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Lithium metatitanate enhanced solid-solid reaction in a lithium-nitrogen-hydrogen system

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It is first time to decrease the end temperature under 260 °C and the lowest peak temperature was occurred at 223 °C, since Li-N-H system was investigated as hydrogen storage material in 2002. -*+

Lithium metatitanate (Li_2TiO_3) is a technologically important material with many practical applications. For example, it has been used as a double layer cathode material in molten carbonate fuel cells[1], and as an electrode material in lithium-ion batteries[2, 3]. In the area of lithium-ion batteries, Li_2TiO_3 usually combines with $LiMO_2$ (M=Fe, Mn, Cr, Ni) to create a solid-solution, with formulas $xLiMO_2$-(1-x)Li_2TiO_3. This has been reported to be able to stabilize the structure of high-capacity cathode materials.[4-7] As a solid breeder material in the blanket of fusion reactors[8], Li_2TiO_3 is the most preferred material for test blanket module for its attractive characteristics, such as high thermal stability, high lithium density, and tritium recovery at low temperature compared to lithium zirconates (Li_2ZrO_3) and lithium-silicate (Li_2SiO_3).[9-11] Because of its many important applications, the mechanical and thermal properties of Li_2TiO_3 have been well investigated.

Recently, the detailed diffusion pathways of lithium in the bulk and the occupancy of lithium in the lattice as well as the effects of the defects have been investigated by Vijayakumar et al.[12] The detailed lithium diffusion properties of Li_2TiO_3 has been measured by nuclear magnetic resonance (NMR) and simulated by the method of potential-based molecular dynamics. It is reported that lithium conduction in monoclinic Li_2TiO_3 is three-dimensional which can provide suitable nearby vacancies. Li_2TiO_3 has been extensively investigated due to its many important applications. Herein, we want to introduce Li_2TiO_3 in another area as catalyst because of its structural characteristics.

Titanium compounds have been doped as catalyst in hydrogen storage materials in 1997. Bogdanović and Schwickardi[13] have reported that $NaAlH_4$ can be used as a solid reversible hydrogen storage material after doping Ti(Obutyl)$_4$. Interest in using complex metal hydrides as hydrogen storage materials is dramatically reawakened after that.[14] One of the most frequently used catalysts is $TiCl_3$. The active catalytic species is produced during high-energy ball-milling[14-17,] which is highly dispersed within the materials. This is indicated that Ti worked effectively for the solid-state hydrogen materials. Meanwhile, since the first time report by Chen et al.[18] in 2002, Li-N-H systems have been investigated in terms of their reversibility and relatively high H_2 storage capacity. Theoretically, a large amount (6.5 wt%, this value is on the basis of materials' reaction during experimental condition, not base on tank system.) of hydrogen is accessible in this reaction. Hydrogen can be desorbed through the following solid-solid reaction [Eq.(1)]:

$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$ (1)

However, the system is still limited for practical applications because a high desorption temperature is required and the reaction suffers from slow kinetics. Furthermore, NH_3 is a subsidiary product in the dehydrogenation process according to Equation (2). The main reason is due to $LiNH_2$ decompose at higher temperature.

$2LiNH_2 \rightarrow Li_2NH + NH_3$ (2)

Considering of previous study[19-21], lithium diffusion plays an important role in this solid-solid reaction. The kinetics of this reaction is therefore greatly dependent on the crystal structure and its defects. The mobility of lithium ions can be enhanced during temperature increasing.[22] In this study, we want to introduce the structural characteristics of Li_2TiO_3 into the lithium-nitrogen -hydrogen system, which could help improve the kinetics of reaction. We present results from X-ray diffraction (XRD) and thermogravimetry differential-thermal-analysis thermal gas desorption mass spectrometry (TD-DTA-TDMS) by using Li_2TiO_3 as a catalyst in Li-N-H system.

$LiNH_2$ (95 %), LiH (95 %), $LiCO_3$ (99.997 %), and TiO_2 (99 %) were purchased from Sigma-Aldrich. Single phase Li_2TiO_3 was synthesized by a solid-state reaction.[23] See Equations (3):

$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2$ (3)

Typically, to ensure homogeneous mixing between the starting materials and the additive, $LiNH_2$ and LiH powders (300mg, 1: 1.1 molar ratio) and Li_2TiO_3 (1 mol %) were ball-milled for 2 h (Fritsch P7). Moreover, different molar ratios of Li_2TiO_3 (1 mol%, 2 mol% and 5 mol %) were doped into the mixtures. During high-energy ball-milling process, samples were milled at 400 rpm for 2 h under a hydrogen gas (99.9999 % purity) pressure of 1 MPa at room temperature. The milling was interrupted every 30 min for 15 min to prevent frictional heat during the milling process.

