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## 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 LiNH<sub>2</sub> 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 TiCl<sub>3</sub>·5NH<sub>3</sub>. These results indicated that TiCl<sub>3</sub>·5NH<sub>3</sub> could act as the catalyst. © 2011 American Institute of Physics. [doi:10.1063/1.3606534]

Hydrogen storage in solid state is the key factor that is affecting the use of fuel cell vehicles. Since P. Chen's report,<sup>1</sup> Li-N-H system has been paid much attention for one of the promising hydrogen storage systems.<sup>2-9</sup> Lithium nitride absorbs and desorbs a large amount of hydrogen in the two consecutive reactions as follows:



Theoretically, a large amount (10.4 mass%) of hydrogen (2H<sub>2</sub>/(Li<sub>3</sub>N+2H<sub>2</sub>)) is accessible in these two reactions. Ichikawa *et al.* chose LiNH<sub>2</sub> and LiH as the starting materials and investigated the hydrogenation and dehydrogenation properties of the mixture, focusing on the following reaction:<sup>3,4</sup>



They determined the mechanisms of the reaction and also reported several potential catalysts such as Ti, Fe, Ni, Co (Ref. 3). In addition, two part ammonia mediated reactions were suggested in their work.<sup>4</sup> One is the decomposition of LiNH<sub>2</sub> to Li<sub>2</sub>NH with ammonia emission, the other is the reaction of LiH and the ammonia with hydrogen desorption. Moreover, it was clarified that some catalysts, especially titanium compounds such as TiCl<sub>3</sub>, were effective for improving hydrogen storage kinetics on this system.<sup>3,5</sup> However, we have not been able to characterize the catalysts, which have superior effect on hydrogen desorption, by x-ray diffraction (XRD) measurement.<sup>5</sup> It was difficult to observe the catalysts, because they were quite small amount and highly dispersed in the mixtures. Then, in order to characterize the catalysts, we have performed synchrotron radiation (SR) x-ray absorption spectroscopy (XAS). The results showed that the chemical bonding states of the titanium compounds, which had catalytic effect, were almost same. It is known that TiCl<sub>3</sub> reacts with NH<sub>3</sub> to form TiCl<sub>3</sub>·*n*NH<sub>3</sub> (Ref. 10). This compound could show catalytic effect in the ammonia mediated reaction,

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 LiNH<sub>2</sub> (95%) was from Strem Chemicals. To achieve nanometer-scale contact among LiNH<sub>2</sub>, 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 TiCl<sub>3</sub> (99.999%) and MgCl<sub>2</sub> (99.9%) with micron size were purchased from Sigma-Aldrich. Other additives, the titanium ammine complexes (TiCl<sub>3</sub>·*n*NH<sub>3</sub>), were synthesized from TiCl<sub>3</sub> and NH<sub>3</sub>. TiCl<sub>3</sub> reacted exothermically with sufficient amount (and 1:3 molar ratio) of 0.5 MPa ammonia at room temperature forming TiCl<sub>3</sub>·5NH<sub>3</sub> (and TiCl<sub>3</sub>·3NH<sub>3</sub>, respectively). TiCl<sub>3</sub>·4NH<sub>3</sub> and TiCl<sub>3</sub>·NH<sub>3</sub> were derived by heating of TiCl<sub>3</sub>·5NH<sub>3</sub> under vacuum at 50 and 170 °C, respectively.<sup>10</sup> We have confirmed the chemical composition of TiCl<sub>3</sub>·*n*NH<sub>3</sub> 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.<sup>11</sup> 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/cm<sup>2</sup> 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 TiCl<sub>3</sub>·*n*NH<sub>3</sub> (*n* = 1, 3, 4, and 5). The shape of each spectrum is slightly different. Especially, with respect to the height of pre-edge peak (4965–4970 eV),

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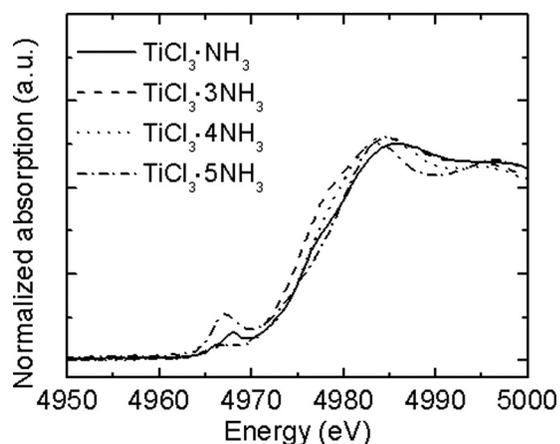


