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Structural phase transitions and adduct release in calcium borohydride

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ABSTRACT

$Ca(BH_4)_2$ compounds were investigated above room temperature by anelastic spectroscopy (AS) and concomitant measurements of thermogravimetry and mass spectrometry (TGA/MS). Both AS and TGA/MS indicate that even after a thermal treatment at 125 °C for 20 h, a non-negligible residual of THF adduct is still present in the sample, which can be removed on a subsequent thermal treatment at temperatures lower than 250 °C. Above 250 °C dehydrogenation takes place. Moreover, AS sensitively detects the occurrence of the $\alpha \rightarrow \alpha'$ structural phase transition around 180 °C, and the $\alpha' \rightarrow \beta$ transformation, which is completed around 330 °C. We also show that both transitions are irreversible and are not accompanied by a latent heat.

1. Introduction

Calcium borohydride, $Ca(BH_4)_2$, has recently attracted much attention as a promising complex hydride for solid state hydrogen storage. Indeed it possesses a theoretical gravimetric hydrogen density of 11.5 mass% and a volumetric hydrogen density of $\sim$130 kg m^{-3}. Moreover, at least a partial rehydrogenation of the decomposition products have been reported [1,2].

Many procedures to synthesize $Ca(BH_4)_2$ have been exploited and most of them leave adducts in the material. Depending on the synthesis and on the procedure to remove the adduct, $Ca(BH_4)_2$ can assume a variety of crystal structures, which change as a function of temperature [3,4]. In the case of the commercially available $Ca(BH_4)_2{\cdot}2THF$ produced by Sigma–Aldrich, the adduct can be removed by means of a thermal treatment around 160 °C in vacuum for a time which, depending on the authors, can last between 1 [5] and 72 h [4]. X-ray diffraction measurements show that on heating the adduct-free powder above room temperature, two structural phase transitions are observed [4]. Indeed, with increase of T the cell parameters a and c of the α-phase approach each other, and at $\sim$220 °C, a second order $\alpha \rightarrow \alpha'$ transition takes place resulting in a tetragonal α'-phase of space group I-42d, a supergroup of F2dd. On further heating, the α' phase progressively transforms into the β phase and at 320 °C only the latter is present [4].

In the present paper we report a study of the structural phase transitions above room temperature conducted with anelastic spectroscopy measurements. In addition, combined experiments of thermogravimetry, differential thermal analysis and mass spectrometry suggest the possible presence of THF in commercial $Ca(BH_4)_2$ even after a thermal treatment, which was expected to remove the adduct.

2. Experimental

To prepare pure $Ca(BH_4)_2$, $Ca(BH_4)_2{\cdot}(THF)_2$ was purchased from Sigma–Aldrich, and extraction of THF was accomplished by a thermal treatment in vacuum at 125 °C for 20 h. Such temperature was chosen because different polymorphs of $Ca(BH_4)_2$ can be obtained by modifying the reaction conditions. If the sample is heated at temperatures below $\sim$130 °C for a few hours, a significant amount of α-$Ca(BH_4)_2$ will be formed; on the contrary, by thermal treatments at higher temperature one obtains only the β structural phase. Therefore, in order to study the structural phase transition from the α to the β phase we chose the particular thermal treatment previously described. XRD measurements excluded the presence of THF in the treated sample, at least within the sensitivity of this technique (a few percent). We found that the distribution of polymorphs was approximately $\sim$25% α-phase and $\sim$75% β-phase.

Concomitant measurements of thermogravimetry (TGA), differential thermal analysis (DTA) and mass spectrometry (MS) were performed by means of a Setaram Setsys Evolution 1200 TGA System coupled through vacuum components to a Pfeiffer Prisma analyzer, maintained at a pressure lower than 10^{-4} mbar by a differential

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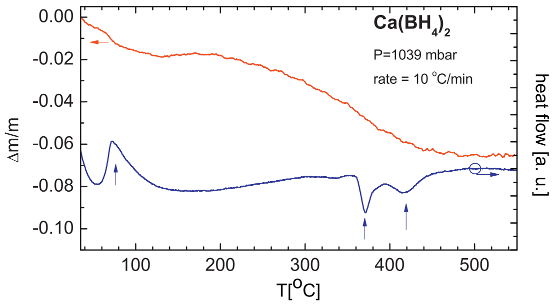

Fig. 1. Relative mass variation and heat exchange of $Ca(BH_4)_2$ heated at atmospheric pressure at 10 °C/min.

pumping. In order to identify all possible gaseous products, survey scans in the mass range 1–100 amu were recorded during the TGA/DTA measurements. After mounting the sample in a Al_2O_3 crucible, the system was evacuated and flooded with high purity argon. All DTA–TGA data were collected on ∼3–7 mg of powder during heating above room temperature.

