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Hydrogen storage properties of various carbon supported $NaBH_4$ prepared via metathesis

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ABSTRACT

Sodium borohydride nanoparticles prepared via the metathesis reaction between $LiBH_4$ and NaCl were successfully deposited on various carbon supporting materials such as graphite, graphene oxide and carbon nanotubes. The X-ray diffraction analyses were conducted to identify the phase of $NaBH_4$ deposited on various carbon supporting materials. The transmittance electron micrograph analyses were also conducted to investigate the particle size and dispersion of $NaBH_4$ within carbon supporting materials. The particle size and size distribution of $NaBH_4$ on graphite were observed to be larger and broader than of other two supporting materials, graphene oxide and CNT due to the lower surface energy as compared to GO and CNT. The bonding state of $NaBH_4$ was confirmed by the Fourier-transformed infrared spectroscopy analysis. The TG and PCT results show that the hydrogen desorption of the $NaBH_4$ deposited on carbon supports takes place at temperature (130 °C~) significantly lower than that of pure $NaBH_4$ (above 500 °C) and the amount of desorption was in the order of graphene oxide (12.3 mass %) > CNT (9.8 mass %) > graphite (5.7 mass %). The reversibility of hydrogen adsorption after five cycles of adsorption-desorption showed that $NaBH_4$/GO and $NaBH_4$/CNT were much better than that of pure $NaBH_4$ due to excellent structural stability.

Introduction

The global energy demand is continuously increasing as a result of economic development. Fossil fuels are a depleting resource, and the risks involved with nuclear power generation are considered a threat due to the recent incident in Fukushima, Japan. Research into the development of safe and environmentally friendly renewable energy has therefore intensified significantly. Hydrogen has been considered as an energy carrier for the storage of renewable energy, as it has a high energy density and no harmful emissions; it is an encouraging alternative to conventional energy sources,

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although a number of technical challenges must first be overcome. Currently, hydrogen storage technology involves either compressing hydrogen gas with up to 900 bar of pressure, or liquefying hydrogen at $-251\ ^\circ C$ in super-insulated cryotanks. However, the energy (in)efficiency and safety risks, together with a volumetric hydrogen density limit of less than 30 kg/m^3, are major drawbacks of the currently used systems. Therefore, hydrogen storage research is currently focused on hydrogen sorption within materials in order to provide a safe, stable, efficient, and hydrogen dense storage [1–6].

Hydrogen storage materials include metal hydrides and complex hydrides, which have the advantage of high volumetric hydrogen density and stability. Complex hydrides are hydrogens covalently bound to anions such as alanates (Al), amides (N), or borohydrides (B). The borohydrides contain up to 20% by mass of hydrogen in some stable compounds. Sodium borohydride ($NaBH_4$) is an interesting compound in this regard, especially due to its high hydrogen storage capacities (up to 10 wt%), low toxicity, and the release of high purity hydrogen [7–13]. However, $NaBH_4$ has a high enthalpy for hydrogen release and a significant activation energy for the re- and dehydrogenation reactions. Furthermore, the hydrogen desorption reaction leads to several phases that tend to separate and prevent rehydrogenation of $NaBH_4$. Various attempts have been made to solve these problems, such as: the synthesis of a nanostructured hydride in order to improve the dehydrogenation/rehydrogenation reaction rate and reversibility [14–18]; and the changing of properties by encapsulation of the hydride particles in a nanoporous substrate [19,20].

Nanostructured and nanosized materials greatly reduce the thermodynamics and kinetics of hydrogen uptake and desorption by reducing the diffusion length, therefore increasing the reaction rate. Nanostructured materials also have several advantages; they have a large surface area, and demonstrate physisorption, rapid kinetics, low temperature desorption, hydrogen dissociation, and molecular diffusion along the surface [21]. However, the high reactivity of the nanosized materials often results in particle agglomeration. Agglomeration can be prevented in structured nanomaterials by the use of various supports [22,23]. Carbon has been reported to be a suitable support material for nanosized hydrides; the carbon support stores hydrogen with a low enthalpy through physisorption [24–27], and may be decorated with hydrides containing chemisorbed hydrogen. Therefore, the combination of carbon and hydrides leads to an increased overall hydrogen content [28,29]. It is of great importance to obtain a uniform size distribution of the hydride on the support to achieve well defined properties of the hydrides. Recently, Li et al. [30] reported that a uniform size could be obtained by direct synthesis of $NaBH_4$, utilizing the self-printing method.

In this study, $NaBH_4$ nanoparticles were directly formed on a carbon support by the metathesis reaction between $LiBH_4$ with NaCl. Various carbon supports such as graphite, carbon nanotubes (CNTs), and graphene oxide (GO) were used to investigate the effect of the size and dispersion of $NaBH_4$ on hydrogen storage capacity. In addition, the possibility of lowering the hydrogen desorption temperature and reversibility arising from the interactions between carbon support and $NaBH_4$ nanoparticles was investigated.

Experimental

Preparation of $NaBH_4$ and carbon support particles

At a 1:1 M ratio, $LiBH_4$ (95%, Sigma-Aldrich, USA) and NaCl (99.9%, Sigma-Aldrich, USA) were mixed with various carbon supports at a mass ratio of 10:1 under an argon atmosphere by ball milling. $NaBH_4$ nanoparticles were synthesized according to the reaction: $LiBH_4 + NaCl \rightarrow NaBH_4 + LiCl$. Ball milling was performed at 400 rpm in a planetary ball mill for 10 h [30]. The four types of carbon support used were graphite (Timcal, Ltd., Switzerland), as-prepared GO [31], and CNTs (95.0%, Plasmachem, USA). A schematic of the synthesis process of $NaBH_4$ particles on the carbon support is shown in Fig. 1. The metathesis reaction is below.

$$\mathrm{NaCl}(\Delta G = -384.05\mathrm{kJ/mol}) + \mathrm{LiBH_4}(\Delta G = -124.77\mathrm{kJ/mol}) \rightarrow \mathrm{NaBH_4}(\Delta G = -127.11\mathrm{kJ/mol}) + \mathrm{LiCl}(\Delta G = -384.05\mathrm{kJ/mol}):$$
$$\Delta G = -2.34\mathrm{kJ/mol}$$

Characterization

$NaBH_4$ nanoparticles deposited onto various carbon supports were structurally characterized by powder X-ray diffraction (XRD, Bruker D8) with CuK_α radiation (40 kV and 40 mA); the size of the $NaBH_4$ nanoparticles was identified. Changes to the chemical bonds upon the reaction were investigated by Fourier-transform infrared spectroscopy (FTIR, Spectrometer Spectrum Two, PerkinElmer). The hydrogen desorption reaction was followed by thermogravimetric analysis (TGA, Model 8000, PerkinElmer) at a heating rate of $5\ ^\circ C\ min^{-1}$ under N_2 flow. The particle size, morphology, and dispersion of $NaBH_4$ nanoparticles were investigated by high resolution transmission electron microscopy (TEM, FEI Tecnai G2 Spirit Twin). The sample was prepared by mixing 0.01 g of each sample in 1 ml tetrahydrofuran (THF, Fisher chemical, UK) for 30 min by sonication and dispersion on a carbon grid type-B. XPS was performed at with a Mg X-ray source and a hemispherical analyzer (Phoibos 100, SPECS), at a passing energy of 20 eV for the narrow scans. The samples are conductive thus no charging correction is needed.

Hydrogen ab- and desorption flow measurements

The adsorption/desorption flows of samples were identified by pcT mass flow measurements using a manual advanced

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