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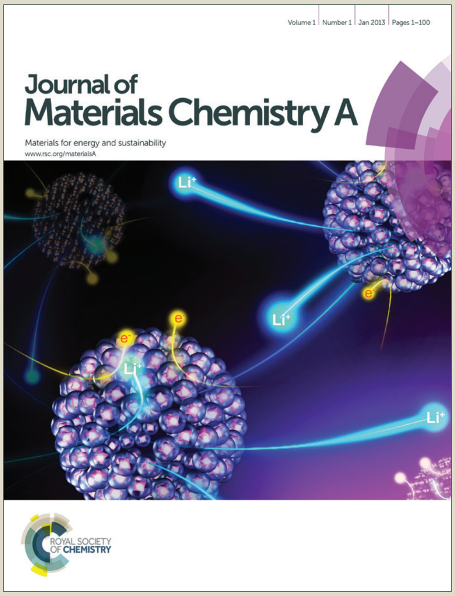

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A metal-oxide catalyst enhanced the desorption properties in complex metal hydrides

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In this study, $LiTi_2O_4$ was synthesized as a possible catalyst in the complex metal hydrides. $LiTi_2O_4$ was stable in the sample after high-energy ball milling and heat treatment. $LiTi_2O_4$ exhibited a catalytic effect among the samples of MgH_2, $LiAlH_4$ and $LiNH_2$. The desorption kinetics and the purity of the desorbed hydrogen gas have been improved by doping $LiTi_2O_4$. Furthermore, the catalytic mechanism of $LiTi_2O_4$ was discussed in accordance with the experimental results.

1. Introduction

Hydrogen is a kind of independent carrier compared to conventional ones such as fossil fuels. It accompanies following advantages such as clean, environmental friendliness and forming water as a non-polluting product during practical application.[1] Accordingly, reductions of dependence on fossil fuels and emissions of pollutants and greenhouse gases could be realized after using hydrogen as a primary fuel successfully. This would have a great influence on both changing energy structure and improving global warming. Recently hydrogen energy has been investigated actively in terms of production, storage and application (comprising combustion engines in vehicles and power application).[2] Nowadays compressed gaseous hydrogen is used in prototype and liquid form in advanced tank systems.[3] However, storing hydrogen in solid-state materials has definite advantages on accessible hydrogen content and energy efficiency compared to complex system which using high-pressure gas or cryogenic liquid. A series of storage materials have been proposed, such as metal-hydrides, alanates and amides. While the hydrogen capacity of complex metal hydrides is reasonable (often in the 3-12 wt. % range), relatively high thermal stability, slow kinetics of the pure hydrides, undesirable by-product gases (e.g. ammonia) and irreversibility on cycling are still limitations for on-board applications.[4]

Extensive efforts are currently being made to approach for the improvement of hydrogen storage properties on improving the absorption/desorption kinetics, reducing the operating temperatures and improving the purity of the desorbed hydrogen gas.[5] One of strategies for the improvement of the hydrogen storage properties is addition of catalyst. Ti compounds have been well known to catalyze the dehydrogenation of complex aluminium hydrides in solution. Wieberg et al. firstly in 1951 observed Ti catalysed the dehydrogenation of $LiAlH_4$ in a diethyl ether suspension.[6] A breakthrough came when Bogdanović and Schwickardi certificated that doping a few mol % Ti in the complex metal hydride $NaAlH_4$ lowered the dehydrogenation temperature, improved the kinetics and allowed rehydrogenation of the decomposition products.[7] This is indication that Ti worked effectively for the solid-state $NaAlH_4$. Interest in using complex metal hydrides as hydrogen storage materials is dramatically reawakened. Meanwhile, the catalytic effect of Ti compound was also found in $LiH/LiNH_2$ system which could be reversibility and have a high hydrogen capacity of 6.5 wt %.[8] The absorption/desorption kinetics and the purity of the desorbed hydrogen gas had been improved. Among the system of metal hydrides, MgH_2 exhibits a high hydrogen capacity up to 7.6 wt %. However, the absorption and desoption reaction of Mg/MgH_2 itself is too slow. Barkhordarian et al. reported that Ti compounds had a catalytic effect for the absorption and desorption.[9-11] Subsequently, Hanada et al. reported the valence state of the Ti compounds which doped in MgH_2.[12] However, the catalyst state of Ti compound is not as same as the original after ball-milling and/or heat treatment. [12, 13] In this case, the mechanism of catalytic effect is difficult to understand clearly due to the instability of Ti compounds.