The consolidated samples necessary to carry out anelastic spectroscopy measurements were obtained by pressing the powders in a die at pressure lower than 2 kbar, following a successful procedure recently introduced to study complex hydrides [6–10]. The samples were shaped as rectangular bars 40 mm long, 5 mm wide and 0.7–1.5 mm thick. All the material handling was performed in a glove bag in flowing argon atmosphere to avoid formation of oxides and hydroxides and to prevent reactions with oxygen or water vapour.

Anelastic spectroscopy measurements are conducted suspending the samples on thin wires located at the nodal lines of flexural vibration modes, and electrostatically exciting their corresponding mechanical resonances. The measurement of the dynamic Young modulus E' is obtained from the angular vibration frequency

$$\omega^2 = kE'/\rho, \qquad (1)$$

where ρ is the mass density, and k a numerical factor depending on the sample geometry [11]. The elastic modulus is extremely sensitive to the formation of new phases or of atomic complexes in materials, and it has been shown that its measurement allows the monitoring of the evolution of phase transitions [12] or chemical reactions [6–10,13] as a function of temperature and time. A phase transformation is usually revealed by a slope variation or a jump of the Young modulus at the transformation temperature.

3. Results and discussion

3.1. TGA–DTA–MS measurements

TGA–DTA experiments at ambient pressure, performed in an argon atmosphere with a temperature rate of 10 °C/min are reported in Fig. 1.

Measurements show that upon heating, calcium borohydride looses about 2% of its initial mass below ∼150 °C, and displays an exothermic peak in the heat flow. Due to the presence of the argon atmosphere, the concomitant mass spectrometry measurements were not conclusive to determine the gaseous species released during this first stage of the decomposition of $Ca(BH_4)_2$. For this reason the TGA measurement was repeated in vacuum in the range of 10^{-4} mbar. In this condition the mass spectrometer recorded effusion of THF between 60 °C and 220 °C (Fig. 2), with a consequent decrease of the initial mass of about 5%. It should be noted that THF has several fragments which can be observed in the mass spectrometry measurements (m/Z = 71,72, 41, 42); in particular, one of them is located at $m/Z = 2$, not to be confused, however, with effusion of hydrogen from the sample. The oscillations in the mass spectrometry curves below 250 °C can be attributed to the fact that the measurements are conducted in vacuum and therefore the heating rate is not rigorously constant, especially because at lower temperature the heat exchange for the sample heating proceeds essentially via conduction.

From Fig. 2 it is seen that the total weight loss is $\Delta m/m \sim -14\%$. Considering that ∼−5% is due to the THF loss taking place below 200 °C, we can conclude that heating the $Ca(BH_4)_2$ sample in vacuum up to ∼550 °C results in a hydrogen release of 9 wt%. A qualitatively similar result is obtained when heating in argon atmosphere at ambient pressure; however, in this case the corresponding weight loss is 4 wt%. The large difference between the above values suggests that the equilibrium pressure between $Ca(BH_4)_2$ and THF(H_2) gas is lower than 1 bar, so that more adduct or hydrogen are released at pressure lower then this value.

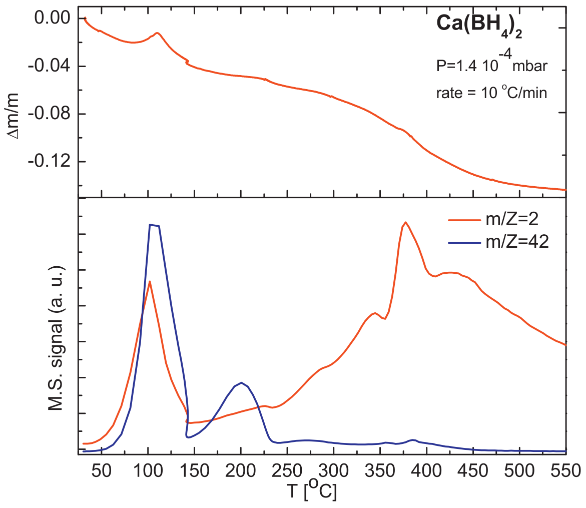

Fig. 2. Relative mass variation and concomitant mass spectrometry measured at $m/Z = 2$ and $m/Z = 42$ (THF). The average heating rate was 10 °C/min.

