Effect of Ti catalyst with different chemical form on Li–N–H hydrogen storage properties

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Abstract

The effect of some different type Ti additives on kinetics of the reaction, $LiH + LiNH_2 \leftrightarrow Li_2NH + H_2$, was intensively investigated in this work. The mixture of LiH and $LiNH_2$ powders with the 1:1 molar ratio and Ti additives with different chemical form were mechanically ball milled under a hydrogen gas atmosphere of 1 MPa at 400 rpm for 2 h and the measurements of thermal hydrogen desorption spectrum (TDS), thermogravimetry (TG) and X-ray diffraction (XRD) were performed. Here, we used Ti (nano particle), Ti (micro particle), $TiCl_3$, TiO_2 (nano particle) and TiO_2 (micro particle) as the additives. The results indicated that the Ti^{nano}, $TiCl_3$ and TiO_2^{nano} doped composites revealed a superior catalytic effect on the TDS properties, while the Ti^{micro} and TiO_2^{micro} did not show so good catalytic effect being similar to the sample without any additives. In the XRD profiles, there are traces of Ti and TiO_2 phases in the Ti^{micro} and TiO_2^{micro} doped composites, respectively, whereas no trace of Ti, $TiCl_3$ and TiO_2 was found in the Ti^{nano}, $TiCl_3$ and TiO_2^{nano} doped composites. These results indicate that the uniform distribution of nano particle Ti metal between LiH and $LiNH_2$ plays an important role for catalytic effect.
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1. Introduction

Hydrogen energy systems have been proposed as a means of energy independence from fossil fuels, which can reduce greenhouse gas and other harmful emissions from stationary and mobile sources. For realizing hydrogen energy systems in the near future, we have to establish the energy storage and transportation technologies. One of the key technologies is to develop high-performance hydrogen storage materials [1–18]. So far, we have studied Mg-based metal hydrides [19–21] and carbon-related material systems [22–24] with high-capacity absorbing hydrogen to improve the hydrogen storage properties.

Since Chen et al.'s report [25], lithium–nitrogen–hydrogen (Li–N–H) compounds have been paid much attention for one of the new hydrogen storage systems [28,29]. Lithium nitrides can absorb/desorb a large amount of hydrogen in the two consecutive reactions (1) as follows:

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH. \tag{1}$$
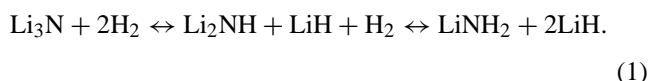
Theoretically, a large amount (10.4 wt.%) of reversible hydrogen $(2H_2/(Li_3N + 2H_2))$ is accessible in these two reactions. However, it should be noted that the original reactions (1) had been discovered at the beginning of 20th century [26,27]. Recently, we chose $LiNH_2$ and LiH as starting materials and have investigated its hydrogenating/dehydrogenating properties [28,29], paying attention to the following reaction,

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH \tag{2}$$

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The reason is because the reaction (2) can more easily absorb/desorb 6.5 wt.% of hydrogen due to the smaller enthalpy change ΔH. We have already reported that some catalysts, especially $TiCl_3$, were effective for improving H storage properties on this system. In this paper, we examined the effect of some different type Ti-based additives on the kinetics of the reaction (2) in detail.

2. Experimental

The starting materials, LiH and $LiNH_2$ with 95% purity, were purchased from Sigma–Aldrich and from Strem Chemicals, respectively. We used Ti^{nano} with smaller than one nanometer particle size, Ti^{micro} (Rare Metallic, 99.9% purity) with several ten to hundred micrometer particle size, $TiCl_3$ (Sigma–Aldrich, 99.999% purity) with micron meter size, TiO_2^{micro} (Sigma–Aldrich, 99.999% purity) and TiO_2^{nano} (Millennium, 82.8% purity) with a specific surface area of $\sim 180\, m^2/g$ as the dry additives. The synthesis and properties of Ti^{nano} have been described in ref. [30]. According to the EXAFS measurements, the colloidal Ti particles are two-shell clusters of only 13 Ti atoms which are stabilized by ligands of the solvent tetrahydrofuran (THF). The formal composition of the colloid is Ti–0.5 THF, the particle size is less than 1 nm.

In order to mix starting materials and the additive homogeneously, we used ball milling (Fritsch P7). All the samples were handled in a glovebox filled with purified argon to minimize contact with oxygen and water. Three hundred milligrams of $LiNH_2$ and LiH powders with 1:1 molar ratio and 1 mol% additive were mixed for 2 h by ball milling. In the milling process, the powders and 20 pieces of steel balls with a diameter of 7 mm were brought into a Cr steel pot and milled at 400 rpm under a hydrogen gas (99.9999% purity) pressure of 1 MPa at room temperature.

