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Characterization of titanium based catalysts in the Li-N-H hydrogen storage system by X-ray absorption spectroscopy

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Abstract

A lithium-nitrogen-hydrogen (Li-N-H) system has been reported as one of the attractive hydrogen storage systems. So far, it was clarified that some catalysts, especially titanium-based compounds, were significantly effective for improving the hydrogen storage kinetics in the Li-N-H system. In this research, the chemical bonding states of the titanium compounds in the mixture of LiH and $LiNH_2$ were examined by X-ray absorption spectroscopy (XAS) as the characterization of the catalysts. The results of X-ray absorption near-edge structure (XANES) indicated that the Ti atoms in the titanium compounds, which revealed the catalytic effect on the hydrogen desorption (H-desorption) properties, had a common electronic (chemical bonding) state.

Keywords: Hydrogen absorbing materials; Solid state reactions; Catalysis; EXAFS; NEXAFS; SEXAFS

1. Introduction

Since in Chen et al's report [1], the Li-N-H compound has been paid much attention for one of the new hydrogen storage systems [2–11]. Lithium nitride absorbs and desorbs a large amount of hydrogen in the two consecutive reactions as follows:

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH. \quad (1)$$

Theoretically, a large amount (10.4 mass%) of hydrogen ($2H_2/(Li_3N+2H_2)$) is accessible in these two reactions. Ichikawa et al. chose $LiNH_2$ and LiH as starting materials and have investigated the hydrogenating and dehydrogenating properties of the mixture [2,4], focusing on the following reaction:

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH. \quad (2)$$

The reason is that reaction (2) can more easily absorb/desorb 6.5 mass% of hydrogen due to the smaller enthalpy change (ΔH).

So far, it was clarified that some catalysts, especially titanium compounds such as $TiCl_3$, were effective for improving hydrogen storage kinetics on this system [2,3]. However, we have not been able to characterize the catalysts, which have superior effect on hydrogen desorption, by X-ray diffraction (XRD) measurement of the laboratory-type equipment [3]. It was difficult to observe the catalysts because they were quite small in amount, highly dispersed in the mixtures and their crystalline sizes were extremely small. In this work, the chemical bonding states of the titanium compounds in the mixture were examined by synchrotron radiation (SR) X-ray absorption spectroscopy (XAS) for characterizing the catalysts.

1.1. Experimental procedure

The powder of LiH (95% purity) was purchased from Sigma–Aldrich and $LiNH_2$ (95%) was from Strem Chemicals. To achieve nanometer-scale contact among $LiNH_2$, LiH and 1 mol% additive, the mixtures were mechanically ball-milled (P7, Fritsch) at 400 rpm under hydrogen (99.99999 %) atmosphere of 1 MPa at room temperature for 2 h [2]. The several kinds of additives; Ti^{nano} with smaller particle size than one nanometer, Ti^{micro} (Rare Metallic, 99.9%) with several ten to hundred micrometer particle size, $TiCl_3$ (Sigma–Aldrich, 99.999%) with micron size, TiO_2^{micro} (Sigma–Aldrich, 99.999%) with micron size and TiO_2^{nano} (Millennium, 82.8%) with a specific surface area of ~180 m^2/g were used. Ti^{nano} was

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synthesized by Fichtner et al. [12]. The H-desorption properties of the composites prepared by ball-milling were examined by thermal desorption mass spectroscopy (TDMS) (Anelva M-QA200TS) combined with thermogravimetry (TG) (Rigaku TG8120) at the temperature range from 25 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 TDMS without exposing the samples to air at all.

The XAS measurements were carried out at the BL19B2 beam-line of SPring-8 SR facility in Japan [13]. This beam-line is a hard X-ray bending magnet beam-line. All the sample preparations were performed in the glovebox, which is filled with purified Ar gas. The samples were formed to the 1 cm diameter pellet by 600 kg/cm^2 press. To avoid the oxidation of the sample during the XAS measurement, the samples could be protected by the polyimide film with 8 μm thickness.

