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Direct synthesis and NMR characterization of calcium alanate

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Abstract

In this work, we present a new synthesis path and characterization results of the alanate, $Ca(AlH_4)_2$. We have synthesized for the first time, calcium alanate, directly from starting mixtures of AlH_3 and CaH_2 using mechanosynthesis. $Ca(AlH_4)_2$ has been identified using magic angle spinning nuclear magnetic resonance (MAS-NMR) and Fourier transform infrared (FTIR) measurements.

Keywords: Hydrogen storage materials; Mechanochemical synthesis; Nuclear resonances

1. Introduction

Complex hydrides have recently shown promise for high gravimetric densities beyond those of traditional metal hydrides, and those that are composed of light elements are of particular technological interest. Calcium alanate is one such system as it has a total capacity of 7.8 wt.% hydrogen. However, dehydrogenation takes place over several steps, and only the first two reactions can be considered for practical applications. These reactions are listed below with the approximate temperature indicated [1].

$$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + 1.5H_2 \qquad (200\,^{\circ}C) \qquad (1)$$

$$CaAlH_5 \rightarrow CaH_2 + Al + 1.5H_2 \qquad (260\text{–}550\,^{\circ}C) \qquad (2)$$

$$CaH_2 \rightarrow Ca + H_2 \qquad (600\text{–}700\,^{\circ}C) \qquad (3)$$

If we consider the first two reactions (which occur at technologically viable temperatures), 5.9 wt.% hydrogen would be released.

Historically, calcium alanate was first synthesized in THF following the reaction ($4CaH_2 + 2AlCl_3 \rightarrow Ca(AlH_4)_2 + 2CaCl_2$) [2,3]. In those works, attempts to purify the alanate were unsuccessful. While little interest has been shown in this compound since the initial work, more recent work has studied alternative synthesis paths. Wet chemical synthesis under inert processing conditions has been the recent approach to producing nearly pure calcium alanate. Typically, a solvent adduct is first formed, $Ca(AlH_4)_2 \cdot x$ (solvent) (solvent = THF, DEE, ...) [4–8], the solvent is then removed by moderate heating under vacuum. Mechanochemical synthesis [8] has also been reported using mixtures of $NaAlH_4$ and $CaCl_2$. This approach also results in the successful synthesis of calcium alanate but NaCl is present as a by-product.

The structure of the solvent adducts has been determined using monocrystal X-rays diffraction [5] while the structure of the nearly pure calcium alanate, once the solvent has been removed, could not be solved. Attempts have been made through the use of DFT calculations to suggest different hypothetical structures [9]. The most stable of these proposed structures was found to be similar to the CaB_2F_8 structure (space group *Pbca*).

The focus of this paper is to present a new simple synthesis path for calcium alanate by the mechano-reaction of CaH_2 and AlH_3, and the characterization of the products using IR and NMR methods.

2. Experimental

The synthesis of calcium alanate was performed using both the metathesis reaction (Eq. (4)) [8] or the direct synthesis (Eq. (5)) for the first time using

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ball-milling technique.

$$2\,LiAlH_4 + CaCl_2 \rightarrow Ca(AlH_4)_2 + 2\,LiCl \quad (4)$$

$$2\,AlH_3 + CaH_2 \rightarrow Ca(AlH_4)_2 \quad (5)$$

For the first synthesis path, a mixture of 2.27 g of anhydrous $CaCl_2$ (Alfa Aesar, 96%) and 1.518 g of $LiAlH_4$ (Alfa Aesar, 95%) were used without further purification. These compounds were placed in an 80 mL steel vessel, with five 0.5 in. diameter steel balls. The vessel was sealed using a rubber gasket in an Argon glove box. The Argon filled vessel was then placed in a Fritsch-pulverisette 6 planetary mill. The mixture was subsequently milled at 500 rpm for either a continuous 3 h mix, or for a 3 h mix during which the system was allowed to cool for 5 min every 15 min. We did not notice significant differences between those two procedures.

For the second path, a mixture of 0.618 g of CaH_2 (Alfa Aesar, 98%) and 0.882 g of AlH_3 was ball-milled in the same set up than previously at different speeds (from 200 to 500 rpm) and different times (from 1 to 10 h). We used α-AlH_3 originally synthesized by the Dow Chemical Company in the early 1970s and provided by Brookhaven National Laboratory.

Solid state FTIR spectra were recorded using a Nicolet 860 Magna series FTIR spectrometer, under ambient conditions and in air over the range 400–4000 cm^{-1}.

Solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) measurements were performed using a Bruker Avance 500 MHz spectrometer equipped with a Bruker 4 mm CPMAS probe. MAS-NMR samples were loaded in a 4 mm ZrO_2 rotor and sealed with a tightly fitting kel-F cap inside an Argon glove box in order to avoid any contact with air. The spectral frequencies were 500.23 and 130.25 MHz for ^{1}H and ^{27}Al nuclei, respectively. A typical MAS spectrum was recorded under MAS spinning rate of 12–14 kHz after a short (0.3 μs ∼ 8° pulse) single pulse at room temperature using either dried N_2 or air. Use of compressed air was found not to be influential in our experimental setup. NMR shifts were externally referenced to 1.0 M of $Al(NO_3)_3$ aqueous solution at 0 ppm for ^{27}Al nucleus.

3. Results and discussion

Wet chemistry routes can lead to calcium alanate formation. However, the real formulation of the synthesized compound is $Ca(AlH_4)_2 \cdot x$ (solvent). Some solvent always remains within the structure in the as synthesized product and subsequent extraction of the solvent is difficult to achieve without alanate decomposition. A narrow temperature window is generally necessary to purify the compound without decomposition [4,5], making reproducible synthesis difficult. Therefore, a simple and straightforward “dry” method without by product is of great interest because potential candidates for hydrogen storage such as the calcium alanate and other complex hydrides are typically synthesized using solvents.

In this work, a new synthesis path for calcium alanate formation has been accomplished using mechanically milled mixtures of calcium hydride and aluminium hydride in stoichiometric proportions (Eq. (5)). Different parameters have been used for the mechano-synthesis including milling speed and duration. The products have been characterized using FTIR and ^{27}Al MAS NMR.

As a baseline for our spectroscopic results, we have used calcium alanate prepared using the mechano-chemical metathesis reaction of $LiAlH_4$ and $CaCl_2$. The final products are a mixture of the calcium alanate with LiCl. ^{27}Al NMR and FTIR spectra are presented in Figs. 1 and 2, respectively. The shift in the NMR spectrum at 105.6 ppm corresponds to previously reported values for calcium alanate, and is in good agreement with reported NMR data [8]. $LiAlH_4$ and $NaAlH_4$ spectra are also shown in Fig. 1 for comparison. The peak of the lithium alanate (95.8 ppm), used as starting material, is clearly distinct from the calcium alanate peak, and is not evident in the final product spectrum. The FTIR spectrum consists mainly of two wide bands, of which the ∼1800 cm^{-1} band corresponds to the Al–H vibrations. Again, our data are consistent with previously reported values [5,8]. X-ray diffraction indicated the presence of LiCl peaks but the quality of the diffractogram did not allow for further conclusions on a possible alanate structure.

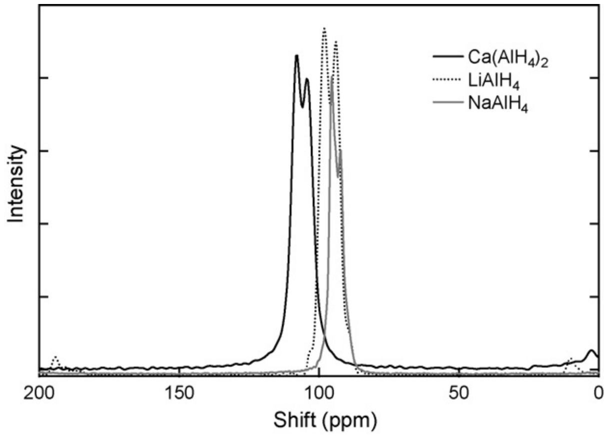

Fig. 1. ^{27}Al NMR spectra of the calcium alanate (105.6 ppm) obtained with the metathesis reaction, compared with $LiAlH_4$ (95.8 ppm) and $NaAlH_4$ (92.9 ppm).

