

# ROLES OF $\text{TiCl}_3$ , $\text{TiO}_2$ , $\text{Ti}$ AND $\text{Ti}(\text{OBU})_4$ ON THE HYDROGEN DESORPTION AND REVERSIBILITY OF $\text{NaAlH}_4$

**Rangsunvigit P.**<sup>(1,2)\*</sup>, **Suttisawat Y.**<sup>(1,2)</sup>, **Kitiyanan B.**<sup>(1,2)</sup>, **Kulprathipanja S.**<sup>(3)</sup>

<sup>(1)</sup> The Petroleum and Petrochemical College, Chulalongkorn University,  
Chula Soi 12, Phyathai Road, Bangkok 10330, Thailand

<sup>(2)</sup> Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University,  
Chula Soi 12, Phyathai Road, Bangkok 10330, Thailand

<sup>(3)</sup> UOP, A Honeywell Company, Des Plaines, Illinois, 60017 USA

\*Fax: 66 (2) 215 4459 E-mail: Pramoch.R@chula.ac.th.

## Introduction

Sodium alanate or sodium aluminium hydride ( $\text{NaAlH}_4$ ) has shown promising properties for hydrogen storage after the effects of a metal catalyst on the hydride reversibility were reported [1, 2]. Its maximum reversible hydrogen capacity is close to 4 wt%  $\text{H}_2$  compared to 5.6 wt%  $\text{H}_2$  achieved from the first desorption. In our previous work, the hydrogen desorption/re-absorption of  $\text{NaAlH}_4$  doped with chlorides of different transition metals was investigated and  $\text{TiCl}_3$  was found to be the best catalyst among the tested four transition metal chlorides with the reversible hydrogen capacity about 3.5 wt%  $\text{H}_2$  (3.85 wt%  $\text{H}_2$  based on hydride weight). Doping  $\text{TiCl}_3$  in the hydride system poses the formation of  $\text{NaCl}$  as a by-product, which is believed to be one of many reasons for the incomplete reversibility of  $\text{NaAlH}_4$  [1, 2]. This work was carried out with the hypothesis that the formation of the by-product during the hydrogen desorption/re-absorption would be the culprit for the decrease in the reversible hydrogen capacity and using other forms of Ti compound would somehow avoid the by-product formation. Effects of using  $\text{TiO}_2$  and metallic Ti as catalysts were then investigated in the hydrogen desorption/re-absorption of  $\text{NaAlH}_4$ . Results were also compared with that using  $\text{Ti}(\text{OBU})_4$  and  $\text{TiCl}_3$ .

## Results and Discussion

Fig. 1 shows the comparison of temperature program desorption in the 1<sup>st</sup> cycle of undoped  $\text{NaAlH}_4$ ,  $\text{NaAlH}_4$  doped with 4 mol%  $\text{Ti}(\text{OBU})_4$  ( $\text{Ti}(\text{OBU})_4\text{-NaAlH}_4$ ),  $\text{NaAlH}_4$  doped with 4 mol%  $\text{TiCl}_3$  ( $\text{TiCl}_3\text{-NaAlH}_4$ ),  $\text{NaAlH}_4$  doped with 4 mol%  $\text{TiO}_2$  ( $\text{TiO}_2\text{-NaAlH}_4$ ), and  $\text{NaAlH}_4$  doped with 4 mol% metallic Ti ( $\text{Ti-NaAlH}_4$ ). All doped samples exhibit the hydrogen desorption at the lower temperature than that of the undoped sample. The result shows that  $\text{Ti}(\text{OBU})_4\text{-NaAlH}_4$  starts to desorb hydrogen at the temperature around 100°C, while the onset temperature of the hydrogen desorption of  $\text{TiCl}_3\text{-NaAlH}_4$  and  $\text{Ti-NaAlH}_4$  are

higher, at 110°C and 160°C, respectively. Surprisingly, it can be clearly observed that the hydrogen desorption behavior of  $\text{TiCl}_3\text{-NaAlH}_4$  is quite similar to that of  $\text{TiO}_2\text{-NaAlH}_4$  after the temperature is raised to 120°C.

