NH₃ concentration in the outlet gas. Mass 16 contains both NH₂ and O species; however, the intensity of NH₂ species is 80% of the NH₃ intensity, whereas the intensity of O is only 1% of the H₂O intensity. As a result, the intensity of Mass 16 is very sensitive to the alternation of the NH₃ concentration. In contrast, the change in the H₂O concentration only induces negligible alternation in the intensity of Mass 16, as shown in the MgH₂ only sample above.

Analysis of NH₃ Concentration in the Effluent Gases using Residual Gas Analyzer

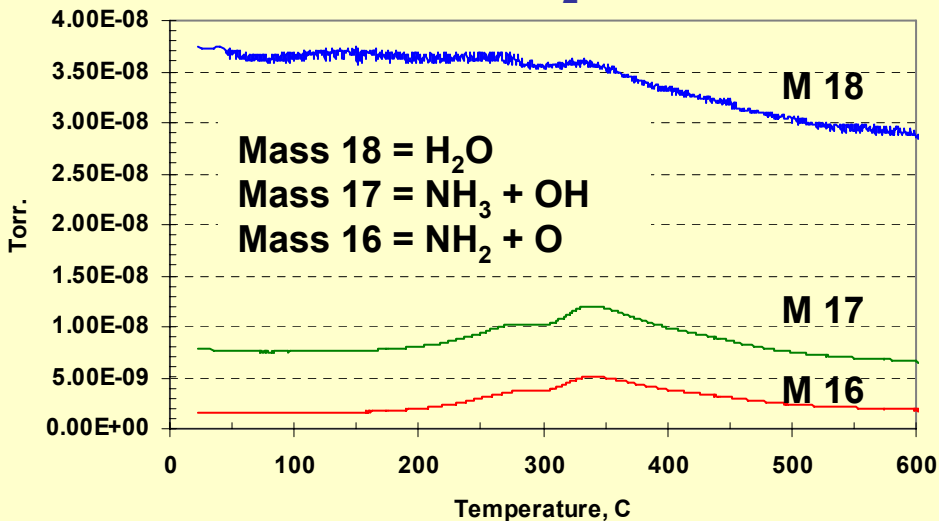
Milled 2 LiNH₂ + MgH₂ in TGA



Milled LiNH₂ + LiH₂ in TGA



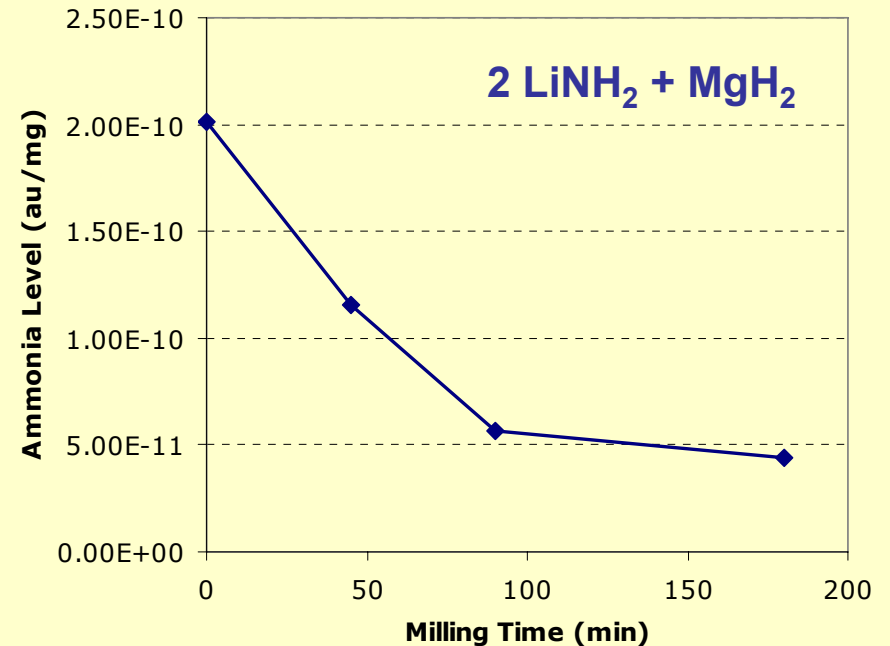
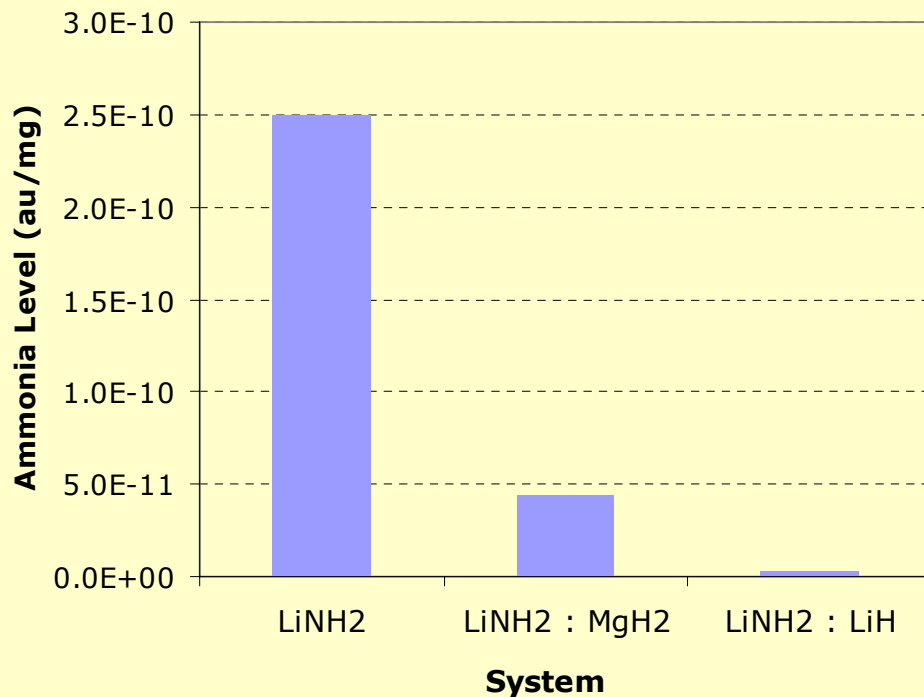
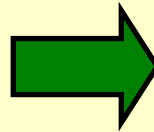
Milled LiNH₂ in TGA



- The LiNH₂ + MgH₂ mixture releases NH₃, whereas the LiNH₂ + LiH system does not, as indicated by the change in the signal of Mass 16.
- LiNH₂ only releases NH₃, and this is reflected in the substantial change of the Mass 16 signal.

