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# Catalytic and inhibitive effects of Pd and Pt decorated MWCNTs on the dehydrogenation behavior of LiAlH<sub>4</sub>

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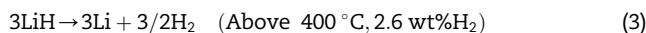
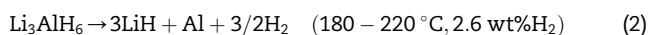
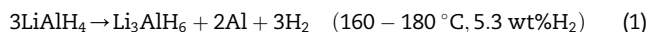
## ABSTRACT

A novel catalyst was developed to modify the dehydrogenation behavior of LiAlH<sub>4</sub> (lithium alanate). Using a chemical reduction method, Pd and Pt nano-particles were decorated on multi-walled carbon nanotubes (MWCNTs). The homogeneity and surface morphology of Pd and Pt decorated MWCNTs were examined by using transmission electron microscopy and scanning electron microscopy. The dehydrogenation behavior of LiAlH<sub>4</sub> admixed with Pd and Pt decorated MWCNTs was investigated by thermal gravimetric analysis (TGA) and the in-situ synchrotron X-ray diffraction (XRD) technique. The TGA results revealed that the addition of Pd or Pt decorated MWCNTs would have either catalytic or inhibitive effects on the dehydrogenation of LiAlH<sub>4</sub>, which were concentration dependent. The in-situ XRD analysis confirmed the catalytic power of Pd or Pt decorated MWCNTs and the corresponding dehydrogenation reaction pathway of LiAlH<sub>4</sub>. The TGA results showed that both Pd and Pt decorated MWCNTs acted not only as a catalyst for LiAlH<sub>4</sub>, but also a hydrogen absorber.

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## Introduction

Lithium aluminum hydride (LiAlH<sub>4</sub>) is a promising complex metal hydride used for solid state hydrogen storage due to its high gravimetric hydrogen density. The dehydrogenation reactions and the corresponding temperatures of LiAlH<sub>4</sub> are as follows [1–4]:



The theoretical amount of hydrogen released from LiAlH<sub>4</sub> resulting from both the first and the second dehydrogenation reactions is 7.9 wt%. Nevertheless, the dehydrogenation temperature of the LiAlH<sub>4</sub> is still far from the target operation temperature set by the U.S. Department of Energy (DOE) [5]. Therefore, a number of studies have aimed to develop catalysts to improve the dehydrogenation properties (such as operation temperature and reaction kinetics) of LiAlH<sub>4</sub>. Some of the effective catalysts are carbon nano materials, such as carbon nano-fibers (CNFs) [6,7], single-walled carbon

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nanotubes (SWCNTs) [8] and multi-walled carbon nanotubes (MWCNTs) [9–11]. These carbon nano-materials have been confirmed to possess the property of nano-confinement [12–16], have destabilization effects [17–19] and are able to serve as effective forms of transit that provide an efficient pathway for hydrogen diffusion [20]. Moreover, the electron affinity of carbon materials can affect the H-removal energy during dehydrogenation reactions [21]. Previous studies have shown that the addition of MWCNTs would modify the thermodynamic and kinetic properties of  $\text{LiAlH}_4$ , lowering its dehydrogenation temperature to as low as  $120^\circ\text{C}$  [11].

It has been reported that MWCNTs is a promising solid state hydrogen storage material if decorated with Pt or Pd [22–28]. The Pd or Pt decorated MWCNTs can absorb up to 2.7 wt% of hydrogen at room temperature under 7 MPa of hydrogen pressure [28]. The “spill-over” effect induced by the decorated metal particles provides an efficient pathway for hydrogen molecules to dissociate and the atoms to diffuse in and out of the carbon material [22,29,30].

Since MWCNTs can serve as an effective catalyst for the dehydrogenation of  $\text{LiAlH}_4$ , it is of interest to examine whether the decoration of Pt or Pd can further affect the catalytic power. A recent study proposed decorating Fe, Ni and Pd nano-particles on carbon nano-materials to produce an effective catalyst for dehydrogenation of  $\text{LiAlH}_4$  [31]. The aim of the current study is to further clarify the effects of Pd or Pt decorated MWCNTs on the dehydrogenation behavior of  $\text{LiAlH}_4$ , and especially the catalytic and/or inhibitive effects. Using a chemical reduction method, both Pd and Pt particles can be successfully decorated on MWCNTs. Thermogravimetric analysis (TGA) was utilized to reveal the dehydrogenation behaviors of  $\text{LiAlH}_4$  with various additions of Pd or Pt decorated MWCNTs. *In-situ* XRD analysis was used to identify the reaction pathways of the dehydrogenation reactions.