After that, the samples were measured by TG-DTA (Hitachi Bruker TAPS3000S) combined with TDMS upon heating to 400 °C with a heating rate of 5 °Cmin^{-1}. TG-DTA equipment was installed in glovebox to avoid exposing the sample to air during the measurements. Furthermore, the structure properties were characterized by XRD measurements.

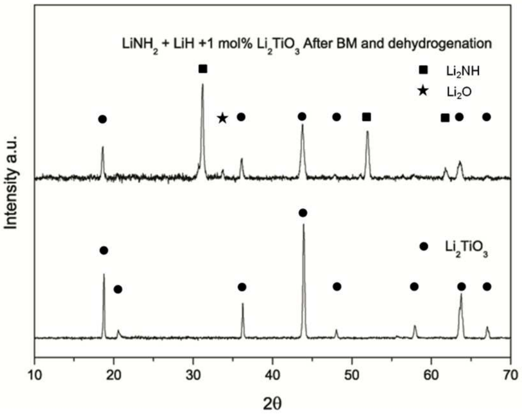

Figure 1. XRD patterns for the single phase of Li_2TiO_3 and $LiNH_2$ + LiH with 1mol % Li_2TiO_3 ball-milled for 2 h after TG measurement up to 400 °C.

Li_2TiO_3 was synthesized by sintering a mixture of Li_2CO_3 and TiO_2 at 700 °C. The powder XRD profile is shown in Figure 1. XRD pattern presented no apparent impurities in the product of single phase of Li_2TiO_3. The color of this single phase was off-white, which is consistent with previous report.[24] The stability of Li_2TiO_3 is also reflected by the XRD patterns in Figure 1. After high-energy ball-milling and dehydrogenation, the structure of Li_2TiO_3 was the same as that of the single phase of raw Li_2TiO_3. This indicates that the Li_2TiO_3 in the cycled sample essentially remains in the same state.

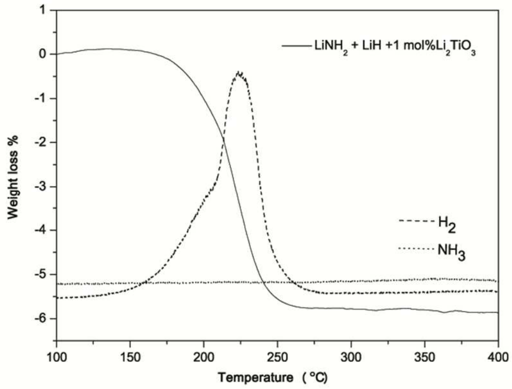

Figure 2. TDMS and corresponding TG results for the $LiNH_2$ + LiH mixture ball milled for 2 h with 1 mol % Li_2TiO_3 during dehydrogenation.

In order to clarify the thermal desorption properties of the mixture with additive, the desorption gas and weight loss was studied by TG-DTA-TDMS equipment. The TDMS result from sample with catalyst is shown in Figure 2. The LiH + $LiNH_2$ composite with additive showed only a sharp H_2 peak. The peak temperature was at 223 °C. No NH_3 was detected by TDMS. Comparing to the sample without catalyst which released H_2 and NH_3 at higher temperature[20], it clearly demonstrates that doping Li_2TiO_3 had an effect on the whole system (The results of sample without catalyst is shown in ref 20). Furthermore, the doping of Li_2TiO_3 led to full desorption within the temperature range from 150 to 260 °C. Compared with other famous catalyst, such as $TiCl_3$, $LiTi_2O_4$ (as shown in Figure 3), Ti^{Nano}, TiO_2 (as shown in ref 25), BN and TiN (as shown in ref 26), the peak temperature of DTA is the lowest (223 °C) among these catalysts. Accordingly, the lower dehydrogenation temperature implied that the properties of desorption could be enhanced greatly by doping Li_2TiO_3 as catalyst. The temperature of reaction range is also the shortest (150~260 °C), compared with $TiCl_3$ (150~300 °C) and $LiTi_2O_4$ (150~310 °C). From the above results, it can be concluded that Li_2TiO_3 has the highest catalytic efficiency in Li-N-H system. It is first time to decrease the end temperature to 260 °C since the system is first reported by Chen et al.[18]