After homogenizing the mixed powders by the above methods, the composites were examined by thermal desorption mass spectroscopy (TDS) (Anelva M-QA200TS) combined with thermogravimetry (TG) (Rigaku TG8120) upon heating up to 450 °C with a heating rate of 5 °C/min. This equipment was especially designed and built up for using it inside the glovebox filled with purified argon, which permitted simultaneous measurements by TG and TDS without exposing the samples to air. We examined the structural characters of the produced composites by X-ray diffraction (XRD) measurements (Rigaku RINT2000, Cu Kα).

3. Results and discussion

Fig. 1 shows the TDS profiles for the hydrogen and ammonia gases from each composite prepared by planetary ball milling of the mixture of LiH, $LiNH_2$ and several kinds of additives for 2 h under a 1.0 MPa hydrogen gas atmosphere. We can see a broad shaped hydrogen desorption curve (with a
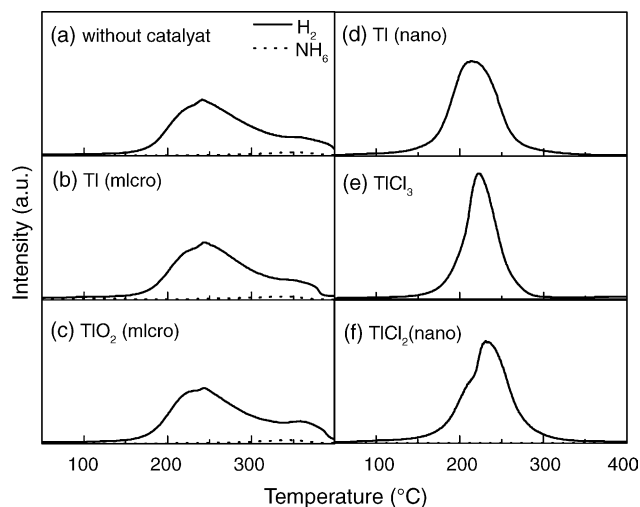

Fig. 1. The TDS profiles for hydrogen and ammonia gas from each sample made of LiH, $LiNH_2$ and additive: (a) none, (b) Ti^{micro}, (c) TiO_2^{micro}, (d) Ti^{nano}, (e) $TiCl_3$ and (f) TiO_2^{nano}, heating rate 5 °C/min.

peak temperature $T_p = \sim 250$ °C) in the TDS profiles for the samples doped with no additives (a), Ti^{micro} (b) and TiO_2^{micro} (c), in which a small amount of ammonia emission was detected around 330 °C. These results indicate that the additives Ti^{micro} and TiO_2^{micro} do not act as a suitable catalyst, judging from the fact that they showed almost the same TDS profiles as the composite without any additives. On the other hand, the composites doped with Ti^{nano} (d), $TiCl_3$ (e) and TiO_2^{nano} (f) exhibited sharp hydrogen desorption peaks with $T_p = \sim 220$ °C as is shown in Fig. 1 and no ammonia emission could be detected within our experimental accuracy. These results indicate that Ti^{nano}, $TiCl_3$ and TiO_2^{nano} effectively act as a good catalyst on the reaction of hydrogen desorption. Therefore, we suggest that the particle size of the precursor may be one of the important factors for acting as effective catalyst. A similar effect has been also observed with other complex hydrides [30].

For all of the above composites, we examined the structural properties by XRD analysis which is shown in Fig. 2. First of all, we notice that the $LiNH_2$ and LiH phases are identified in all the XRD profiles. It should be noted that the reflection peaks corresponding to Ti and TiO_2 are observable in the XRD profiles for Ti^{micro} (b) and TiO_2^{micro} (c) doped composites, which exhibited worse hydrogen desorption properties as mentioned above. On the other hand, no trace of the Ti, $TiCl_3$ and TiO_2 phases was found in the XRD profiles for the composites including Ti^{nano} (d), $TiCl_3$ (e) or TiO_2^{nano} (f), which exhibited superior hydrogen desorption properties. These results suggest that Ti, $TiCl_3$ and TiO_2 are highly dispersed in the nanoscale and act as an effective catalyst on the reaction of hydrogen desorption.

Furthermore, we would mention impurity phases in the composites. We easily find trace of the LiOH phase in all the XRD profiles as shown in Fig. 2, which may be originated from moisture in air during the measurement of XRD.