Normally, the reactions which occur between solid phases for complex metal hydrides are solid-state reaction. Diffusion plays an important role in solid-state reactions since they require the coming together of reactive species. The rigid structure makes solids different from liquids and gases. The kinetics of solid-state reactions is therefore greatly dependent on the crystal structure and its defects. Based on these results, one proposal for improving the kinetics of solid-state reaction is increasing the mobility of ions, such as Li^+, Na^+ and H^- in the complex metal hydrides. This process would progress by doping catalyst, especially Ti compounds. Our previous study suggested that, $LiTi_2O_4$ was discovered by transmission electron microscope (TEM) in the Li-N-H sample which doped $TiCl_3$ as the catalyst.[13] The catalytic Ti compounds were active at the interface between LiH and $LiNH_2$. Herein, we choose $LiTi_2O_4$ as the catalyst for hydrogen storage materials in lithium alanate, magnesium hydride and lithium amides. As the result of their investigation, hydrogen can be desorbed via the following reaction:

$LiAlH_4 \leftrightarrow LiH + Al + 3/2H_2$ (1)
$MgH_2 \leftrightarrow Mg + H_2$ (2)
$LiH + LiNH_2 \leftrightarrow Li_2NH + H_2$ (3)

For the case of $LiAlH_4$, the equation (1) can be recast as a two step reaction as the following reaction:

$LiAlH_4 \rightarrow 1/3\ Li_3AlH_6 + 2/3\ Al + H_2$ (4)
$1/3\ Li_3AlH_6 \rightarrow LiH + 1/3\ Al + 1/2\ H_2$ (5)

Consequently, the catalytic effect of $LiTi_2O_4$ will be discovered for samples with the aim of enhancing hydrogen desorption properties in this study.

2. Experimental

2.1 Sample preparation

The powder of $LiAlH_4$ (95 %), Li_2CO_3 (99.997%), TiO_2 (99%), Ti_2O_3 (99.9%), LiH (95%) and $LiNH_2$ (95%) were purchased from Sigma-Aldrich. MgH_2 (98%) powder was purchased from Alfa Aesar. The single phase of $LiTi_2O_4$ was synthesized by a two-step solid-state reaction. $Li_2Ti_2O_5$ will form as an intermediate compound.[14] The reaction equations used here are:

$Li_2CO_3 + 2TiO_2 \rightarrow Li_2Ti_2O_5 + CO_2$ (6)

$Li_2Ti_2O_5 + Ti_2O_3 \rightarrow 2LiTi_2O_4$ (7)

The synthesis method of $LiTi_2O_4$ is according to Xu et al. introduced before.[15] Considering the volatility of Li, it was hard to get the exact composition of Li. Here the excess molar fraction 0.15 of Li_2CO_3 is added in equation (6) for $LiTi_2O_4$. An additional factor is sensitivity of $LiTi_2O_4$ to air. This issue was mentioned by several groups, [16-18] regardless of the preparation method used. The aging reaction is the topotactic oxidation of $LiTi_2O_4$. $LiTi_2O_4$ reacts with oxygen or H_2O in air and is progressively transformed into $Li_{1-x}Ti_2O_4$ ($0 \leq x \leq 0.8$). The polycrystalline sample is stored in Ar atmosphere in order to avoid the aging reaction with oxygen and moisture.

Typically, in order to ensure a homogeneous mixing between the starting materials and the additive, a ball-milling equipment (Fritsch P7) was used. Samples of $LiAlH_4$ and 0.5 mol % $LiTi_2O_4$ were milled for 2 h. The samples, mixtures of MgH_2 and 1 mol % $LiTi_2O_4$, were milled for 20 h. $LiNH_2$ and LiH powders with 1: 1.2 molar ratio and 0.5 mol % $LiTi_2O_4$ were milled for 2 h. The total weight for each ball-milled sample was 300 mg. In the high energy ball-milling process, powder and 20 steel balls (SUJ-2) with a diameter of 7 mm were brought into a Cr steel pot (SKD-11) and milled at 400 rpm under a hydrogen gas (99.9999 % purity) pressure of 1 MPa at room temperature. The ball-to-powder ratio was 100:1. The milling was interrupted every 1 h for 30 min in order to prevent frictional heat during the milling process.