2. Results and discussion

Fig. 1 shows the TDMS profiles of hydrogen and ammonia gases from each composite of LiH + $LiNH_2$ and several kinds of additives prepared by ball-milling for 2 h under a 1.0 MPa hydrogen gas atmosphere. A broad shaped H-desorption curve (with a peak temperature $T_p = \sim 250$ °C) is observed in the TDMS 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 were detected around 330 °C. These results indicate that the additives Ti^{micro} and $TiO_2{}^{micro}$ do not act as a suitable catalyst, because they showed almost the same TDMS 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) exhibit similar sharp H-desorption peaks with $T_p = \sim 220$ °C as is shown in Fig. 1, in which no ammonia emission could not be detected within our experimental accuracy. We concluded that the additives of $TiCl_3$, Ti^{nano} and $TiO_2{}^{nano}$ can act as a suitable catalyst on the H-desorbing reaction in the composite of LiH and $LiNH_2$. However, the composites had no traces corresponding to the additives in the XRD profiles. Above results have already reported in Ref. [3].

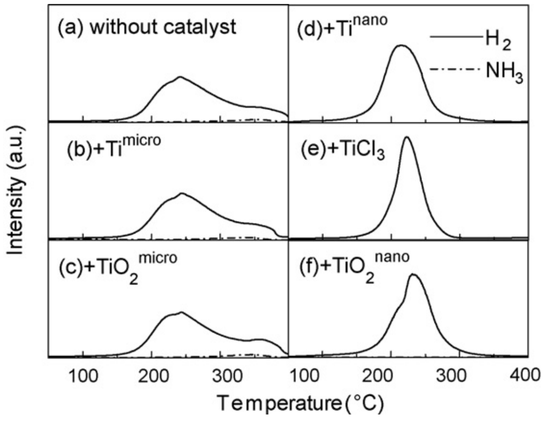

Fig. 1. TDMS profiles with heating rate 5 °C/min for hydrogen and ammonia gases from the composites of LiH + $LiNH_2$ (a) and LiH + $LiNH_2$ with some additive; Ti^{micro} (b), $TiO_2{}^{micro}$ (c), Ti^{nano} (d), $TiCl_3$ (e) and $TiO_2{}^{nano}$ (f).

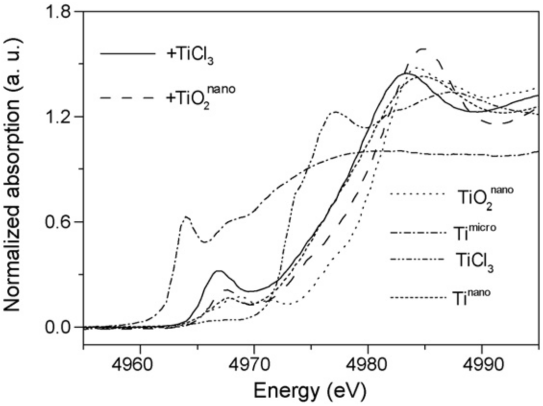

Fig. 2. XANES profiles of Ti K-edges for the composites of LiH + $LiNH_2$ catalyzed by $TiCl_3$ and $TiO_2{}^{nano}$ and XANES profiles for $TiO_2{}^{nano}$, Ti^{micro}, $TiCl_3$ and Ti^{nano} themselves as references.

X-ray absorption near-edge structure (XANES) profiles of the Ti K-edges corresponding to some Ti species in the composite prepared by ball-milling respective mixtures of LiH and $LiNH_2$ with 1 mol% $TiCl_3$ (labeled as +$TiCl_3$) and 1 mol% $TiO_2{}^{nano}$ (+$TiO_2{}^{nano}$) are shown in Fig. 2, in which those of the Ti K-edges of $TiO_2{}^{nano}$, Ti^{micro} and $TiCl_3$ themselves are also shown as the references. The profiles of the Ti K-edges for +$TiCl_3$ and +$TiO_2{}^{nano}$ seem to be in quite similar shape to each other. However, it should be noted that the profiles of +$TiCl_3$ and +$TiO_2{}^{nano}$ are quite different from their original profiles. These results indicate that the original valences corresponding to $TiCl_3$ and $TiO_2{}^{nano}$ are, respectively, in 3+ and 4+ states, while the Ti K-edges of the catalysts +$TiCl_3$ and +$TiO_2{}^{nano}$ in the mixture are really in a similar intermediate valence state between 3+ and 4+ valences, leading to a suitable catalytic effect. In the case of +Ti^{nano}, the XANES profile is a similar shape to those of +$TiCl_3$ and $TiO_2{}^{nano}$ as well. Meanwhile, the XANES profiles of +Ti^{micro} and +$TiO_2{}^{micro}$, which have no improvement on the H-desorption kinetics shown in Fig. 1, are quite similar to those of TiH_2 and $TiO_2{}^{micro}$, respectively. These results indicate that Ti^{micro} in the composite is changed to TiH_2 during ball-milling under hydrogen atmosphere and $TiO_2{}^{micro}$ is not changed, leading to different results from the cases of $TiCl_3$ and $TiO_2{}^{nano}$.

