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Mechanochemical synthesis and XPS analysis of sodium alanate with different additives

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Abstract

$NaAlH_4$ was mechanochemically synthesized under high hydrogen pressure. Additives can be added to $NaAlH_4$ directly during the milling process. In situ monitoring of the pressure and temperature was used to provide an insight into the reactions occurring in the vial during synthesis—a process so far based purely on empirical considerations. This method was then applied to directly compare different additives during synthesis. The following trend was obtained for the effectiveness of the additives: $TiCl_3 > CeCl_3 > ScCl_3 \gg Ti$. This trend was also verified for desorption by differential scanning calorimetry and by monitoring decomposition at room temperature during long-term storage. In addition, the direct comparison by X-ray photoelectron spectroscopy of the chemical state of the additive after milling illustrated indirectly the importance of the reduction of the chloride—and the formation of NaCl—during synthesis. These reactions can be linked to the formation of vacancies necessary for fast diffusion of hydrogenated species within the material.

Keywords: In situ characterization; Complex hydrides; Hydrogen storage; Mechanochemical synthesis; X-ray photoelectron spectroscopy

1. Introduction

Hydrogen as energy carrier appears as an attractive solution for the development of new sustainable energy sources. The establishment of a hydrogen economy requires safe and reliable storage such as solid-state storage in lightweight hydrides [1]. Complex hydrides have attracted much interest in recent years because of their large hydrogen storage capacities (e.g. $LiBH_4$ can store up to 18 wt.% H_2) [2–5]. Among the complex hydrides, $NaAlH_4$ has been widely studied since Bogdanovic and Schwickardi [6] discovered its reversibility at moderate temperatures using $TiCl_3$ as additive (see reactions (1) and (2) below). Note that the decomposition of NaH is usually not considered for practical applications because it requires very high temperature.

$$NaAlH_4 \leftrightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \quad (1)$$

$$\leftrightarrow NaH + Al + \frac{3}{2}H_2 \quad (2)$$

Early studies on $NaAlH_4$ involved complicated multi-step chemical processes for the synthesis of $NaAlH_4$ with $TiCl_3$ as additive. Later, ball milling was proven to enhance the desorption kinetics of sodium alanate and facilitate rehydrogenation under moderate pressures [7,8]. This technique was also used to mix efficiently different additives with $NaAlH_4$ [9]. The beneficial influence of high hydrogen pressure during reactive ball milling was demonstrated for the synthesis of magnesium hydrides [10]. Bellosta von Colbe et al. [11] succeeded in synthesizing catalyzed $NaAlH_4$ in one step by milling of NaH, Al and $TiCl_3$ under ~80 bar H_2. In this case, the mechanochemical synthesis occurs at room temperature because of the creation of highly reactive fresh surfaces and new interfaces during the continuous fracture/cold-welding processes [12,13]. These conditions facilitate the adsorption and dissociation of

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hydrogen molecules on the surfaces of the particles. In addition, the diffusion of hydrogen inside the particles is promoted by the defects that appear during milling and by the reduction in particle size.

In addition to the development of new synthesis techniques, much work has been done on the screening of suitable additives. The use of pure Ti was put forward by Wang et al. [14,15] to avoid the formation of by-products such as NaCl and therefore to maintain a high gravimetric capacity. A variety of chloride compounds were also tested by Anton [16] who milled the additive together with $NaAlH_4$ for 15 min. The highest reaction rates were obtained for Ti(III) and Ti(IV). Nevertheless, current understanding of the reaction mechanism and of the detailed role played by the additive is limited. Most recently, it has been shown that the use of $ScCl_3$ and $CeCl_3$ leads to improved kinetic and cycling properties [17–19]. The synthesis of $NaAlH_4$ with these additives has been recently proposed by high-pressure ball milling but no direct comparison of the different additives has so far been reported.

