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LETTERS

Ultrafast Reaction between LiH and NH_3 during H_2 Storage in Li_3N

Yun Hang Hu* and Eli Ruckenstein

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260

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Li_3N is a potential H_2 storage material due to its high theoretical H_2 capacity (10.4 wt %). A critical potential issue regarding this N-based storage material is the generation of NH_3, which consumes some H_2 and also constitutes a poison for the downstream processes. In this Letter, by using the temperature-programmed decomposition of a two-layer material ($LiNH_2$ and LiH), we demonstrate that NH_3 produced via the decomposition of $LiNH_2$ is completely captured by LiH even at very short contact times (25 ms) with the carrier gas. This ultrafast reaction between NH_3 and LiH inhibits NH_3 formation during the hydrogenation of Li_3N and also prevents the NH_3 generated during the dehydrogenation of the hydrogenated Li_3N to escape into the H_2 stream. However, if the hydrogenated Li_3N was previously exposed to the atmosphere, some NH_3 could escape into the H_2 stream during the H_2 desorption, due to the partial oxidation of LiH by the water present in air.

Introduction

Hydrogen is a promising clean fuel for vehicles, which can use hydrogen for propulsion either directly, or through fuel cells. In both cases, a suitable hydrogen-storage material is needed to make this source of energy economically viable. There are economical issues with the traditional H_2 storage methods, such as the liquefaction process, because the compression and cooling of the hydrogen to 20 K consumes almost 30% of the hydrogen energy.[1] The H_2 adsorption on activated carbon, which has a very high surface area (1500−2000 m^2/g), also requires a low temperature (77 K) and a high pressure (∼50 atm).[1] Low H_2 storage capacities and slow desorption kinetics are the drawbacks of the metal hydrides. In recent years, the high, reversible adsorption of H_2 onto carbon nanotubes[2−4] has stimulated both experimental and theoretical work for H_2 storage in carbon nanomaterials.[2−11] However, it is still unclear how high hydrogen-storage capability can be reached by these nanostructured carbon materials.[5,6]

As early as 1910, Dafert and Miklauz[12] reported that the reaction between Li_3N and H_2 generated Li_3NH_4 (a mixture of 2LiH and $LiNH_2$[13])

$$Li_3N + 2H_2 = Li_3NH_4$$

Consequently, Li_3N can theoretically store 10.4 wt % hydrogen. Furthermore, they found that Li_3NH_4 can be partially decomposed to release H_2.[12] Therefore, the hydrogenation of Li_3N and the dehydrogenation of the hydrogenated Li_3N constitute a reversible process, which can be used for H_2 storage.[14] Our experiments have shown that the complete recovery of Li_3N from the hydrogenated compounds is a difficult process that requires high temperatures (above 430 °C) and long times. The use of such high temperatures produces sintering and the recovered Li_3N becomes ineffective. For this reason, the reversible storage capacity of Li_3N is about 5 wt %.

However, one critical issue with this N-based material is the possibility of NH_3 generation during the hydrogenation of Li_3N and during the decomposition of the hydrogenated Li_3N, because the NH_3 formation from H_2 and Li_3N is thermodynamically a

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* To whom correspondence should be addressed. Phone: 716-6452911ext.2266. Fax: 716-645-3822. E-mail: yhu@buffalo.edu.

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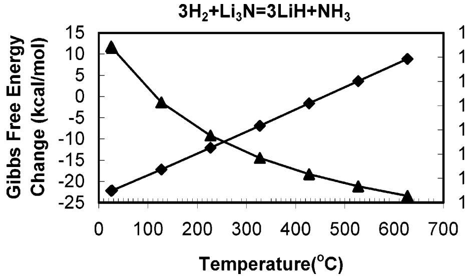

Figure 1. Thermodynamics of Li_3N hydrogenation to NH_3: (◆) Gibbs free energy change; (▲) $P_{NH_3}/P_{H_2}^3$).

very favorable process at temperatures below 400 °C (see Figure 1). In this paper, by using two-layer materials and short contact times between them and the carrier gas (He), we found that the ultrafast reaction between NH_3 and LiH inhibits the NH_3 generation during the hydrogenation of Li_3N and prevents NH_3 to escape into the H_2 stream during dehydrogenation.