2.2 Characterization measurements

Structure properties were characterized by X-ray diffraction (XRD) measurement. Sample was firstly put on a glass plate in the glove box. Then the glass plate was covered with a plastic film to protect the sample from air contact. The plastic film does not have any obvious influence to the obtained XRD patterns. The samples measured with a diffraction 2θ angle from 10° to 90° under a speed of 0.04° per step. Furthermore, after the milling process, the mixtures were examined by Thermo gravimetry and differential thermal analysis (TG-DTA) equipment (HITACHI BRUKER TAPS3000S) combined with Thermal gas desorption mass spectrometry (TDMS). TG-DTA equipment was installed in another glove box to avoid exposing the sample to air in their measurements.

3. Results and Discussion

$LiTi_2O_4$ synthesized by sintering the mixture of $Li_2Ti_2O_5$ and Ti_2O_3 at 880 °C under the pressure less than 10^{-4} Pa. Figure 1 gave the powder X-ray diffraction (XRD) profile. There were no apparent impurities in the product of the single phase of $LiTi_2O_4$. The color of this single phase was black, which was consistent with the previous reports.[19] The stability of $LiTi_2O_4$ is reflected by the XRD patterns in Figure 2. Three kinds of samples after high-energy ball milling and dehydrogenation, the 0.5 mol % $LiTi_2O_4$ + 99.5 mol % $LiAlH_4$ mixture, the 1 mol % $LiTi_2O_4$ + 99 mol % MgH_2 mixture and the composite of LiH and $LiNH_2$ with 0.5 mol % $LiTi_2O_4$, were prepared for the XRD experiment. The results indicated that the structure of $LiTi_2O_4$ was as the same as the single phase of the raw $LiTi_2O_4$ after high-energy ball milling and dehydrogenation.

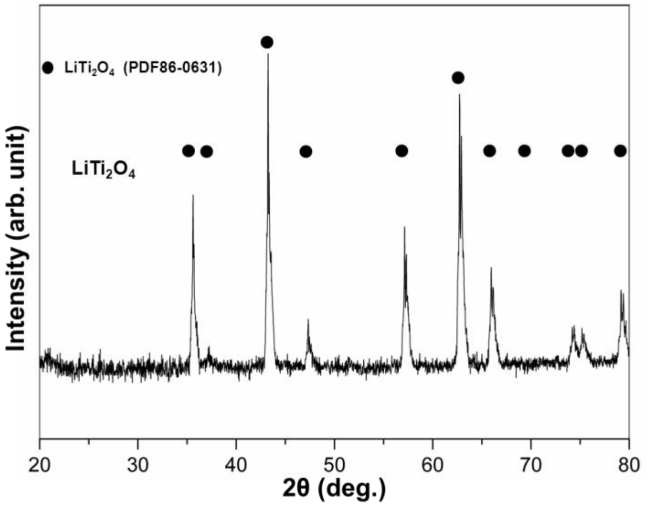

Figure 1. XRD pattern of the single phase of $LiTi_2O_4$.

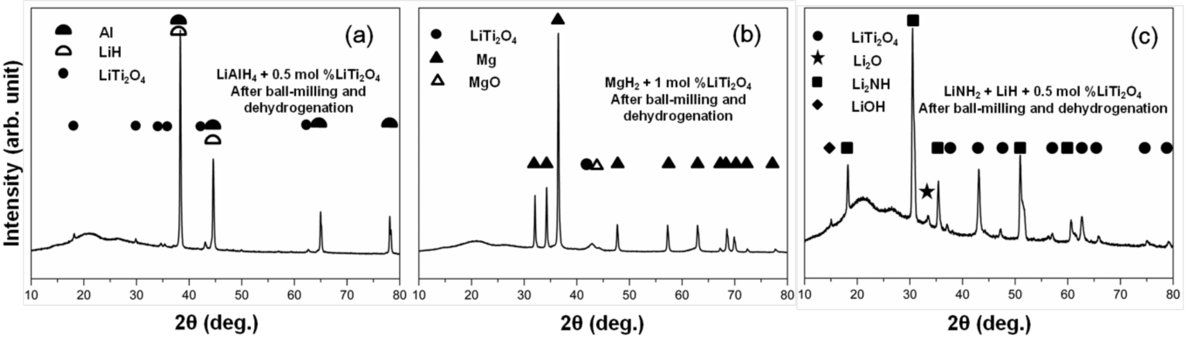

Figure 2. XRD pattern of the samples after high-energy ball milling and dehydrogenation: (a) the 0.5 mol % $LiTi_2O_4$ + 99.5 mol % $LiAlH_4$ mixture, (b) the 1 mol % $LiTi_2O_4$ + 99 mol % MgH_2 mixture, (c) the composite of LiH and $LiNH_2$ with 0.5 mol % $LiTi_2O_4$.