FIG. 1. Ti *K*-edge XANES spectra of  $\text{TiCl}_3 \cdot n\text{NH}_3$  ( $n = 1, 3, 4,$  and  $5$ ).

the order is  $\text{TiCl}_3 \cdot 5\text{NH}_3 > \text{TiCl}_3 \cdot 4\text{NH}_3 \approx \text{TiCl}_3 \cdot 3\text{NH}_3 > \text{TiCl}_3 \cdot \text{NH}_3$ . This order should be originated from the difference in symmetry of environmental atoms around titanium atom.<sup>9</sup> 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  $\text{TiCl}_3 \cdot n\text{NH}_3$  ( $n = 1, 3, 4,$  and  $5$ ) is almost the same. Figure 2 shows Ti *K*-edge XANES spectra of  $\text{TiCl}_3 \cdot 5\text{NH}_3$ ,  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  and  $\text{TiCl}_3$  itself. As reported in Ref. 6, the hydrogen desorption property of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  is superior than  $\text{LiH} + \text{LiNH}_2$ , the Ti *K*-edge XANES spectrum of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  is quite different from  $\text{TiCl}_3$  itself. Here, the unidentified Ti *K*-edge XANES spectrum of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  completely agrees with that of  $\text{TiCl}_3 \cdot 5\text{NH}_3$ . This means the chemical bonding state of  $\text{TiCl}_3$  ballmilled with  $\text{LiH} + \text{LiNH}_2$  is quite similar with that of  $\text{TiCl}_3 \cdot 5\text{NH}_3$ . Figure 3 shows TDMS and TG profiles with heating rate 5 °C/min for hydrogen and ammonia gases from the composites of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  and  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3 \cdot 5\text{NH}_3$ . The hydrogen desorption properties of them are quite similar with each other, which means that  $\text{TiCl}_3 \cdot 5\text{NH}_3$  has catalytic effect. Figure 4 shows Ti *K*-edge XANES spectra of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3 \cdot n\text{NH}_3$  ( $n = 1, 3, 4,$  and  $5$ ). Those results indicate that the chemical bonding states of  $\text{TiCl}_3 \cdot n\text{NH}_3$  are changed to be a particular state by ballmilled with  $\text{LiH} + \text{LiNH}_2$ . The particular state agrees with

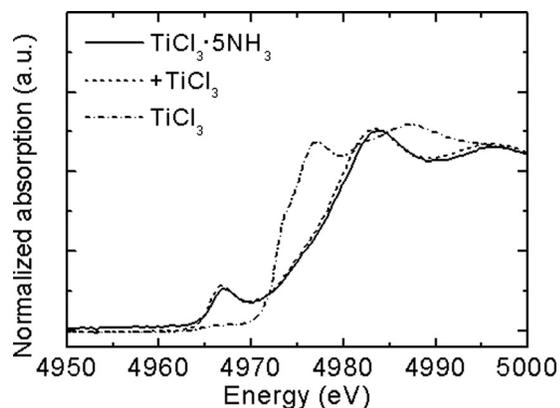


FIG. 2. Ti *K*-edge XANES spectra of  $\text{TiCl}_3 \cdot 5\text{NH}_3$ ,  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  and  $\text{TiCl}_3$  itself.

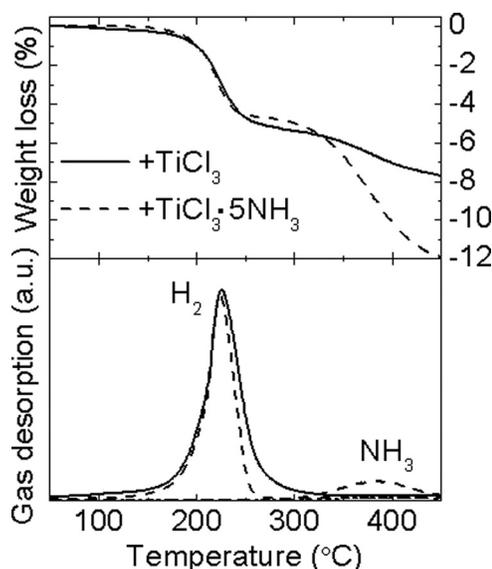


FIG. 3. TDMS and TG profiles with heating rate 5 °C/min for hydrogen and ammonia gases from the composites of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3$  and  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3 \cdot 5\text{NH}_3$ .