Fig. 2 displays the reversibility and stability of  $\text{Ti}(\text{OBU})_4\text{-NaAlH}_4$  (Fig. 2a),  $\text{TiCl}_3\text{-NaAlH}_4$  (Fig. 2b),  $\text{TiO}_2\text{-NaAlH}_4$  (Fig. 2c), and  $\text{Ti-NaAlH}_4$  (Fig. 2d). The subsequent hydrogen desorption behavior of  $\text{TiO}_2\text{-NaAlH}_4$  and  $\text{TiCl}_3\text{-NaAlH}_4$  seems to reproduce their 1<sup>st</sup> hydrogen desorption except the lower reversible hydrogen capacity, around 3.8 wt% (H/M). The onset temperatures in the subsequent hydrogen desorption of  $\text{Ti}(\text{OBU})_4\text{-NaAlH}_4$  are in the range of 80-100°C as well as the reversible hydrogen capacity is around 2 wt%. In the case of  $\text{Ti-NaAlH}_4$ , the subsequent hydrogen desorption shifts to a higher temperature, 200°C, while the reversible hydrogen capacity decreases to only 1 wt% (H/M). Comparison between the subsequent desorption of  $\text{Ti-NaAlH}_4$  with its 1<sup>st</sup> hydrogen desorption shows that the onset desorption temperature of the subsequent cycle is close to the 2<sup>nd</sup> decomposition temperature of the 1<sup>st</sup> cycle. Moreover, the curve shape of the subsequent desorption profile of  $\text{Ti-NaAlH}_4$  is identical with its 1<sup>st</sup> desorption in the second step of the reaction. This indicates that the hydrogen desorption in the subsequent cycle results from the hydrogen desorption of  $\text{Na}_3\text{AlH}_6$ .

The BET surface area analysis was conducted with the desorbed samples of  $\text{TiO}_2\text{-NaAlH}_4$  and  $\text{TiCl}_3\text{-NaAlH}_4$ . The surface area of the desorbed sample doped with  $\text{TiO}_2$  is 147.65  $\text{m}^2 \text{g}^{-1}$ , while that of the desorbed sample doped with  $\text{TiCl}_3$  is 56.76  $\text{m}^2 \text{g}^{-1}$ . Thus, it can be deduced that not only does  $\text{TiO}_2$  improve the hydrogen reversibility of  $\text{NaAlH}_4$ , its porosity and surface area (geometric effect) also increase the surface area of the hydride sample, which facilitates the hydrogen diffusion in the desorbed sample.

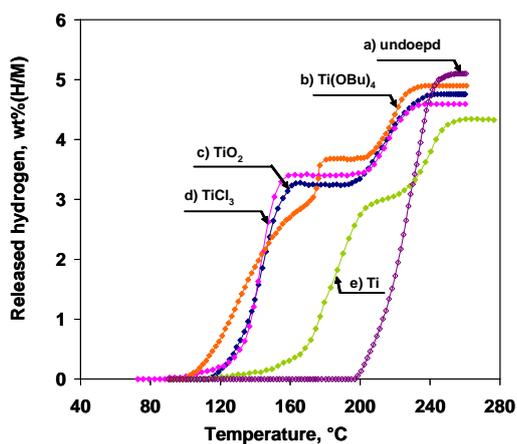


Fig. 1 Correlation between temperature and hydrogen capacity, during the 1<sup>st</sup> hydrogen desorption on: a) undoped NaAlH<sub>4</sub>, b) Ti(OBu)<sub>4</sub>-NaAlH<sub>4</sub>, c) TiO<sub>2</sub>-NaAlH<sub>4</sub>, d) TiCl<sub>3</sub>-NaAlH<sub>4</sub> and e) Ti-NaAlH<sub>4</sub>.