Figure 3 showed the thermo gravimetry and differential thermal analysis (TG-DTA) results of the as received $LiAlH_4$ and the 0.5 mol % $LiTi_2O_4$ + 99.5 mol % $LiAlH_4$ mixture. It could be confirmed that during the examined temperature range, dehydrogenation process showed rather different behavior from these two samples. In the case of the as received sample, two conspicuous peaks were around 165 – 180 °C. The endothermic peak (170 °C) was for the melting of $LiAlH_4$. After the endothermic peak, there was an exothermic peak (179.5 °C) that indicated the decomposition of liquid $LiAlH_4$. The reaction started at 160 °C and ended at 240 °C. The total amount of weight loss was 6.4 wt. %. In the case of the mixture sample, the hydrogen desorption started at 100 °C, and the whole decomposition of $LiAlH_4$ completed at around 220 °C. Two endothermic peaks could be seen from the DTA curve. The peak temperature of each peak was 160 °C and 210 °C. Accordingly, some of the authors have calculated in their reports that the enthalpy of the first dehydrogenation of $LiAlH_4$ with additive is in agreement with the enthalpy difference between the melting transition and the exothermic decomposition immediately following it for as received $LiAlH_4$.[20, 21, 22, 23] Consequently, the composite endothermic-exothermic peak at 170 – 180 °C in the sample without additive is in agreement with the absorption of latent heat of melting by $LiAlH_4$ with fast decomposition of the Li_3AlH_6 and desorption of H_2, and immediate releasing the latent heat of fusion Li_3AlH_6 with desorption of H_2. Hence, the first dehydrogenation of $LiAlH_4$ is intrinsically endothermic. Doping $LiAlH_4$ with $LiTi_2O_4$ improved its thermal decomposition, bringing this dehydrogenation below the melting point of $LiAlH_4$ and separating it from the complex melting-desorption-solidification event that appears at 170 °C for the undoped sample. This result indicated the $LiTi_2O_4$ has some catalytic effect on the lithium alanate.

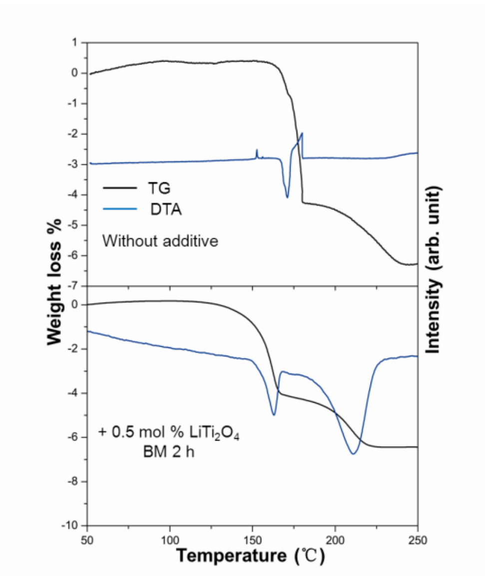

Figure 3. Differential thermal analysis and corresponding weight loss for the dehydrogenation of the as received $LiAlH_4$ and the 0.5 mol % $LiTi_2O_4$ + 99.5 mol % $LiAlH_4$ mixture.

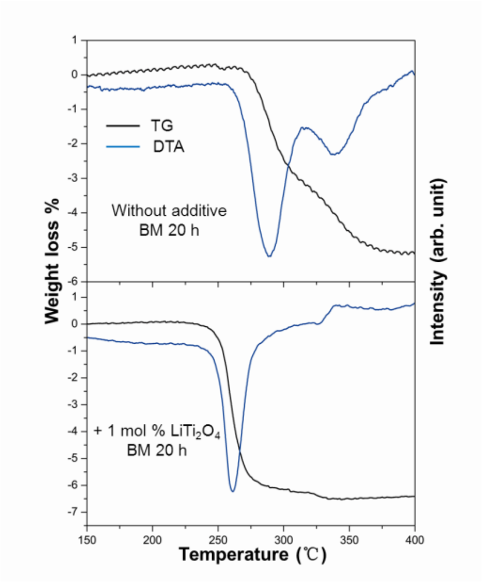

Figure 4. Differential thermal analysis and corresponding weight loss for the dehydrogenation of the milled MgH_2 and the 1 mol % $LiTi_2O_4$ + 99 mol % MgH_2 mixture.