Experiments

Two types of two-layer materials were used: in one, denoted TLM-1, $LiNH_2$ was the first layer and LiH the second one; in the other (TLM-2), the order of the layers was inverted. The mole ratio of LiH to $LiNH_2$ was in both cases equal to 2. The temperature-programmed decomposition mass spectrum (TPDMS) of these two-layer materials was performed as follows: A carrier gas (He) was allowed to flow at 1 atm pressure through the two-layer material (0.03 g; with an exception of 0.003 g for the shortest contact time experiment), which was placed in a fixed bed reactor located in an electric furnace, programmed to heat at a rate of 3 °C/min. The gaseous products of the decomposition of the first layer were passed by the carrier (He) through the second layer, and finally, all the gaseous molecules, including those produced in the second layer, were carried into a mass spectrometer (HP Quadrupole, 5971 series mass selective detector) equipped with a fast response inlet capillary system to detect NH_3. Very high space velocities of the carrier gas were used to achieve very short contact times between the gas molecules and the two-layer materials (as short as 2.4 ms).

Results and Discussion

During the temperature-programmed decomposition of TLM-1, in which the carrier gas (He) has passed first through the $LiNH_2$ layer and then through the LiH layer, no NH_3 was detected (Figure 2a). In contrast, for the reverse two-layer material (TLM-2), in which the carrier gas (He) has passed first through the LiH layer and then through the $LiNH_2$ layer, NH_3 was detected in the broad temperature range between 60 and 500 °C (Figure 2b). This means that NH_3 was formed through the decomposition of $LiNH_2$ but was captured by LiH. To examine how fast LiH has captured the NH_3 formed via the $LiNH_2$ decomposition, millisecond contact times were employed. For a contact time as short as 25 ms, NH_3 was still completely captured by LiH at all temperatures (Figure 2c). Even when the contact time was as short as 2.4 ms, 99.7% of NH_3 resulted from the $LiNH_2$ decomposition could be captured. Only 0.3% of the NH_3 resulted from $LiNH_2$ decomposition passed into the gas-phase stream (Figure 2d). This demonstrates that LiH can capture ultrafast the NH_3 formed during the H_2 release process of the hydrogenated Li_3N. Furthermore, in practice, the contact times are much longer than 10^3 ms, and hence no NH_3 impurity is expected to escape into the H_2 stream when Li_3N is used as storage material.

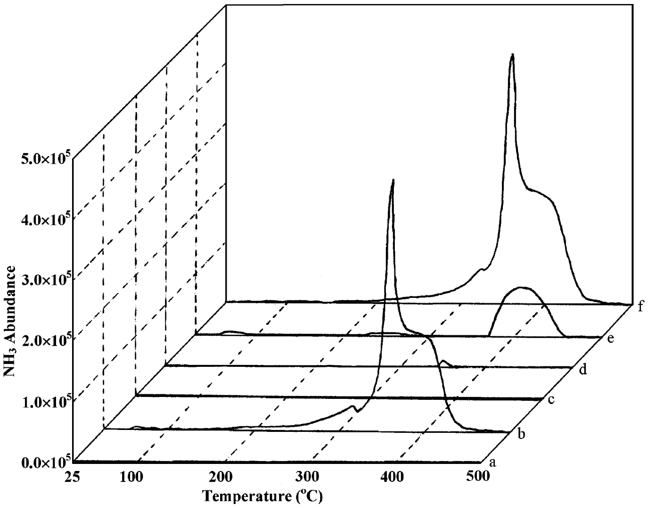

Figure 2. Temperature-programmed decomposition mass spectra: (a) TLM-1 with a contact time of 110 ms; (b)TLM-2 with a contact time of 110 ms; (c) TLM-1 with a contact time of 25 ms; (d) TLM-1 with a contact time of 2.4 ms; (e) TLM-1 with a contact time of 110 ms (exposed to air for 24 h before the experiment); (f) the two-layer material, with $LiNH_2$ as the first layer and Li_2O as the second one.