IR data are presented in Fig. 1 for the alanate prepared by direct synthesis. The position of the different bands compares well with the metathesis reaction IR data. However, IR data do not allow us to clearly differentiate calcium alanate peaks from those of aluminium hydride, which might be among the final products if the reaction is not complete. Thus, NMR data are also important in order to distinguish the two phases. These are presented in Fig. 3 for a selection of syntheses prepared at

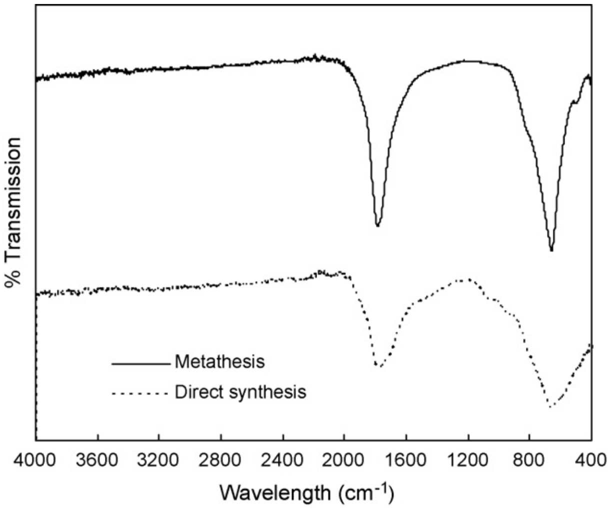

Fig. 2. FTIR spectra of the metathesis reaction products (black line) and the direct synthesis products (dotted line). We can note the similarities. The band around 1800 cm^{-1} corresponds to the Al–H bonds vibrations.

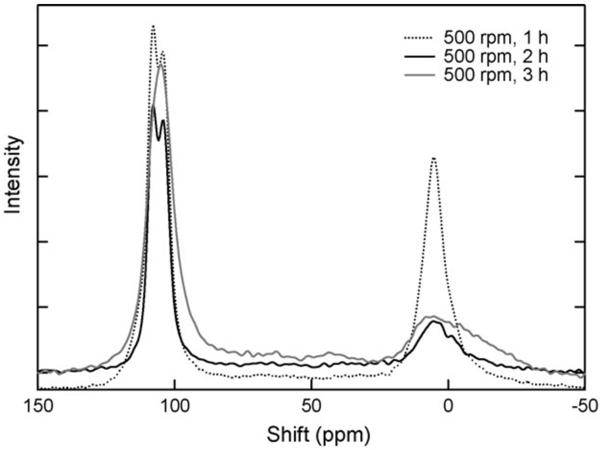

Fig. 3. ^{27}Al NMR spectra of the direct synthesis reaction products for different ball-milling times at 500 rpm: 1 h (dotted line), 2 h (black line) and 3 h (grey line).

Table 1
Parameters used for direct synthesis and effect on the ratio of the final products

Parameters	Ratio $Ca(AlH_4)_2/AlH_3/Al$
500 rpm, 1 h	1/0.73/0.01
500 rpm, 2 h	1/0.37/0.015
500 rpm, 3 h	1/0.36/0.03

500 rpm using various ball-milling time (1, 2 and 3 h). In contrast to the metathesis reaction, two peaks appear at ∼105.2 ppm and ∼6 ppm, corresponding to the calcium alanate and an aluminium hydride, respectively. The latter is clearly identified as α-AlH_3, in agreement with NMR work reported in the literature [10]. We also note the presence of a weak intensity peak at around ∼1600 ppm corresponding to aluminium metal. This aluminium metal can either come from the α-AlH_3 that is partly decomposed or from the decomposition during the ball-milling. Nevertheless, when reasonable times of ball-milling are used, the ratio of aluminium metal in the final product is negligible.

The relative peak area by integrating the different peaks that contribute to the spectra can be calculated. In this way, we can determine the ratio between each species that contains aluminium. The results for different syntheses are presented Table 1. With the Dow Chem α-AlH_3, the best synthesis (i.e. highest ratio for calcium alanate), is obtained when the 500 rpm speed is used for 2 h. We note improvement compared to that of the 1 h ball-milled sample at the same speed. We note also that longer milling time (3 h total) does not improve the reaction. We note a small decrease in the proportion of calcium alanate and, in parallel, slightly more aluminium metal is observed. If the time of ball-milling is increased up to 6 h at the same speed, the calcium alanate phase decomposes almost completely.

While we are exploring other parameters in order to improve the alanate ratio, we note that so far, the use of lower milling speed and longer ball-milling have not improved the reaction ratio. Also, very low speeds (200 rpm) with up to 10 h milling time led to no reaction.

4. Conclusion

We have synthesized the calcium alanate, $Ca(AlH_4)_2$ for the first time by direct synthesis using CaH_2 and AlH_3 ball-milled together. The compound was characterized by means of NMR and FTIR. The synthesis using freshly made α-AlH_3 can potentially improve the reaction rate and this work is currently in progress.

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