Analysis of NH₃ Concentration in the Effluent Gases using Residual Gas Analyzer

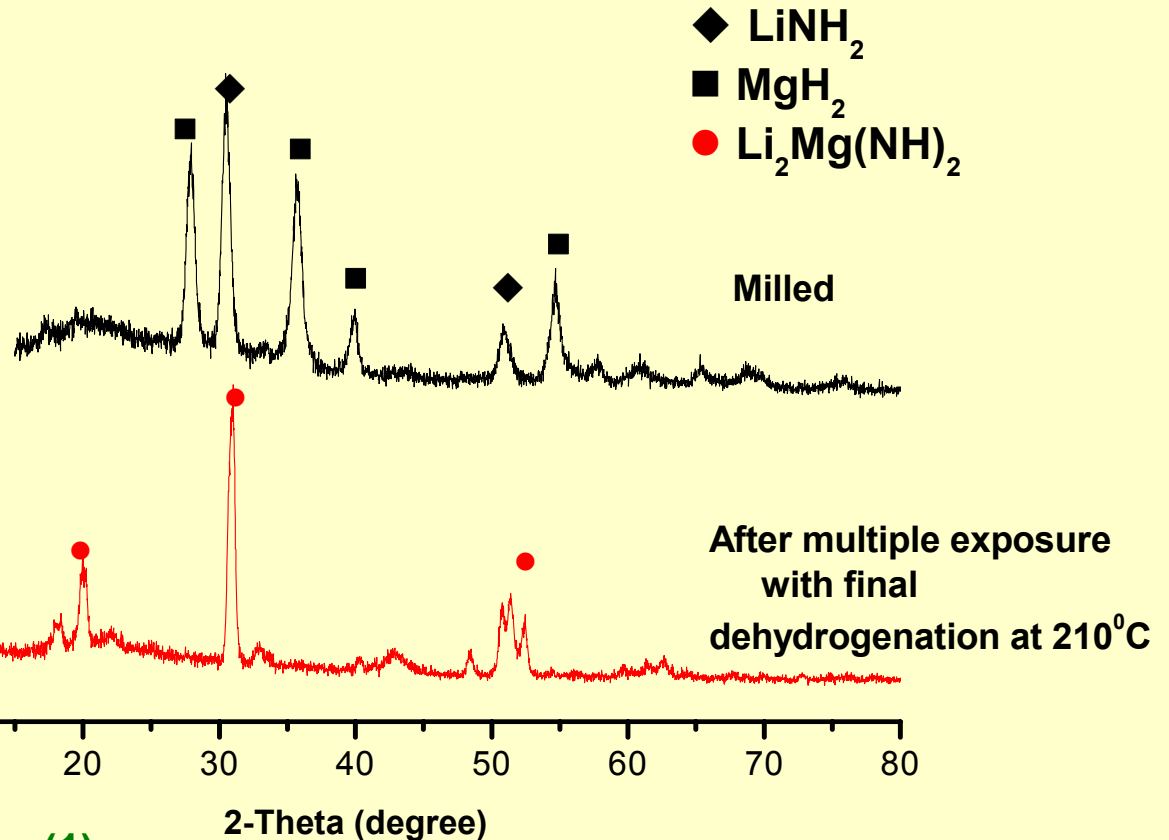
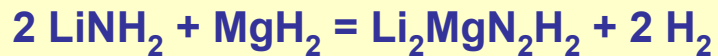
The NH₃ escape issue in the LiNH₂ + MgH₂ system can be alleviated by ball milling, but cannot be eliminated because of the slow reaction between NH₃ and MgH₂.



- LiNH₂ releases the largest amount of NH₃ per unit weight, which is followed by the LiNH₂ + MgH₂ system.
- The LiNH₂ + LiH system has almost no NH₃ escape problem because the reaction between NH₃ and LiH is very fast after mechanical activation.

XRD Analysis of the LiNH₂ and MgH₂ Mixture after Dehydrogenation at 210⁰C

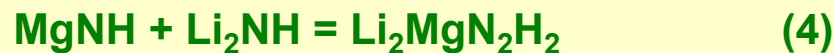
XRD patterns indicate that the following reaction has taken place in the dehydrogenation process of the LiNH₂ and MgH₂ mixture:



Based on TGA, RGA, and XRD analyses, it is proposed that the overall reaction above proceeds with the following steps:

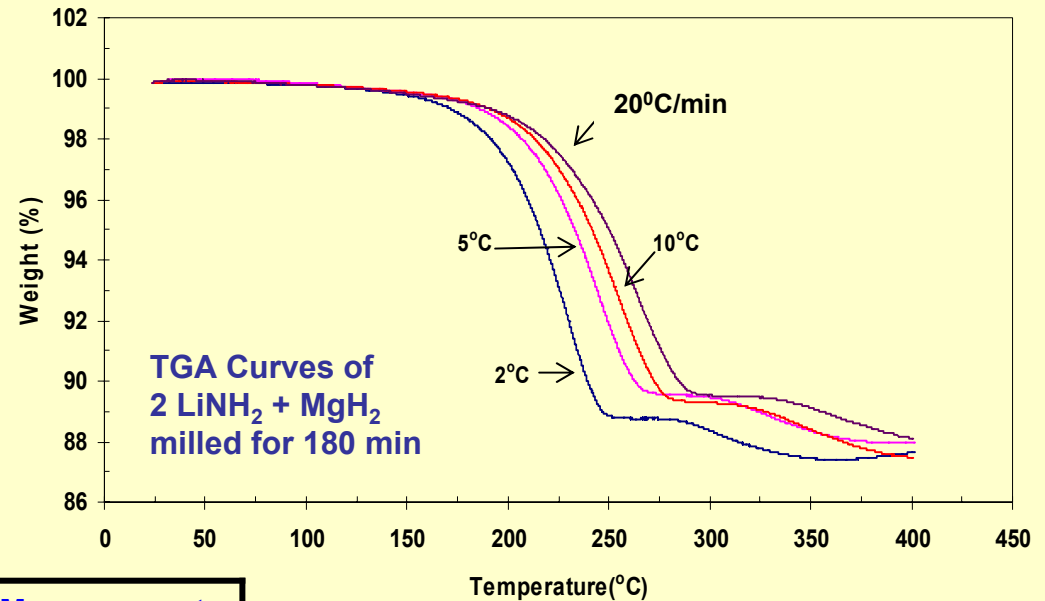


(Repeating Reactions (2) and (3) until all NH₃ and MgH₂ are converted to H₂ and MgNH)



Activation Energy Comparison between the LiNH_2 and MgH_2 and the LiNH_2 and LiH Systems

The activation energies of dehydrogenation for $\text{LiNH}_2 + \text{MgH}_2$ and $\text{LiNH}_2 + \text{LiH}$ systems were determined using the Kissinger method (DSC data) and Flynn-Wall method (TGA data), as indicated in the table below.