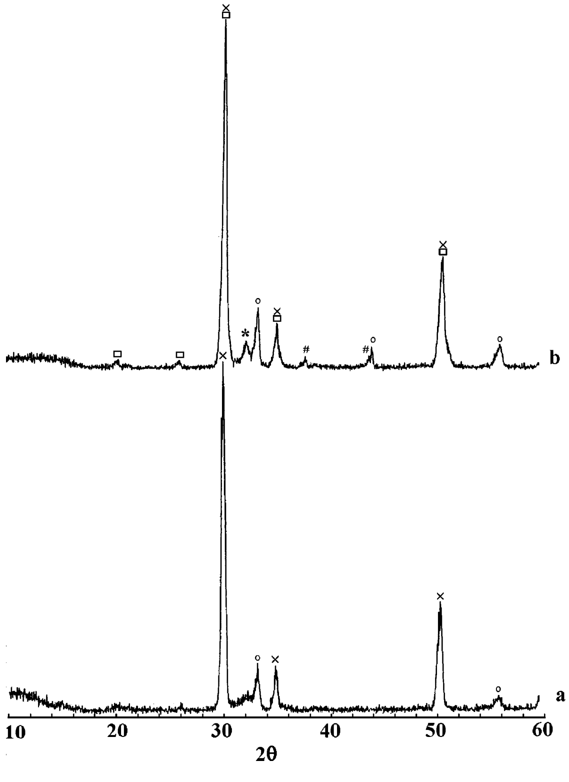

Figure 3. XRD patterns of TLM-1 after the temperature-programmed decomposition: (a) first layer; (b) second layer (×) Li_2NH; (□) $LiNH_2$; (#) LiH; (*) LiOH; (○) Li_2O.

XRD was used to examine the phase transformations of the two-layer material (TLM-1) after the decomposition reaction. As shown in Figure 3, $LiNH_2$ of the first layer has decomposed to Li_2NH, whereas LiH of the second layer was transformed to Li_2NH and $LiNH_2$. The presence of Li_2O and LiOH was a result of the exposure of the sample to the atmosphere during the XRD measurements and the reaction of LiH with the water from the atmosphere. Consequently, the following transformations occurred:

$$2LiNH_2 \rightarrow Li_2NH + NH_3$$
$$NH_3 + LiH \rightarrow LiNH_2 + H_2$$

The complete hydrogenation of Li_3N generated a mixture of 2LiH and $LiNH_2$ ($Li_3N + 2H_2 \rightarrow LiNH_2 + 2LiH$).[12−14] The generation of a $LiNH_2$ molecule was accompanied by the formation of two LiH molecules. Because LiH reacts quickly with NH_3, the LiH generated via the Li_3N hydrogenation could capture all the NH_3 formed via the $LiNH_2$ decomposition, and NH_3 could not escape into the H_2 stream during the H_2 release process.

The ultrafast reaction between NH_3 and LiH affected also the product composition and prevented the formation of a NH_3 impurity during the hydrogenation process of Li_3N. Because Li_2NH was detected during the hydrogenation of Li_3N,[14] the hydrogenation of Li_3N is a multistep process: Li_3N was first hydrogenated to Li_2NH and LiH. Further, Li_2NH was hydrogenated to $LiNH_2$ and LiH, and $LiNH_2$ was hydrogenated to LiH and NH_3. This means that for each NH_3 molecule generated, three LiH molecules were formed. Because the reaction between LiH and NH_3 to $LiNH_2$ is ultrafast, all NH_3 was transformed to $LiNH_2$. Consequently, the products of the complete hydrogenation of Li_3N are $LiNH_2$ and LiH. In other words, the ultrafast reaction between NH_3 and LiH also inhibits the NH_3 formation during the hydrogenation of Li_3N.

However, for a two-layer TLM-1 that was previously exposed to the atmosphere for 24 h, NH_3 was detected during the TPD (Figure 2e). This occurred because TLM-1 absorbed water from the atmosphere, which oxidized LiH to Li_2O. The Li_2O formed could no longer capture NH_3. Indeed, when LiH in TLM-1 was completely replaced by Li_2O, three NH_3 peaks were identified in the TPD (Figure 2f). This observation indicates that if a hydrogenated Li_3N was previously exposed to the atmosphere, NH_3 is expected to escape into the H_2 stream during the desorption process. Indeed, NH_3 was detected during H_2 desorption from a hydrogenated Li_3N, which was previously exposed to the atmosphere for 24 h.

In conclusion, the ultrafast reaction between LiH and NH_3 prevents a NH_3 impurity to escape into the H_2 flow during the entire H_2 storage process. However, if the hydrogenated Li_3N was previously exposed to the atmosphere, some NH_3 is expected to escape into the H_2 stream during the H_2 desorption, due to the partial oxidation of LiH.

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