In this paper, the one-step mechanochemical synthesis of $NaAlH_4$ with different additives and using reactive ball milling is described. The millings were performed under H_2 pressures between 10 and 140 bar. Monitoring of the pressure and temperature during milling provided insights into the reactions occurring during mechanochemical synthesis, which has been so far—though very widely used for a large variety of functional materials—a purely empirical process. It is demonstrated how this information can be used to effectively screen different additives for $NaAlH_4$. In addition, X-ray photoelectron spectroscopy (XPS) helps to shed light on the differences in the chemical state of the various additives. From these results, we report experimental support for the catalytic mechanism of $NaAlH_4$ proposed by first-principles calculations.

2. Materials and methods

2.1. Synthesis by high-pressure reactive milling

NaH (Aldrich, 95%) and Al (MaTeck, $-100+200$ mesh) powders (1:1) were mixed with 4 mol.% of additive powder. The mixture was reactively ball milled under H_2 (grade 5.0) in a planetary monomill Fritsch Pulverisette P6. The additives were $TiCl_3$ (Aldrich, 99.999%), $ScCl_3$ (Aldrich, 99.9%), $CeCl_3$ (Alfa Aesar, 99.9%) or Ti (Alfa Aesar, 99.9%, −150 mesh). Millings of NaH and Al without additive and of pure Al were also performed for 5 h for comparison. The milling parameters are summarized in Table 1. A specially designed "intelligent" vial (Evicomagnetics) was developed to operate in a pressure range of 1–150 bar for various gases. This vial is designed for in situ monitoring of the temperature and pressure during milling by using a gas-temperature measurement system integrated into the vial lid. Powder handling was done in argon atmosphere inside a glovebox with oxygen and water content less than 1 ppm.

2.2. Materials characterization

The characterization of the as-milled samples was carried out by X-ray diffraction (XRD) analysis using a Philips 1050 diffractometer (Co K_α radiation). The samples were covered by a Kapton® foil to avoid any contact with air during the measurements. Differential scanning calorimetry (DSC) measurements were performed using a Netzsch apparatus (DSC 204 HP Phoenix), which was placed inside a dedicated glovebox under argon. The heating rate was fixed at 5 K min^{-1} for all the samples and the measurements were performed under 3 bar Ar. XPS analysis was carried out on as-milled samples using a PHI 5600 CI apparatus (Physicals Electronics) using a monochromatic Al K_α source (1486.6 eV) and operating under high vacuum (3×10^{-10} mbar). The powder was placed in a molybdenum sample holder inside the glovebox and transferred without contact with air inside the XPS apparatus using a closed chamber. Hydrocarbon contamination was too low in the sample to use the C 1*s* line as internal calibration, and therefore we calibrated the spectra using the Cl $2p_{3/2}$ line at 200.7 eV as reference [20]. High-resolution scans were performed on Ti 2*p*, Sc 2*p* and Ce 3*d* binding energy regions. Analysis of the sample under the surface was done after ion beam sputtering of the surface (Ar^+, 1.5 keV, 2.4 μA) for 17 min.

3. Results and discussion

3.1. Synthesis by high-pressure reactive ball milling

3.1.1. Energy input during milling

The first attempt to prepare $NaAlH_4$ in a one-step reaction was done using $TiCl_3$ as additive. The initial milling parameters (milling type 1) are given in Table 1. The

Table 1
Summary of the milling parameters used in this study.

Milling type	Compound	Balls number (diam.)	BPR[a]	p (H_2) (bar)	Rotational speed (rpm)
1	NaH + Al + 4 mol.% $TiCl_3$	7 (15 mm)	50/1	110	500
2	NaH + Al + 4 mol.% $TiCl_3$	37 (10 mm)	50/1	110	550
3	NaH + Al + 4 mol.% $TiCl_3$	37 (10 mm)	50/1	10, 50, 100, 140	550
4	NaH + Al + 4 mol.% $TiCl_3$, Ti, $ScCl_3$ or $CeCl_3$	37 (10 mm)	50/1	100	550

[a] Ball-to-powder ratio.