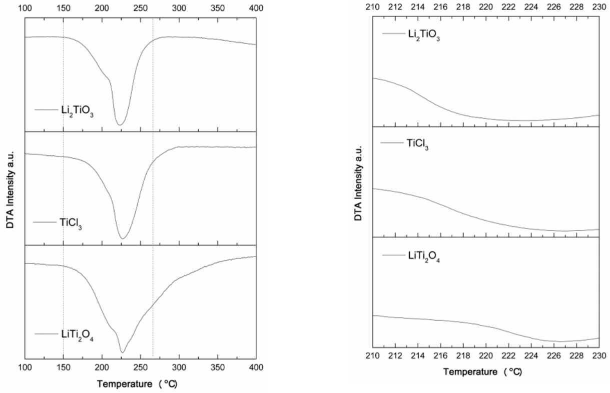

Figure 3. DTA results for the dehydrogenation of samples: $LiNH_2$ + LiH + 1 mol % Li_2TiO_3; $LiNH_2$ + LiH + 1 mol % $TiCl_3$; $LiNH_2$ + LiH + 0.5 mol % $LiTi_2O_4$ (left figure). Detail parts of peak temperature (right figure).

Different amounts of Li_2TiO_3 were doped into the mixtures to illustrate the appropriate amount of Li_2TiO_3 in the system (Figure 4). According to the TG-DTA data, the peak temperature for H_2 desorption of a 1 mol % doped Li_2TiO_3 sample was the same as that of a 2 mol % doped Li_2TiO_3 sample and a 5 mol % doped Li_2TiO_3 sample, that is, 223 °C. The DTA curves of both samples were similar to each other. The experiment weight loss for the 1, 2 and 5 mol% doped Li_2TiO_3 samples was 5.8 wt%, 5.1 wt% and 4.4 wt % (these values were based on reaction of materials during experimental condition), respectively. A minor impurity of the starting material, such as Li_2O, could explain the lower experimental hydrogen-storage-capacity than theoretical value. In accordance with these results, it indicates that there is no simple linear correlation between the catalytic effect and the amount of catalyst. The appropriate amount of Li_2TiO_3 should be 1 mol % considering of the higher storage capacity.

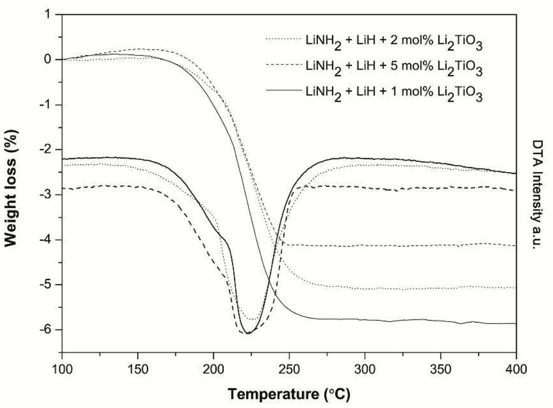

Figure 4. Corresponding TG and DTA results for the mixtures milled for 2 h with different amounts of Li_2TiO_3 as an additive.

In order to clarify the catalytic effect on hydrogenation process, the reversibility, recyclability, and the hydrogenation rate have been investigated. The addition effect of Li_2TiO_3 on hydrogen absorption has been examined by a series of experiments. The dehydrogenated samples were hydrogenated at the same temperature (200 °C) and hydrogen pressure (1 MPa) for 10 min, 100 min, 200 min, and 500 min, respectively. Figure 5 shows the corresponding hydrogen-uptake amount for samples from the extent of reaction. The hydrogenation rate of the samples with/without Li_2TiO_3 addition was shown in Table 1(The result of sample without catalyst is shown in ref 27). The hydrogenation rate of the sample with Li_2TiO_3 addition is obviously higher than that of the reference sample by 4.8 times for 10 min, 2.5 times for 100 min, and 2.0 times for 200 min hydrogenation, respectively.

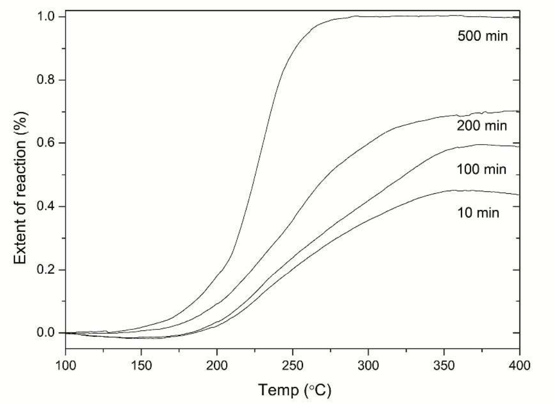

Figure 5. Extent of reaction after the samples with Li_2TiO_3 addition rehydrogenated at 200 °C, 1MPa H_2 for 10 min, 100 min, 200 min, and 500 min, respectively.