The release of a small quantity of THF from the pre-treated samples can be due to the great difference of mass between the sample used for the thermal treatment at 125 °C for 20 h (m∼5 g) and the specimen for TGA–DTA experiments (m = 3-7 mg). Indeed, the effusion process is expected to be limited by the diffusion of THF out of the sample. Therefore, the release of the adduct from a massive sample may be not completed even after 20 h at 125 °C; on the contrary in a smaller sample, like the one used for TGA–DTA measurements, one can observe the effusion of THF even at temperature lower then 125 °C. A similar behaviour has been observed for the release of ammonia from Li amide, during the transformation into imide [14,15].

Two endothermic peaks are present in the DTA curves centered around 360 and 420 °C, which suggest a multi-step dehydrogenation process, in agreement with previous diffraction measurements [16–19].

3.2. Anelastic spectroscopy measurements

The vibration frequency of the $Ca(BH_4)_2$ sample after the heating treatment at 125 °C to remove THF, was measured as a function

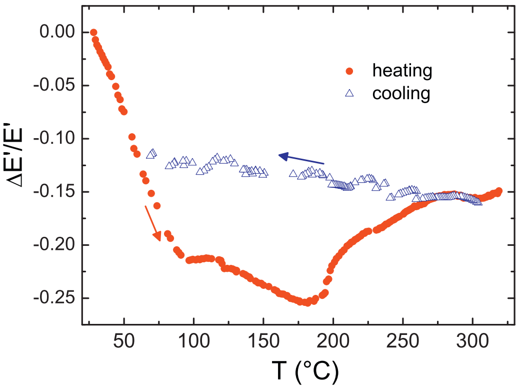

Fig. 3. Relative variation of the Young modulus of the $Ca(BH_4)_2$ sample.

of temperature, with a temperature rate of ~1.2 K/min. Considering the quadratic relation between vibration frequency and elastic modulus (Eq. (1)), we plotted the value $\Delta f^2/f_0^2 = \Delta E'/E'_0$ in Fig. 3, in order to monitor the direct fractional variation of the elastic modulus vs temperature; f_0 is the frequency value at room temperature.

In the quasi harmonic approximation, the Young modulus is expected to decrease almost linearly with increasing temperature. Phase transitions or decomposition processes may drastically modify this monotonically decreasing behaviour, and indeed those processes are most sensitively revealed by slope changes in the elastic modulus. The 22% decrease of the modulus on heating between room temperature and 90 °C is huge and is certainly due to the release of THF, in agreement with the TGA measurements of Fig. 2. Between 120 °C and 180 °C the linear behaviour and the slope of the modulus curve are consistent with a trend essentially driven by the Debye model (see subsequent cooling curve), indicating that the evolution of THF was practically ended. On heating an inversion of the decreasing trend of *E*' starts at about 180 °C. This abrupt change of slope is the signature of the α to α' phase transformation first detected by diffraction measurements [4]. The higher temperature reported by those authors (220 °C) is well explained by the lower sensitivity inherent the diffraction observations. On heating above the α to α' transformation temperature, the α' phase progressively transforms into the β phase [4]. This transformation is responsible for the big deviation of modulus from the standard behaviour. The fact that at 330 °C the modulus curve does not reassume the decreasing behaviour on heating definitely indicates that the α' to β transition is not yet completed, even though the tendency of the *E*'-curve to saturation suggests that the massive part of transformation already occurred. The corresponding value determined by XRD is rather lower (300 °C), what we again ascribe to the different sensitivity of measurements.

On subsequently cooling from 320 °C, the modulus curve displays the monotonic increase expected from the Debye model for a material not undergoing phase transformations, indicating that α → α' and α' → β transformations are irreversible.

The DTA curve of Fig. 1 does not display any heat exchange around 180 °C, the temperature of slope inversion in the *E*' curve. This demonstrates that the α → α' → β transitions are second order phase transformations, as already reported in literature. We point out here that, although calorimetric measurements are inadequate in this case, Young modulus experiments are extremely effective to detect the occurrence of phase transitions, regardless of their order.

4. Conclusions

We obtained a mixture of α and β phase of calcium borohydride by means of a thermal treatment at 125 °C for 20 h of the commercially available $Ca(BH_4)_2 \cdot 2THF$. Even after this procedure to remove THF, a small quantity (a few wt%) of the adduct is retained in the sample and can be released on further heating below 250 °C. Dehydrogenation takes place above 250 °C and the amount of H_2 released depends on the pressure inside the experimental cell. Anelastic spectroscopy measurements can identify two non reversible structural phase transitions which are not detected by differential scanning calorimetry. The first one takes place on heating around 180 °C (α → α'), while the second one completes around 320 °C (α' → β transformation).

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