that of  $\text{TiCl}_3 \cdot 5\text{NH}_3$ . 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  $\text{LiH} + \text{LiNH}_2$  hydrogen storage system, as reported by Ichikawa *et al.*<sup>4,7</sup> Moreover,  $\text{TiCl}_3$  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  $\text{LiNH}_2$  (Ref. 12). Therefore, we considered that the role of  $\text{TiCl}_3$  catalyst was a kind of ammonia carrier in this system.  $\text{TiCl}_3$  would make the reaction kinetics of  $\text{LiH} + \text{NH}_3$  faster and then promote the decomposition of  $\text{LiNH}_2$  to  $\text{Li}_2\text{NH}$ . Here, it was expected that  $\text{MgCl}_2$  could be a good catalyst in this system, because  $\text{MgCl}_2$  could absorb  $\text{NH}_3$  and form ammine complex just like  $\text{TiCl}_3$  (Ref. 13). Figure 5 shows TDMS profiles of the composites of  $\text{LiH} + \text{LiNH}_2$  and  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{MgCl}_2$  shown in Fig. 5 (Heating rate: 5 C/min;

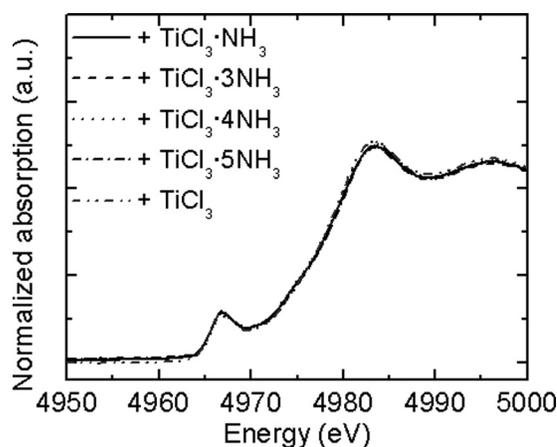


FIG. 4. Ti *K*-edge XANES spectra of  $\text{LiH} + \text{LiNH}_2$  with 1 mol.%  $\text{TiCl}_3 \cdot n\text{NH}_3$  ( $n = 1, 3, 4,$  and  $5$ ).

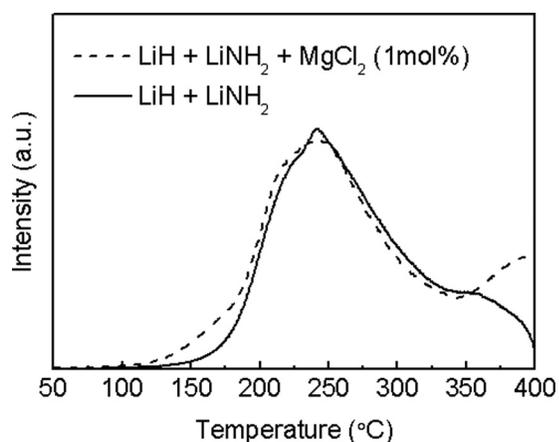


FIG. 5. TDMS profiles with heating rate 5 °C/min for hydrogen and ammonia gases from the composites of LiH + LiNH<sub>2</sub> and LiH + LiNH<sub>2</sub> with MgCl<sub>2</sub>.

Detected gases: H<sub>2</sub>, NH<sub>3</sub>), two profiles show almost the same desorption property in each composite. Consequently, MgCl<sub>2</sub> 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 TiCl<sub>3</sub>·5NH<sub>3</sub> 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 TiCl<sub>3</sub>·5NH<sub>3</sub>. Then, we considered the catalytic role of TiCl<sub>3</sub> to be a kind of

ammonia carrier, and thus examined the catalytic effect of MgCl<sub>2</sub>, which similarly reacted with ammonia to TiCl<sub>3</sub>. It was found that the existence of titanium element was required to be effective catalysts, because MgCl<sub>2</sub> could not act as a good catalyst in this system.

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