Temperature and pressure		200 °C, 1 MPa H_2		
Hydrogenation Time (min)		10	100	200
Hydrogenation Rate (%)	w/o catalyst	9	23	34
	w/ catalyst	44	59	70

Table 1. The catalytic effect of hydrogenation is showed from the hydrogenation ratio.

Furthermore, the recyclability and durability of the catalytic effect of Li_2TiO_3 was examined by 10-cycle test (Figure 6). The weight loss (5.8 %) and peak temperature (223 °C) are the same as the 1st cycle. From these results, it is evident that the catalyst not only had effect on dehydrogenation process, but also on the hydrogenation process.

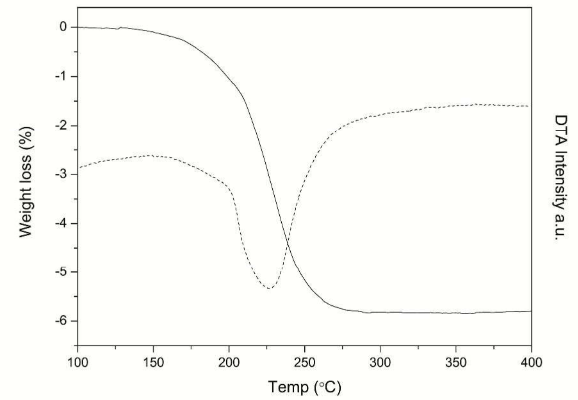

Figure 6. Corresponding weight loss of $LiNH_2$ + LiH + 1 mol% Li_2TiO_3 mixture de/hydrogenated for 10-cycle (solid line) and differential thermal analysis (dash line).

On the basis of the above results, it can be concluded that Li_2TiO_3 can effectively catalyze the solid-solid reaction between LiH and $LiNH_2$ upon de/hydrogenation. In order to understand the catalytic mechanism of Li_2TiO_3 in the Li-N-H system, some investigations were performed. During temperature increasing in dehydrogenation, the thermal vibration of ion become more active, and the density of vacancy become higher. In this case, the lithium-ion mobility could be increased. Some of the authors have proposed in their reports that the solid-solid reaction between LiH and $LiNH_2$ based on Li^+ migration across reactive interfaces between the LiH particles and the $LiNH_2$ particles in high temperature dehydrogenation.[19, 20, 28] In the present study, Li_2TiO_3 was experimentally doping into Li-N-H system. According to the structural characteristics of Li_2TiO_3 (Figure 7), a nonstoichiometric Li_2TiO_3 can cause lithium vacancies in both the $LiTi_2$ layers and the pure Li, lithium diffusion should happen in the xy plane and along the z axis. Lithium mobility in monoclinic Li_2TiO_3 is three-dimensional which could provide suitable nearby vacancies during temperature increasing in dehydrogenation. [12] The doping Li_2TiO_3 with vacancies was around by solid particles, such as $LiNH_2$ and LiH. These vacancies help destabilize the stability of lithium-ions in the crystal-lattice of $LiNH_2$ and LiH which could increase the mobility of lithium-ions and make the reaction happen at lower temperature. Furthermore, the improvement in the kinetics could lead to consume $LiNH_2$, and therefore, the emission of ammonia at high temperatures could be restricted.

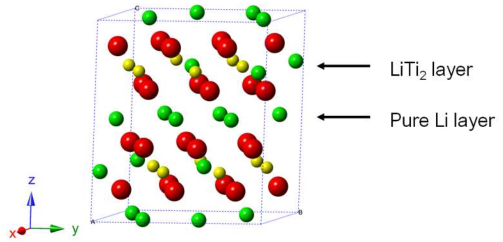

Figure 7. The crystal structure of monoclinic $LiTi_2O_3$ (as reported in ref 29). Lithium atoms are shown in green, oxygen atoms in red, and titanium atoms in yellow.

Conclusions

In summary, we have reported the discovery of Li_2TiO_3 as a catalyst in a solid-solid reaction for hydrogen storage materials for the first time. The catalytic effect, appropriate amount and stability of Li_2TiO_3 in the system were confirmed by the results of TG-DTA-MASS and XRD. Since the Li-N-H system was investigated as hydrogen storage material in 2002, it is first time to decrease the end temperature under 260 °C and the lowest peak temperature was occurred at 223 °C. A storage capacity of 5.8 wt % H_2 was obtained during dehydrogenation. Meanwhile, the catalytic effect on hydrogenation process has also been investigated. The catalytic effect of Li_2TiO_3 probably results from an increase in the mobility of the lithium-ions between the $LiNH_2$ and LiH solid phases. The results presented here are the first to appear in the literature. It is hoped that they will be helpful in achieving deeper insight into metal oxide nanoparticles catalyzed solid-solid reaction for hydrogen storage.

Notes and references

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