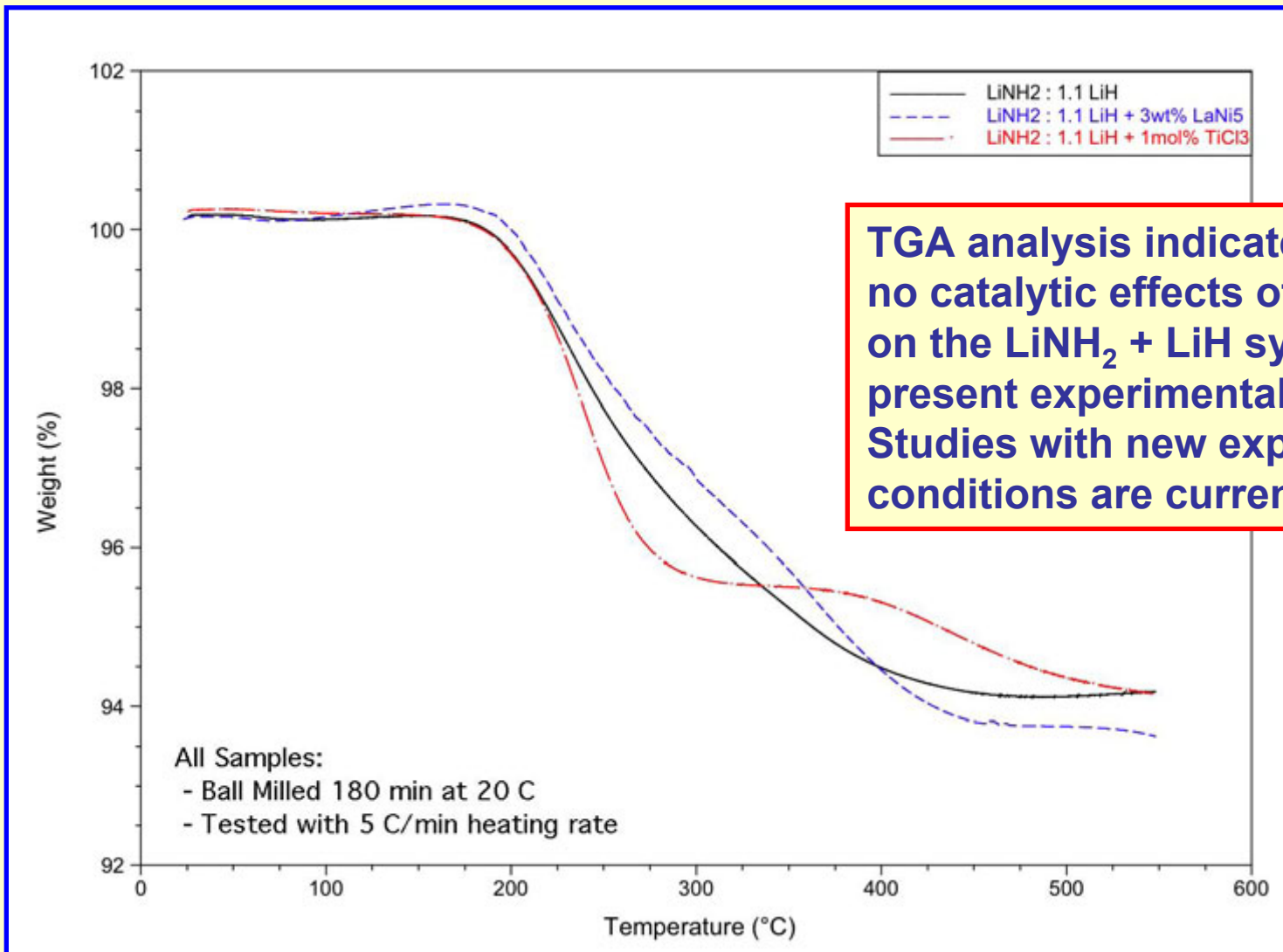
Materials	Processing Conditions	Activation Energy (kJ/mol)	Measurement Method
$\text{MgH}_2 + 2 \text{LiNH}_2$	No milling	182	4 wt.% loss of TGA
$\text{MgH}_2 + 2 \text{LiNH}_2$	Milling for 180 min	133	4 wt.% loss of TGA
$\text{LiH} + \text{LiNH}_2$	Milling for 180 min	118	4 wt.% loss of TGA
$\text{LiH} + \text{LiNH}_2$	Milling for 180 min	113	Peak temperature of DSC
$\text{LiH} + \text{LiNH}_2$	No Milling	164	Peak temperature of DSC

