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

Shigehito Isobe, Satoshi Hino, Takayuki Ichikawa, and Yoshitsugu Kojima

Graduate School of Engineering, Hokkaido University, N-13 W-8, Sapporo 060-8628, Japan
Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

(Received 9 March 2011; accepted 11 June 2011; published online 5 July 2011)

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 measurement as the characterization of 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.

To achieve nanometer-scale contact among LiNH2, LiH, and the ammonia, mechanical ball-milled (P7, Fritsch) TiCl3 (99.999%) and MgCl2 (99.9%) 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 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 (99.9999%) 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),
the order is TiCl₃₅NH₃ > TiCl₃₄NH₃ > TiCl₃₃NH₃ > TiCl₃NH₃. This order should be originated 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 TiCl₃ₙNH₃ (ₙ = 1, 3, 4, and 5) is almost the same. Figure 2 shows Ti K-edge XANES spectra of TiCl₃₅NH₃, LiH + LiNH₂ with 1 mol.% TiCl₃ and TiCl₃ itself. As reported in Ref. 6, the hydrogen desorption property of LiH+LiNH₂ with 1 mol.% TiCl₃ is superior than LiH + LiNH₂, the Ti K-edge XANES spectrum of LiH + LiNH₂ with 1 mol.% TiCl₃ is quite different from TiCl₃ itself. Here, the unidentified Ti K-edge XANES spectrum of LiH + LiNH₂ with 1 mol.% TiCl₃ completely agrees with that of TiCl₃₅NH₃. This means the chemical bonding state of TiCl₃ ballmilled with LiH + LiNH₂ is quite similar with that of TiCl₃₅NH₃. Figure 3 shows TDMS and TG profiles with heating rate 5 °C/min for hydrogen and ammonia gases from the composites of LiH + LiNH₂ with 1 mol.% TiCl₃ and LiH + LiNH₂ with 1 mol.% TiCl₃₅NH₃. The hydrogen desorption properties of them are quite similar with each other, which means that TiCl₃₅NH₃ has catalytic effect. Figure 4 shows Ti K-edge XANES spectra of LiH + LiNH₂ with 1 mol.% TiCl₃ₙNH₃ (ₙ = 1, 3, 4, and 5). Those results indicate that the chemical bonding states of TiCl₃ₙNH₃ are changed to be a particular state by ballmilled with LiH + LiNH₂. The particular state agrees with that of TiCl₃₅NH₃. Here, the mechanism of the catalytic effect should be discussed. As mentioned in the introduction, the ammonia intermediated reaction was suggested for explaining the hydrogen desorption mechanism in this LiH + LiNH₂ hydrogen storage system, as reported by Ichikawa et al.⁴,⁷ Moreover, TiCl₃ 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 LiNH₂ (Ref. 12). Therefore, we considered that the role of TiCl₃ catalyst was a kind of ammonia carrier in this system. TiCl₃ would make the reaction kinetics of LiH + NH₃ faster and then promote the decomposition of LiNH₂ to Li₂NH. Here, it was expected that MgCl₂ could be a good catalyst in this system, because MgCl₂ could absorb NH₃ and form ammine complex just like TiCl₃ (Ref. 13). Figure 5 shows TDMS profiles of the composites of LiH + LiNH₂ and LiH + LiNH₂ with 1 mol.% MgCl₂ 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.

The authors would like to acknowledge Dr. T. Honma for performing the XAS measurement in SPring-8. This work was partially supported by the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (JSPS), and Hydro Star project of New Energy and Industrial Technology Development Organization (NEDO).

11http://www.spring8.or.jp/