The TG-DTA results of the milled MgH_2 and the 1 mol % $LiTi_2O_4$ + 99 mol % MgH_2 mixture were shown in Figure 4. There were two endothermic peaks for the milled MgH_2 sample during the measurement. Dehydrogenation started around 260 °C and ended at 380 °C. The peak temperature for each peak was 290 °C and 340 °C. The weight loss of 5.1 wt. % was much less than the theoretical value of 7.6 wt. %, which indicated an incomplete decomposition of the milled sample under the condition of heating up to 400 °C at a rate of 5 °C/min. For the sample with an additive the DTA curve showed that hydrogen desorption started at 220 °C and finished at 330 °C. There was only one main endothermic peak for the mixture sample during the measurements. The peak temperature was at 260 °C. The weight loss of 6.6 wt. % was achieved from the TG measurement compared with the theoretical value of 7.0 wt. %. The difference between the experimental value and the theoretical value was caused by the impurity in the original sample, such as MgO. The much better hydrogen desorption kinetics of the mixture sample was attributed to the catalytic effect of $LiTi_2O_4$. Recently, Nb_2O_5 doped MgH_2 has been studied actively. The sluggish sorption kinetics of MgH_2 can be improved dramatically to release 6 wt % of reversible hydrogen at 250 °C.[8, 24, 25] Hanada et al. informed that MgH_2 with 1 mol % Nb_2O_5 milled for 20 h, was able to release 4.5 wt % H_2.[26, 27] After $LiTi_2O_4$ firstly introduced to this system, the kinetics of MgH_2 has been accelerated at the same level compared with previous work.[27]

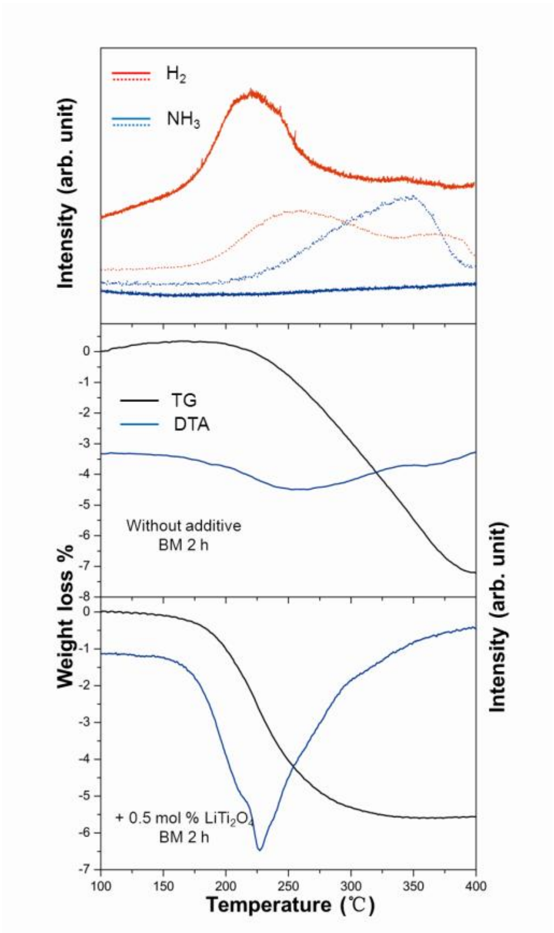

Figure 5. Mass spectra of gas desorption for the dehydrogenation of $LiNH_2$ + LiH mixture without any additive (Dot line) and with 0.5 mol % $LiTi_2O_4$ (Solid line); corresponding weight loss and differential thermal analysis for each sample.

The dehydrogenation process of the composite of LiH and $LiNH_2$ with 0.5 mol % $LiTi_2O_4$ additive was investigated. Figure 5 presented the TDMS result. The sample of LiH and $LiNH_2$ with $LiTi_2O_4$ addition showed a sharp H_2 peak. The peak temperature was at 227 °C. No ammonia was detected during dehydrogenation. To the best of our knowledge, addition of $LiTi_2O_4$ to the system as a catalyst resulted in the lowest desorption temperature observed so far, compared with the well known catalysts (BN, Si, $TiCl_3$).[28] However, hydrogen and ammonia released from the sample without $LiTi_2O_4$. The broad hydrogen desorption curves and obvious ammonia emission can be seen in the temperature range from 200 °C to 400 °C. The results demonstrated clearly that the purity of the desorbed hydrogen gas was improved after doping $LiTi_2O_4$. During heating, the decomposition of the $LiNH_2$ + LiH mixture was observed to start at 200 °C and complete at 400 °C. By contrast, the addition of $LiTi_2O_4$ led to full desorption within the temperature range of 150-310 °C. The total weight loss for $LiNH_2$ + LiH + 0.5 mol % $LiTi_2O_4$ was 5.7 wt. % instead of the 7.5 wt. % for $LiNH_2$ + LiH. Accordingly, a lower dehydrogenation temperature indicated that desorption properties can be improved greatly by adding $LiTi_2O_4$ as the catalyst.

