

# NANOCONFINED MIXED Li AND Mg BOROHYDRIDES AS MATERIALS FOR SOLID STATE HYDROGEN STORAGE

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## SUMMARY

Mixtures of Mg(BH<sub>4</sub>)<sub>2</sub> and LiBH<sub>4</sub> borohydrides in different ratios, prepared by ball milling, have been investigated to test the dehydrogenation kinetics and thermodynamics. Mixed and unmixed borohydrides were dispersed on high specific surface area ball milled graphite by means of the solvent infiltration technique using different borohydride to support ratio contents. It has been observed by thermal programmed desorption measurements that the nanoconfinement of the borohydrides on the supports leads to a lower dehydrogenation temperature compared to unsupported borohydrides. Moreover, a further decrease of the dehydrogenation temperature is observed by increasing the specific surface area of the support. The dehydrogenation process seems to be favoured by the heterogeneous nucleation on the graphite surface of decomposition products or intermediate phases from liquid borohydrides.

## INTRODUCTION

Light metal borohydrides, as LiBH<sub>4</sub> and Mg(BH<sub>4</sub>)<sub>2</sub>, are interesting materials as potential hydrogen storage media due to their theoretical high gravimetric hydrogen capacity [1], but present several limitations of H-exchanging thermodynamics and kinetics which also restrict the reversible dehydrogenation. In order to overcome these limitations, it has been proposed to confine light metal borohydrides in nanoporous scaffolds, exploiting the favourable properties of nanostructured materials and avoiding sintering and agglomeration during cycling [2]. In recent papers it has been shown that LiBH<sub>4</sub> milled with carbon nanotubes [3,4] and included in mesoporous carbon [5] displays a decrease of dehydrogenation temperature. Beneficial effects of carbon addition on the dehydrogenation kinetics have also been observed for the Li-B-Mg-H system [6]. In the present paper it is shown that ball milled mixtures of LiBH<sub>4</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> deposited on graphite exhibit a lower onset dehydrogenation temperature compared to unsupported mixtures.

## EXPERIMENTAL DETAILS

Mixtures of LiBH<sub>4</sub>:Mg(BH<sub>4</sub>)<sub>2</sub> with stoichiometric ratios 1:0, 2:1, 1:1, 1:2, 0:1 were obtained by ball milling in Ar atmosphere using a SPEX 8000M shaker mill with a ball to powder ratio of 10:1. LiBH<sub>4</sub> was purchased from Sigma-Aldrich (purity >95%), while Mg(BH<sub>4</sub>)<sub>2</sub> was synthesised from MgBut<sub>2</sub> and BH<sub>3</sub>SMe<sub>2</sub> [7]. Microporous graphite was obtained by milling for about 15 h "Carlo Erba" graphite and was characterized by the BET method with N<sub>2</sub> adsorption measurements at 77 K using a Nova 1200e analyzer. The milled graphite was then poured into a solution of borohydride mixtures in methyl tert-butyl ether (MTBE) (Sigma-Aldrich, anhydrous, 99.8%). Thermal programmed desorption (TPD) and pressure composition isotherm (PCI) measurements were performed on the produced samples by means of a Sievert's volumetric apparatus supplied by Advanced Materials Co. XRD patterns of milled samples were obtained using a Bruker D8 Advance diffractometer with Bragg-Brentano geometry and Cu K $\alpha$  radiation. The XRD measurements were carried out on samples protected with a thin kapton foil (8  $\mu$ m). All samples were handled into a MBraun glove box equipped with a gas purification system (less than 0.1 ppm water and 1 ppm O<sub>2</sub>).

## RESULTS AND DISCUSSION

All XRD patterns of as milled mixed borohydrides showed a combination of the low temperature stable phases of the two components, while after dispersion on graphite (having a BET measured surface area of about 200 m<sup>2</sup>/g) there is evidence that at least part of the borohydrides nucleates as amorphous or in the form of small particles. After hydrogen desorption the XRD patterns show more or less clearly contributions of the main decomposition products of the two borohydrides.

In Figure 1 are shown the TPD curves of samples after ball milling and after dispersion on graphite. It is evident a noticeable reduction of decomposition temperature when the material is dispersed on microporous graphite.

For comparison, thermogravimetric analysis performed by Fang et al. [8] on similar as ball milled mixed borohydrides gave a behaviour close to that of our as ball milled samples.

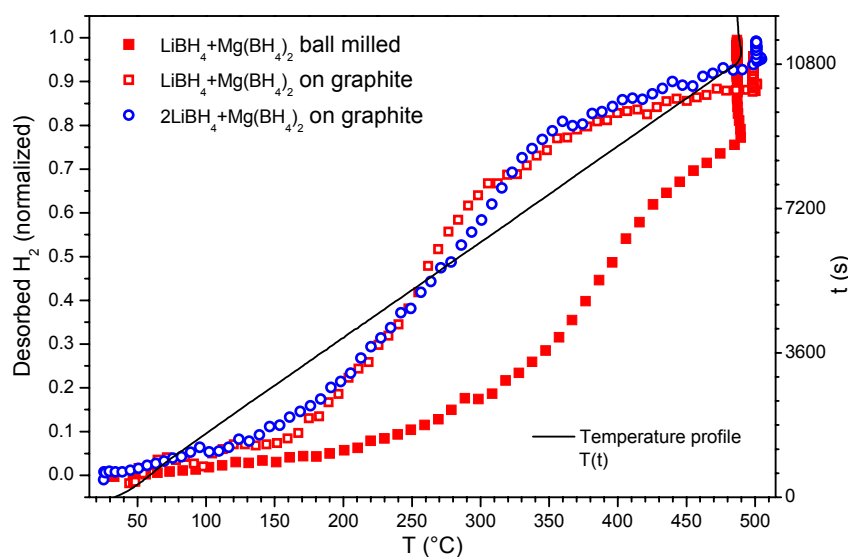


Figure 1: Thermal programmed desorption curves of samples after ball milling and after dispersion on graphite.

The DSC profiles of samples after ball milling show an endothermic peak at about 178 °C, which is most presumably the melting temperature of the mixture. This low melting temperature is supposed to be the cause of the lower decomposition temperature of the studied borohydride mixture when this is nanoconfined on high surface area supports: heterogeneous nucleation of decomposition products from liquid borohydride could be favoured by the presence of small graphite particles. To further support this hypothesis, BET surface area measurements of nanoconfined samples gave values one order of magnitude lower than those measured on the as milled graphite. This can suggest that the active material, the mixed borohydride, was effectively dispersed on the available surface filling the micropores.

## CONCLUSIONS

With the present results it is shown once more that the dehydrogenation temperature of borohydride systems can be consistently lowered by nanoconfinement in supports of high surface area.

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