Particularly, the trace of KBr phase is observed in the XRD profile of Ti^{nano} doped composite (d), where KBr was generated during the preparation of Ti nano particle. Although the other impurities are also present, we assume that KBr would not interfere with the H_2 desorption properties and the catalytic effect.

To understand why these additives act as excellent catalyst, we suppose that the reactions of LiH with $TiCl_3$ and TiO_2 proceed as follows:

$$3LiH + TiCl_3 \rightarrow 3LiCl + Ti + \frac{3}{2}H_2, \tag{3}$$

$$4LiH + TiO_2 \rightarrow 2Li_2O + Ti + 2H_2. \tag{4}$$
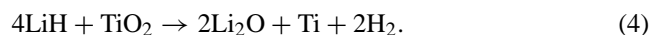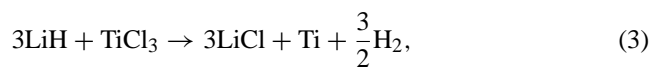
In principle, both the reactions should be possible to proceed during milling or heating as changes of the reaction enthalpy (3) and (4) are calculated to be -476 and $-117\,kJ/mol$ Ti, respectively. Moreover, an increase in entropy due to the release of molecular hydrogen is expected. If both the size of $TiCl_3$ and TiO_2 is of the nanometer order, the above reactions (3) and (4) would quickly proceed by milling treatment or heat treatment. Actually, there are no reflection peaks corresponding to $TiCl_3$ and TiO_2 in the XRD profiles although both the row materials showed clear diffraction peaks corresponding to themselves. Therefore, it seems likely that either the reflection peaks of the precursors are extensively broadened due to the Ti in the above composites is dispersed as Ti metal in nanometer scale or on the atomic level. However, the micrometer scaled TiO_2 might have too large surface potential to completely react with LiH during milling process. Thus, we guess that the Ti metal dispersed in the nanoscale should act as an effective catalyst on the Li–N–H hydrogen storage properties.
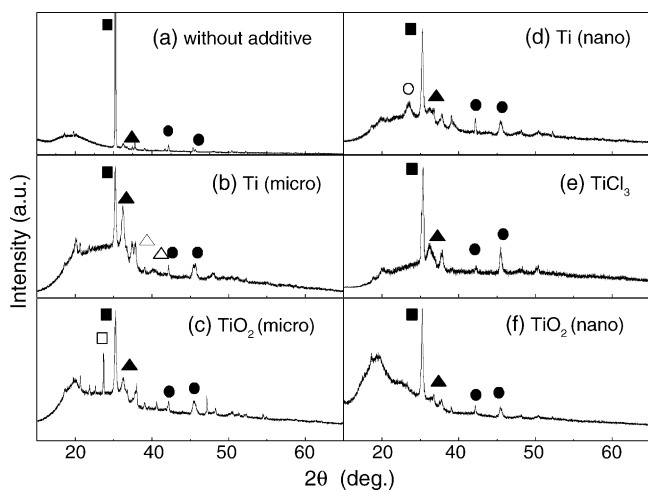

Fig. 2. The XRD profiles of each sample with: (a) no additive, (b) Ti^{micro}, (c) TiO_2^{micro}, (d) Ti^{nano}, (e) $TiCl_3$ and (f) TiO_2^{nano}, prepared by ball milling (($\blacksquare$) $LiNH_2$, ($\bullet$) LiH, ($\blacktriangle$) LiOH, ($\bigcirc$) KBr, ($\triangle$) Ti and ($\square$) TiO_2).

4. Conclusion

In this work, we investigated catalytic effect of some different type Ti additives on H storage properties for the Li–N–H system. The results indicated that the Ti^{nano}, $TiCl_3$ and TiO_2^{nano} doped composites revealed a superior catalytic effect on the TDS properties, while the Ti^{micro} and TiO_2^{micro} did not show so good catalytic effect being similar to the sample without additive. In the XRD profiles, there are traces of Ti and TiO_2 phases in the Ti^{micro} and TiO_2^{micro} doped composites, respectively, whereas no trace of Ti, $TiCl_3$ and TiO_2 was found in the Ti^{nano}, $TiCl_3$ and TiO_2^{nano} doped composites. From the above experimental results, we suggest that the additive particle size is the important factor for improving the kinetics of hydrogen storage, and metallic Ti highly dispersed on the samples in nanometer scale acts as an effective catalyst on the H storage properties for the Li–N–H hydrogen storage system. Particularly, TiO_2^{nano} should be better additive than any other Ti compounds because it has some advantages from the viewpoints of light weight, economical issue and easy treatment.

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