Fig. 3 shows the XANES profiles for the composite of LiH and $LiNH_2$ with 1 mol% $TiCl_3$, and for LiH with 1 mol% $TiCl_3$ and $LiNH_2$ with 1 mol% $TiCl_3$, which were prepared by ball-milling under 1.0 MPa hydrogen atmosphere. The profile of LiH with 1 mol% $TiCl_3$ is similar to that of TiH_2 itself prepared as a reference. This suggests that $TiCl_3$ is first transformed to Ti by reacting with LiH during ball-milling, and then, the generated Ti reacts with hydrogen gas during ball-milling, leading to transformation into TiH_2. On the other hand, the profile of the composite of LiH and $LiNH_2$ with 1 mol% $TiCl_3$ is quite similar to that of $LiNH_2$ with 1 mol% $TiCl_3$. This indicates that a characteristic state of the Ti compound, which has the catalytic effect, is generated by nano-contact between $LiNH_2$ and $TiCl_3$ in the milling process, not LiH and $TiCl_3$.

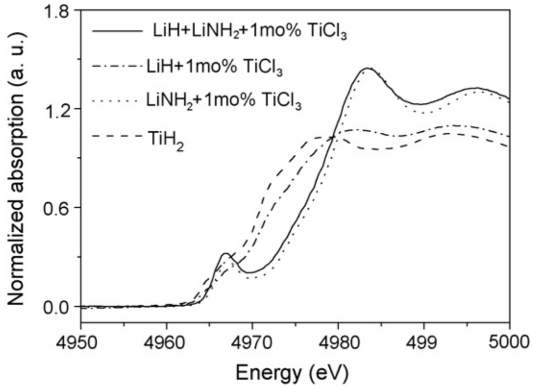

Fig. 3. XANES profiles of Ti K-edges for the composites of LiH and $LiNH_2$ with 1 mol% $TiCl_3$, LiH with 1 mol% $TiCl_3$ and $LiNH_2$ with 1mol% $TiCl_3$ and XANES profile of TiH_2 itself as a reference.

In this work, the extended X-ray absorption fine structures (EXAFS) for the Ti K-edge profiles in the ball-milled mixtures of LiH and $LiNH_2$ doped with Ti^{nano}, $TiCl_3$ and $TiO_2{}^{nano}$ were also examined. The local structure deduced from radial distribution function did not show any common characteristic feature, though all of the above additives showed significant improvements on H-storage properties.

3. Conclusion

We have investigated the catalytic effect of some Ti additives on H-storage properties for the Li-N-H system. The results indicated that the composites $LiH + LiNH_2$ with Ti^{nano}, $TiCl_3$ and $TiO_2{}^{nano}$ revealed a superior catalytic effect on the H-desorption properties, while the Ti^{micro} and $TiO_2{}^{micro}$ did not show any obvious catalytic effect, being similar to the sample without any additives. In this work, the chemical bonding states of the titanium compounds in the composites were examined by XAS measurement in order to characterize the catalysts microscopically. The results of XANES spectra indicated that the Ti atoms in the titanium compounds, which have catalytic effect on the kinetics of H-desorption, have a common onsite electronic state. Moreover, it was clarified that this common state of Ti atom was generated by ball-milling with $LiNH_2$, not LiH.

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