- The activation energy decreases with ball milling.
- $\text{LiNH}_2 + \text{MgH}_2$ system has higher activation energies than $\text{LiNH}_2 + \text{LiH}$ system under the same processing conditions.

Summary for Dehydrogenation Behavior of the LiNH_2 and MgH_2 System

1. The LiNH_2 and MgH_2 system has lower dehydrogenation temperatures than the LiNH_2 and LiH system. This result is consistent with the thermodynamic analysis, i.e., the MgH_2 -containing system has a higher thermodynamic driving force for dehydrogenation and thus lower dehydrogenation temperatures.
2. The reaction rate between MgH_2 and NH_3 is lower than that between LiH and NH_3 . As a result, the escape of NH_3 occurs in the LiNH_2 and MgH_2 system, leading to a substantial weight loss.
3. The $\text{LiNH}_2 + \text{MgH}_2$ system has a higher activation energy than $\text{LiNH}_2 + \text{LiH}$ system under the same processing condition. This is one of the reasons why the reaction rate between MgH_2 and NH_3 is lower than that between LiH and NH_3 .
4. To avoid the escape of NH_3 , the $\text{LiNH}_2 + \text{MgH}_2$ system should be subjected to a slow reaction treatment. The treatment will permit the complete reaction between NH_3 and MgH_2 and convert the $\text{LiNH}_2 + \text{MgH}_2$ mixture to $\text{Li}_2\text{MgN}_2\text{H}_2$ which will change to $\text{Mg}(\text{NH}_2)_2 + 2 \text{LiH}$ mixture in the subsequent hydrogenation step. After such a treatment, there will be no NH_3 escape issue because the fast reaction rate between LiH and NH_3 .

V. Preliminary Studies of Advanced Catalysts for $\text{LiNH}_2 + \text{LiH}$ and $\text{LiNH}_2 + \text{MgH}_2$ Systems



Future Work

- **Remainder of FY 2006:**

- Explore reaction fundamentals of the $\text{MgH}_2 + \text{LiNH}_2$ system: rate-limiting steps, intermediate species, and structure (UConn)
- Investigate the mechanism of mechanical activation in the $\text{LiH} + \text{LiNH}_2$ system: ordering/disordering, phase transformation, bond length, and angle changes with the help of NMR and quantum chemistry calculations at the density function level (PNNL & UConn)
- Develop advanced catalysts: quantum chemistry calculations coupled with experiments (UConn & PNNL)

