

ROLES OF TiCl_3 , TiO_2 , Ti AND $\text{Ti}(\text{OBU})_4$ ON THE HYDROGEN DESORPTION AND REVERSIBILITY OF NaAlH_4

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Introduction

Sodium alanate or sodium aluminium hydride (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% H_2 compared to 5.6 wt% H_2 achieved from the first desorption. In our previous work, the hydrogen desorption/re-absorption of NaAlH_4 doped with chlorides of different transition metals was investigated and 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% H_2 (3.85 wt% H_2 based on hydride weight). Doping TiCl_3 in the hydride system poses the formation of NaCl as a by-product, which is believed to be one of many reasons for the incomplete reversibility of 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 TiO_2 and metallic Ti as catalysts were then investigated in the hydrogen desorption/re-absorption of NaAlH_4 . Results were also compared with that using $\text{Ti}(\text{OBU})_4$ and TiCl_3 .

Results and Discussion

Fig. 1 shows the comparison of temperature program desorption in the 1st cycle of undoped NaAlH_4 , NaAlH_4 doped with 4 mol% $\text{Ti}(\text{OBU})_4$ ($\text{Ti}(\text{OBU})_4\text{-NaAlH}_4$), NaAlH_4 doped with 4 mol% TiCl_3 ($\text{TiCl}_3\text{-NaAlH}_4$), NaAlH_4 doped with 4 mol% TiO_2 ($\text{TiO}_2\text{-NaAlH}_4$), and NaAlH_4 doped with 4 mol% metallic Ti (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 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 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 1st 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 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 Ti-NaAlH_4 with its 1st hydrogen desorption shows that the onset desorption temperature of the subsequent cycle is close to the 2nd decomposition temperature of the 1st cycle. Moreover, the curve shape of the subsequent desorption profile of Ti-NaAlH_4 is identical with its 1st desorption in the second step of the reaction. This indicates that the hydrogen desorption in the subsequent cycle results from the hydrogen desorption of Na_3AlH_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 TiO_2 is 147.65 $\text{m}^2 \text{g}^{-1}$, while that of the desorbed sample doped with TiCl_3 is 56.76 $\text{m}^2 \text{g}^{-1}$. Thus, it can be deduced that not only does TiO_2 improve the hydrogen reversibility of 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.

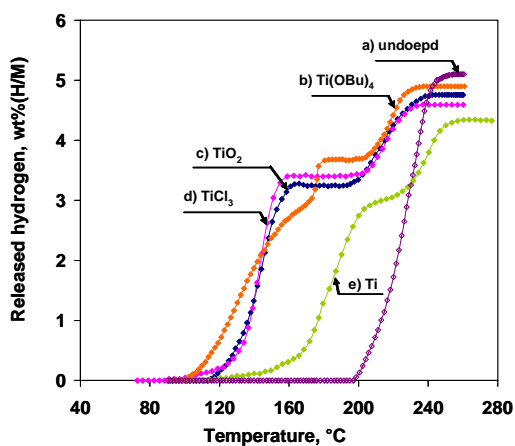


Fig. 1 Correlation between temperature and hydrogen capacity, during the 1st hydrogen desorption on: a) undoped NaAlH₄, b) Ti(OBu)₄-NaAlH₄, c) TiO₂-NaAlH₄, d) TiCl₃-NaAlH₄ and e) Ti-NaAlH₄.

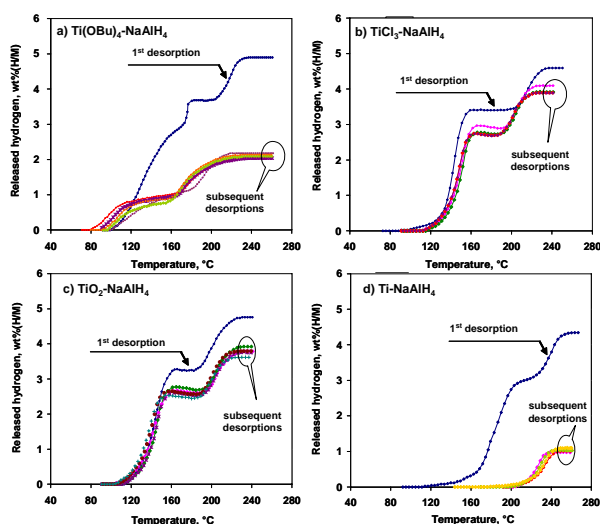


Fig. 2 Correlation between temperature and hydrogen released compared between the 1st desorption and the subsequent desorptions of: a) 4 mol% Ti(OBu)₄-NaAlH₄, b) 4 mol% TiO₂-NaAlH₄, c) TiCl₃-NaAlH₄ and d) Ti-NaAlH₄.

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 Na₂O) in TiO₂-NaAlH₄ and Ti(OBu)₄-NaAlH₄ indicating the reaction between TiO₂ and Ti(OBu)₄ with NaAlH₄. For Ti-NaAlH₄, the metallic Ti becomes TiH_x (1 < x < 2) after the hydrogen desorption. In the case of hydrogen re-absorption, the re-absorbed TiCl₃-NaAlH₄ sample consists of NaAlH₄ and a small amount of Al and NaCl, while the re-absorbed products of TiO₂-NaAlH₄ or Ti(OBu)₄-NaAlH₄ sample are NaAlH₄, Na₃AlH₆, and Al.

From the result, it may be explained that the decrease in the ability of Ti-NaAlH₄ to re-absorb

hydrogen could come from the transformation of metallic Ti to TiH_x. 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 TiCl₃-NaAlH₄ or Ti(OBu)₄-NaAlH₄. It has been early reported that Ti located with Al presenting as an amorphous phase of TiAl₃, which was claimed as a catalyst in the reaction [3]. However, the dissimilar hydrogen desorption/re-absorption behavior of TiCl₃-NaAlH₄ and Ti(OBu)₄-NaAlH₄ 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 Na₂O) in the TiO₂-NaAlH₄ system. This probably occurs from the reduction of TiO₂ by NaAlH₄, and then form NaOH and Na₂O in the hydride system. The reduction of TiO₂ by NaAlH₄, which, in turn, creates the defect sites on the TiO₂ surface, was confirmed by ESR analysis. The Ti³⁺ defect sites on the surface of TiO₂ may act as the active sites of the catalyst for the hydrogen dissociation or recombination into the hydride system [4]. However, the reduction of TiO₂ 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 TiCl₃ ~ TiO₂ > Ti(OBu)₄ > metallic Ti. Despite of the similarity behavior of TiO₂-NaAlH₄ and TiCl₃-NaAlH₄, the former has the superior rate of hydrogen re-absorption.

References

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