Identifying catalyst in Li-N-H system by x-ray absorption spectroscopy

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Chemical bonding states of titanium compounds in LiH and LiNH₂ mixture, which have been a candidate for a hydrogen storage material, have been examined by x-ray absorption spectroscopy to characterize the catalysts. The results of x-ray absorption near-edge structure indicated that the Ti atoms in the Ti compounds, which had the catalytic effect on the kinetics of the hydrogen desorption properties, had a common electronic (chemical bonding) state. Additionally, this common electronic state of the Ti catalysts agrees with that of TiCl₃·5NH₃. These results indicated that TiCl₃·5NH₃ could act as the catalyst.

The powder of LiH (95% purity) was purchased from Sigma-Aldrich and LiNH₂ (95%) was from Strem Chemicals. To achieve nanometer-scale contact among LiNH₂, LiH, and 1 mol. % additive, the mixtures were mechanically ball-milled (P7, Fritsch) at 400 rpm under 1 MPa hydrogen (99.99999%) atmosphere at room temperature for 2 h. As one of the additives, the powder of TiCl₃ (99.9999%) and MgCl₂ (99.9%) with micron size were purchased from Sigma–Aldrich. Other additives, the titanium ammine complexes (TiCl₃·nNH₃), were synthesized from TiCl₃ and NH₃. TiCl₃ reacted exothermically with sufficient amount (and 1:3 molar ratio) of 0.5 MPa ammonia at room temperature forming TiCl₃·5NH₃ (and TiCl₃·3NH₃, respectively). TiCl₃·4NH₃ and TiCl₃·NH₃ were derived by heating of TiCl₃·5NH₃ under vacuum at 50 and 170 °C, respectively. We have confirmed the chemical composition of TiCl₃·nNH₃ by weight change caused by ammonia absorption and desorption. The hydrogen desorption properties of the composites were examined by thermal desorption mass spectroscopy (TDMS) (Anelva M-QA200TS) combined with thermogravimetry (TG) (Rigaku TG8120) at a temperature range from 25°C 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. This beam-line is a hard x-ray bending magnet beam-line. All the samples were prepared in the glove box which is filled with purified Ar gas. The samples were formed to the 1 cm diameter pellet by 600 kg/cm² press. To avoid the oxidation of the samples during the XAS measurement, the samples were protected by the polyimide film with 8 μm thickness.

Figure 1 shows Ti K-edge x-ray absorption near-edge structure (XANES) spectra of TiCl₃·nNH₃ (n = 1, 3, 4, and 5). The shape of each spectrum is slightly different. Especially, with respect to the hight of pre-edge peak (4965–4970 eV), playing a role as a kind of ammonia carrier. In the present work, we identified the chemical bonding state of the titanium compounds, considering that the bonding state should be significant on understanding the catalytic effect.

The results of x-ray absorption near-edge structure indicated that the Ti atoms in the Ti compounds, which had the catalytic effect on the kinetics of the hydrogen desorption properties, had a common electronic (chemical bonding) state. Additionally, this common electronic state of the Ti catalysts agrees with that of TiCl₃·5NH₃. These results indicated that TiCl₃·5NH₃ could act as the catalyst.
the order is TiCl$_3$5NH$_3$ > TiCl$_3$4NH$_3$ > TiCl$_3$3NH$_3$ > TiCl$_3$NH$_3$. This order should be orginated from the difference in symmetry of environmental atoms around titanium atom.9 On the other hand, the position of each K-edge (4965–4970 eV) is almost the same. From these spectra, it is indicated that the valence of titanium in TiCl$_3$-$n$NH$_3$ ($n$ = 1, 3, 4, and 5) is almost the same. Figure 2 shows Ti K-edge XANES spectra of TiCl$_3$5NH$_3$, LiH + LiNH$_2$ with 1 mol.% TiCl$_3$ and TiCl$_3$ itself. As reported in Ref. 6, the hydrogen desorption property of LiH + LiNH$_2$ with 1 mol.% TiCl$_3$ is superior than LiH + LiNH$_2$, the Ti K-edge XANES spectrum of LiH + LiNH$_2$ with 1 mol.% TiCl$_3$ is quite different from TiCl$_3$ itself. Here, the unidentified Ti K-edge XANES spectrum of LiH + LiNH$_2$ with 1 mol.% TiCl$_3$ completely agrees with that of TiCl$_3$5NH$_3$. This means the chemical bonding state of TiCl$_3$ ballmilled with LiH + LiNH$_2$ is quite similar with that of TiCl$_3$5NH$_3$. Figure 3 shows TDMS and TG profiles with heating rate 5 °C/min for hydrogen and ammonia gases from the composites of LiH + LiNH$_2$ with 1 mol.% TiCl$_3$ and LiH + LiNH$_2$ with 1 mol.% TiCl$_3$5NH$_3$. The hydrogen desorption properties of them are quite similar with each other, which means that TiCl$_3$5NH$_3$ has catalytic effect. Figure 4 shows Ti K-edge XANES spectra of LiH + LiNH$_2$ with 1 mol.% TiCl$_3$-$n$NH$_3$ ($n$ = 1, 3, 4, and 5). Those results indicate that the chemical bonding states of TiCl$_3$-$n$NH$_3$ are changed to be a particular state by ballmilled with LiH + LiNH$_2$. The particular state agrees with that of TiCl$_3$5NH$_3$. Here, the mechanism of the catalytic effect should be discussed. As mentioned in the introduction, the ammonia intermediately reaction was suggested for explaining the hydrogen desorption mechanism in this LiH + LiNH$_2$ hydrogen storage system, as reported by Ichikawa et al.4,7 Moreover, TiCl$_3$ catalyst can not only modify the reaction kinetics of hydrogen desorption, but also suppress the ammonia emission during the hydrogen desorption, as shown in Ref. 3. Kim et al. demonstrated that the reaction kinetics determined the product channel in this process without affecting the thermodynamic stability of LiNH$_2$ (Ref. 12). Therefore, we considered that the role of TiCl$_3$ catalyst was a kind of ammonia carrier in this system. TiCl$_3$ would make the reaction kinetics of LiH + NH$_3$ faster and then promote the decomposition of LiNH$_2$ to Li$_2$NH. Here, it was expected that MgCl$_2$ could be a good catalyst in this system, because MgCl$_2$ could absorb NH$_3$ and form ammine complex just like TiCl$_3$ (Ref. 13). Figure 5 shows TDMS profiles of the composites of LiH + LiNH$_2$ and LiH + LiNH$_2$ with 1 mol.% MgCl$_2$ shown in Fig. 5 (Heating rate: 5 °C/min;
Detected gases: H₂, NH₃), two profiles show almost the same desorption property in each composite. Consequently, MgCl₂ does not show any catalytic effect in this Li-N-H system. The results indicate that the existence of titanium element is required to be effective catalysts in this system.

In this paper, we used synchrotron radiation XAS to determine the chemical bonding state of titanium in Li-N-H system. Among them, Ti K-edge XANES spectrum of TiCl₃·5NH₃ agreed with that of Ti-compound in Li-N-H system, indicating that the chemical bonding state of titanium, which has catalytic effect on hydrogen desorption property in Li-N-H system, is quite similar with TiCl₃·5NH₃. Then, we considered the catalytic role of TiCl₃ to be a kind of ammonia carrier, and thus examined the catalytic effect of MgCl₂, which similarly reacted with ammonia to TiCl₃. It was found that the existence of titanium element was required to be effective catalysts, because MgCl₂ could not act as a good catalyst in this system.

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