- **FY 2007:**

- Improve kinetics using mechanical activation, nano-engineering, and advanced catalysts: long milling time (1,440 min & 6,000 min), low-temperature milling (-50°C and -196°C), stability of mechanical activation effects, catalytic effects as a function of processing conditions and cyclic life (UConn & PNNL)
- Determine the mechanism of mechanical activation and its stability: the strength of the hydrogen bond between the host material and the stored H_2 , diffusivity, diffusion paths, and possibly the volume fraction of mobile hydrogen as a function of mechanical activation (PNNL & UConn)

Project Summary

- Relevance:** Explore fundamental mechanisms related to mechanical activation necessary for improving kinetics of reversible hydrogen storage materials.
- Approach:** Quantum-chemical modeling and mechanical activation at different temperatures coupled with (i) chemical modification of lithium amide/imide to destabilize the compounds thermodynamically and (ii) advanced catalysts to enhance hydrogen sorption and desorption kinetically.
- Technical Accomplishments:** (i) Established the effect of mechanical activation; (ii) Demonstrated the dehydrogenation at room temperature for both $\text{LiNH}_2 + \text{LiH}$ and $\text{LiNH}_2 + \text{MgH}_2$ systems; (iii) Identified the NH_3 escaping issue in the $\text{LiNH}_2 + \text{MgH}_2$ system; (iv) Alleviated the NH_3 issue in the $\text{LiNH}_2 + \text{LiH}$ system; (v) Established the sensitivity of LiH to impurities.
- Future Research:** Improve reaction kinetics using mechanical activation, nano-engineering, and advanced catalysts.

Publications and Presentations

- R. Ren, T. Markmaitree, L. Shaw, and Z. G. Yang, “Effects of Mechanical Activation on Lithium Amide/Imide Transition and Hydrogen Sorption/ Desorption,” presented at the Symposium on “Materials for the Hydrogen Economy” in the MS&T '05, Pittsburgh, PA, September 2005.
- T. Markmaitree, R. Ren, and L. Shaw, “Enhancement of Lithium Amide to Lithium Imide Transition via Mechanical Activation,” submitted to J. Phys. Chem. B.
- R. Ren, A. L. Ortiz, T. Markmaitree, W. Osborn, and L. Shaw, “Stability of Lithium Amide and Lithium Hydride in Ambient Atmosphere,” J. Phys. Chem. B, in press.
- R. Ren, T. Markmaitree, L. Shaw, Z. G. Yang, and J. Hu, “Effects of Mechanical Activation on Dehydrogenation of the Lithium Amide and Imide System,” to be submitted to J. Alloys Comp.
- L. Shaw, “Nanostructured Lithium Hydrides, Amides, Imides, and Nitrides for Hydrogen Storage Applications,” an Invited Chapter for a book on “Nanomaterials for Energy Storage Applications,” H. S. Nalwa, Eds., American Scientific Publishers, December 2006.
- L. Shaw, “Hydrogen Economy and Materials Issues,” Invited Presentation at the ASM Hartford Chapter meeting, Hartford, CT, January 2006.

Critical Assumptions and Issues

The present study unambiguously establishes the following two conclusions:

1. Both $\text{LiNH}_2 + \text{LiH}$ and $\text{LiNH}_2 + \text{MgH}_2$ systems exhibit dehydrogenation at room temperature after mechanical activation. This indicates clearly that there is sufficient thermodynamic driving force for hydrogenation and dehydrogenation to occur at room temperature.
2. However, the peak temperature for dehydrogenation is $\sim 250^\circ\text{C}$ for both $\text{LiNH}_2 + \text{LiH}$ and $\text{LiNH}_2 + \text{MgH}_2$ systems. Combining with the first observation, it can be concluded that the reaction rate is too slow for both systems even though there is sufficient thermodynamic driving force for the hydrogenation and dehydrogenation to take place at ambient temperature.

Based on these two conclusions, we believe that:

The key to successfully utilizing these two systems for the on-board hydrogen storage application is the development of advanced catalysts and/or high degree of stable mechanical activation so that hydrogenation and dehydrogenation can occur readily at ambient temperature.