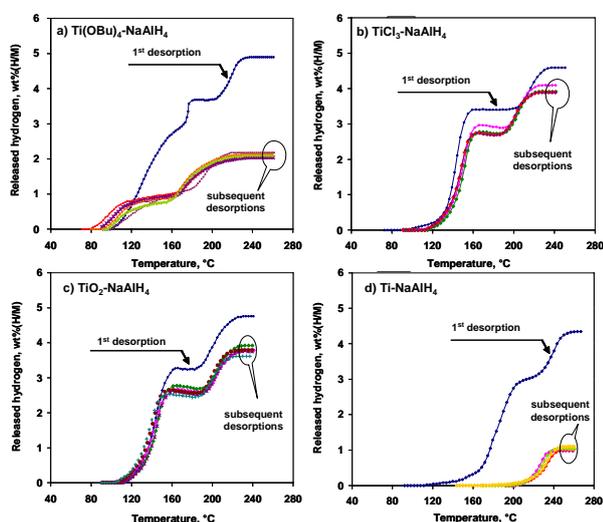


Fig. 2 Correlation between temperature and hydrogen released compared between the 1<sup>st</sup> desorption and the subsequent desorptions of: a) 4 mol% Ti(OBu)<sub>4</sub>-NaAlH<sub>4</sub>, b) 4 mol% TiO<sub>2</sub>-NaAlH<sub>4</sub>, c) TiCl<sub>3</sub>-NaAlH<sub>4</sub> and d) Ti-NaAlH<sub>4</sub>.

XRD results show that the samples after the hydrogen desorption consist of the main products containing Al and NaH. There is also formation of oxide compounds (NaOH and Na<sub>2</sub>O) in TiO<sub>2</sub>-NaAlH<sub>4</sub> and Ti(OBu)<sub>4</sub>-NaAlH<sub>4</sub> indicating the reaction between TiO<sub>2</sub> and Ti(OBu)<sub>4</sub> with NaAlH<sub>4</sub>. For Ti-NaAlH<sub>4</sub>, the metallic Ti becomes TiH<sub>x</sub> (1 < x < 2) after the hydrogen desorption. In the case of hydrogen re-absorption, the re-absorbed TiCl<sub>3</sub>-NaAlH<sub>4</sub> sample consists of NaAlH<sub>4</sub> and a small amount of Al and NaCl, while the re-absorbed products of TiO<sub>2</sub>-NaAlH<sub>4</sub> or Ti(OBu)<sub>4</sub>-NaAlH<sub>4</sub> sample are NaAlH<sub>4</sub>, Na<sub>3</sub>AlH<sub>6</sub>, and Al.

From the result, it may be explained that the decrease in the ability of Ti-NaAlH<sub>4</sub> to re-absorb

hydrogen could come from the transformation of metallic Ti to TiH<sub>x</sub>. That, in turn, reduces the hydrogen dissociation leading to the lower hydrogen re-absorption. No evidence of Ti-species is detected from the XRD results of TiCl<sub>3</sub>-NaAlH<sub>4</sub> or Ti(OBu)<sub>4</sub>-NaAlH<sub>4</sub>. It has been early reported that Ti located with Al presenting as an amorphous phase of TiAl<sub>3</sub>, which was claimed as a catalyst in the reaction [3]. However, the dissimilar hydrogen desorption/re-absorption behavior of TiCl<sub>3</sub>-NaAlH<sub>4</sub> and Ti(OBu)<sub>4</sub>-NaAlH<sub>4</sub> shows the influence of the precursor, as well as results to the different catalytic activity of each system.

The XRD result further reveals the formation of oxide compound (NaOH and Na<sub>2</sub>O) in the TiO<sub>2</sub>-NaAlH<sub>4</sub> system. This probably occurs from the reduction of TiO<sub>2</sub> by NaAlH<sub>4</sub>, and then form NaOH and Na<sub>2</sub>O in the hydride system. The reduction of TiO<sub>2</sub> by NaAlH<sub>4</sub>, which, in turn, creates the defect sites on the TiO<sub>2</sub> surface, was confirmed by ESR analysis. The Ti<sup>3+</sup> defect sites on the surface of TiO<sub>2</sub> may act as the active sites of the catalyst for the hydrogen dissociation or recombination into the hydride system [4]. However, the reduction of TiO<sub>2</sub> also produces the oxide compound as a by-product, which leads to a decrease in the reversible hydrogen capacity of the hydride system.

## Conclusions

The order of catalytic activity is TiCl<sub>3</sub> ~ TiO<sub>2</sub> > Ti(OBu)<sub>4</sub> > metallic Ti. Despite of the similarity behavior of TiO<sub>2</sub>-NaAlH<sub>4</sub> and TiCl<sub>3</sub>-NaAlH<sub>4</sub>, the former has the superior rate of hydrogen re-absorption.

## References

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