## Experimental procedure

### Sample preparation

The Pt and Pd particles were decorated separately on MWCNTs (purity > 95%, outer diameter 20–30 nm; length 5–15  $\mu\text{m}$ , Uni Region, Bio-Tech) by a chemical reduction process. First, 0.3 g of MWCNTs was successively immersed in 0.31 M  $\text{SnCl}_2$  (Merck, >99%) and 1.4 mM  $\text{PdCl}_2$  (Seedchem, >95%) solution and subjected to ultrasonic vibration (Ultrasonic Steri-Cleaner LEO-150; 150 W, 46 kHz) for 10 and 2 min, respectively, for the sensitization and the activation processes. The activated MWCNTs were then added into 150 mg/L of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Acros Organics, 99.9%) or palladium bis-hexafluoroacetylacetonate ( $\text{Pd}(\text{hfa})_2$ ), (Strem Chemicals, 95%) solution, with methanol as the solvent. Borane-dimethylamine complex (DMAB, Acros Organics, 98%) was used as a reducing agent. By slowly adding an adequate amount of DMAB into  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{Pd}(\text{hfa})_2$  solutions, the  $\text{Pt}^{4+}$  and  $\text{Pd}^{4+}$  ions were reduced to form Pt and Pd particles, respectively, and precipitated on MWCNTs.

The treated Pt or Pd decorated MWCNTs (hereafter referred as MWCNTs/Pt or MWCNTs/Pd) were later cleansed by

methanol through a centrifugal sedimentation process and then vacuum dried for 12 h.

The vacuum dried MWCNTs/Pt or MWCNTs/Pd with specific contents (0–20 wt%) was admixed with lithium alanate ( $\text{LiAlH}_4$ , Chemetall, 97% purity) and sealed in a 75 ml stainless steel vessel for milling and mixing treatment. The stainless steel balls contained in this vessel had an average diameter of 4.8 mm. The ball to powder weight ratio was maintained at 10:1. The above sample loading process was carried out in a  $\text{N}_2$  purified glove box. The sealed stainless steel vessel was then cooled in liquid  $\text{N}_2$  before ball milling. The ball milling was performed in a ball milling machine (SPEX 800) at 1700 rpm for 10 min. The cooling and milling processes were repeated three times to ensure full mixing of the powders.

### Thermal dehydrogenation analysis

The dehydrogenation behavior of the  $\text{LiAlH}_4$  admixed with MWCNTs/Pd or MWCNTs/Pt was evaluated by thermogravimetric analysis (TGA) with a high pressure microbalance (Cahn D-110). The sample with an initial weight of ca. 200 mg was loaded in a quartz crucible and transferred into a high pressure chamber. The chamber was evacuated to  $1 \times 10^{-4}$  torr, followed by charging  $\text{H}_2$  gas (99.99% purity) to ambient pressure. As soon as the microbalance system stabilized, heating processes were applied. Two heating processes were adopted in this study, namely (1) continuous heating from room temperature to  $350^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$ , and (2) isothermal heating at  $140^\circ\text{C}$  for 10 h, respectively. The weight change of the sample was continuously measured during each heating process. The weight percentage of hydrogen released from each sample at the specific temperature was then calculated.

### Material characterization

The morphological aspects of MWCNTs/Pt, MWCNTs/Pd and  $\text{LiAlH}_4$  admixed with MWCNTs/Pt or MWCNTs/Pd were examined by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The chemical compositions of MWCNTs/Pt and MWCNTs/Pd were analyzed by an energy dispersive spectrometer (EDS). The transition of the crystal structure during the dehydrogenation reaction was identified by *in-situ* synchrotron X-ray diffraction (*in-situ* XRD) employing beamline 17A, at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. To perform *in-situ* XRD analysis, the sample was first loaded in a 0.5 mm diameter glass capillary tube, and then mounted to the specimen holder.  $\text{N}_2$  gas was introduced at one end of the capillary tube to form a protective atmosphere. The sample was heated from room temperature to  $350^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$  with a hot air blower. During heating, the sample was repeatedly exposed to the synchrotron X-ray with a wavelength of  $1.033105 \text{ \AA}$  at intervals of 240 s. The 2-D diffraction patterns were collected continuously and converted to 1-D patterns by Fit2D software [32]. The transition of the crystal structure during the heating process was thus analyzed.

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