On the basis of these experimental results, it can be figured out that $LiTi_2O_4$ worked catalytically for the reaction among lithium alanate, magnesium hydride and lithium amides on hydrogen desorption. As far as the catalytic mechanism of a Ti compound is concerned, some investigations have been performed. For the situations of lithium alanate and magnesium hydride, the explanation of how Ti compound might work as a catalyst is to destabilize the Metal-H bonds of the complex metal hydrides, such as the bonding between Mg-H or Al-H. Sandrock et al. suggested the Ti compound aided the "breaking and re-forming of covalent Metal-H bonds".[29] Subsequently, starting from 2005, a series of researchers have investigated similar ideas.[30-35] Additionally, Seong Mu Jo certificated that $LiTi_2O_4$ nanofiber could absorb/desorb hydrogen at ambient temperature.[36] That means $LiTi_2O_4$ could probably have a similarly effect on helping weak the Metal-H bond, and suggesting increasing lability of the hydride. The catalytic effect is generated by nanocontact between sample and the $LiTi_2O_4$ in the mechanical milling process.

For the case of lithium-nitrogen-hydrogen system, David et al. proposed in their report that the reaction mechanism based on Li^+ migration across reactive interfaces between LiH and $LiNH_2$.[37] Additionally, our previous results revealed that the catalytic effect is generated by nanocontact between sample and the Ti compound in the interface.[13] In the present studies, $LiTi_2O_4$ has been experimentally proved to have a catalytic effect on the Li-N-H system. The catalytic mechanism might be related to the crystal structure of $LiTi_2O_4$. $LiTi_2O_4$ is a kind of spinel-structures, where Li^+ ions could go through into/out $LiTi_2O_4$ without high energy barriers at ambient temperature.[38] Because of these characteristics of crystal structure, $LiTi_2O_4$ has a high diffusion rate of Li^+ which reported to be 10^{-8} cm^2/sec.[39] All of these could help increase the Li^+ ions mobility in the Li-N-H system. Accordingly, the catalytic effect of $LiTi_2O_4$ probably results from the increasing of the Li^+ ions mobility to improve the reaction kinetics. Meanwhile, the betterment of desorption kinetics could lead to the consumption of $LiNH_2$ and therefore the ammonia emission at high temperature could be restricted.

4. Conclusions

In conclusion, we were able to perform a study on the catalytic effect of $LiTi_2O_4$ in complex metal hydrides, such as magnesium hydride, lithium alanate and lithium amide. The purity and stability of $LiTi_2O_4$ were certificated by XRD results. $LiTi_2O_4$ was stable after high energy ball milling and heat treatment. After adding $LiTi_2O_4$, the dehydrogenation temperature was decreased effectively among the three kinds of materials. The desorption kinetics and the purity of the desorbed hydrogen gas have been improved by doping $LiTi_2O_4$. The catalytic mechanism for complex metal hydrides was also discussed in this study. The results here are the first time to appear in the literature. It is hoped that they are helpful for hydrogen storage materials as well as fuel cell industries.

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Notes and references

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† Electronic Supplementary Information (ESI) available: General experimental procedures, and instrumentations, and characterization are available in the supplementary information. See DOI: 10.1039/c000000x/

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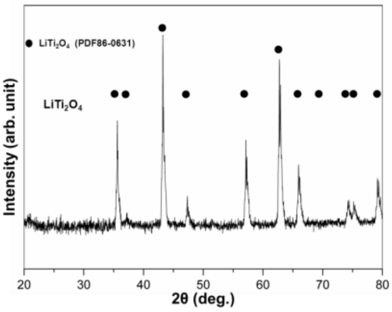

It is the first time that the desorption properties in complex metal hydrides (MgH_2, $LiAlH_4$, and $LiNH_2$) is enhanced by a kind of lithium-ion-battery materials, $LiTi_2O_4$. Three different systems for hydrogen storage are catalysed by one material.