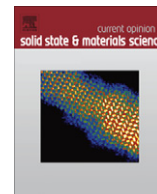




Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cosms

Recent applications of Raman spectroscopy to the study of complex hydrides for hydrogen storage

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ARTICLE INFO

Article history:

Received 26 August 2010

Accepted 19 December 2010

Available online 21 January 2011

Keywords:

Hydrogen storage materials

Raman spectroscopy

Borohydrides

Ammonia borane

Magnesium hydride

ABSTRACT

Raman spectroscopy has been shown to be a powerful and versatile technique for the characterization of certain hydrogen storage materials.

It has been used to investigate the local bonding environments of a range of borohydride compounds, contributing towards the interpretation of diffraction data for the determination of crystal structures: alkali metal (Li, Na, K, Rb, Cs); alkaline earth (Mg and Ca); and transition-metal (Zn and Mn).

Raman has also been used to help identify phases (particularly amorphous) within decomposed borohydride compounds: CaB_6 in decomposed $\text{Ca}(\text{BH}_4)_2$; MgB_2 in decomposed $\text{Mg}(\text{BH}_4)_2$; and $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and boron in decomposed LiBH_4 . In situ Raman measurements on LiBH_4 heated under Ar have shown the orthorhombic to hexagonal phase change, fusion, followed by the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and boron, as a function of temperature.

The Raman vibrational modes for a range of candidate hydrogen storage materials – including borohydrides, ammonia borane, and magnesium hydride – have been tabulated. The data is from the literature and from recent measurements at the University of Birmingham.

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1. Introduction

One of the main challenges for the effective use of hydrogen in automotive applications is the development of a safe and reliable method of storage, which has an acceptable energy density. This has led to research into a range of possible solid-state hydrogen storage media, such as metal hydrides and complex hydrides, which have promising gravimetric hydrogen storage densities.

A crucial part of this research effort is the accurate identification of the crystallographic structure(s) of the phase(s) present, using X-ray and neutron diffraction. Raman spectroscopy can provide information on the local bonding environment, which can help to interpret this diffraction data.

In addition, reversibility in these hydrides (i.e. recombination in hydrogen) is usually only slowly achieved under high pressures of hydrogen at elevated temperatures. Therefore, there is a need to develop techniques which will allow the in situ characterization of (amorphous and/or crystalline) phases present during dehydrogenation and rehydrogenation of the hydride.

Vibrational spectroscopies (e.g. Raman and Infrared) have a number of advantages for the study of hydrogen storage materials, especially complex hydrides such as borohydrides and ammonia borane-based compounds. Firstly the sensitivity to both crystalline

and amorphous materials, and secondly the ability to follow a reaction across a change of state, from solid to liquid or liquid to gas (and *vice versa*). Diffraction methods, in contrast, can only observe changes in crystalline material. While nuclear magnetic resonance (NMR) is capable of measuring crystalline and amorphous material with ease, only a single element can be studied at a time. NMR can also be used for both solids and liquids it cannot easily follow a reaction that involves a change of state (with a single experimental setup). Raman and Infrared, however, probe the bonding between all the elements present and with the appropriate experimental setup (e.g. Raman microscopy), can investigate reactions that have a large volume change (such as foaming) and involve the transition between states of matter and degrees of crystallinity.

It has also been shown that the measurement of the change in energy of the q bands in molecular hydrogen, allows the heat of adsorption of hydrogen onto high-surface porous materials (e.g. MOFs, PIMs, activated carbons, etc.) at 77 K to be calculated [1]. The use of variable temperature high-pressure sample cells may increase the use of Raman spectroscopy in this area.

However, the focus of this review will be on the use of Raman spectroscopy for the evaluation of complex hydrides, principally borohydrides and ammonia borane. An excellent review by Marks and Kolb discussed the structure, bonding and synthesis of a large number of borohydride compounds [2]. Recently, a comprehensive review of the application of vibrational spectroscopy – encompassing Raman, Infrared and Inelastic Neutron Scattering (INS) – to

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potential hydrogen storage materials, such as complex and metal hydrides, was given by Parker [3].

In particular, this review will concentrate on materials being investigated as hydrogen storage media, such as ionic alkali and alkaline earth metal and relevant transition metal borohydrides. This will also include a number of observed and potential decomposition products and reaction intermediates that occur upon thermal decomposition, including metal borides (M_xB_y) and boranes (B_xH_y).

2. Experimental techniques

Lithium borohydride ($LiBH_4$, 95%), lithium borodeuteride ($LiBD_4$, >95%), calcium borohydride ($Ca(BH_4)_2$) and ammonia borane (NH_3BH_3 , 97%) were obtained from Sigma-Aldrich Company Ltd. $K_2B_{12}H_{12}$ and $K_2B_{10}H_{10}$ samples were obtained from Katchem Ltd. Magnesium hydride (MgH_2 , 95%) was obtained from Degussa-Goldschmidt. The samples were handled in an argon-filled glove box (LABstar, MBraun) in which water and oxygen levels were below 1 ppm.

Raman spectra were collected using a Renishaw InVia reflex Raman microscope. A 488 laser was focused using a long working distance $20\times$ objective onto the sample with a spot diameter of approximately $50\ \mu m$ and a beam power of around 20 mW. Around 10 mg of sample was loaded into an aluminium crucible in an Instec HCS621 V sample cell with a fused silica window; the cell allows inert loading in a glove box and atmosphere control. The samples were heated and cooled under argon gas flowing at 100 ml/min, and heated at $2\ ^\circ C/min$. Temperature was measured using a thermocouple situated within the heater block.

3. Recent developments

3.1. Borohydrides

Borohydrides, or tetrahydroborates (containing a BH_4 unit), as a class of compound have been known since the 1940s [4–6]. They have been the subject of numerous studies due to their uses as common reducing agents in organic chemistry [7–10]. There is great interest in borohydrides as hydrogen storage materials [11–14] as they offer both high volumetric and gravimetric hydrogen storage densities.

The borohydride ion, $[BH_4]^-$, is the simplest known boron hydrogen anion. It is able to form both ionic compounds with alkali and alkaline earth metals and covalent complexes with transition metals. Bonding between the borohydride ligand and a metal centre invariably involves a three-centre, two-electron bridging hydrogen in either a monodentate, a bidentate or a tridentate manner. Fig. 1 shows the four main bonding configuration of the BH_4 unit with a metal centre (M).

Specifically, the vibrational spectra of these four different modes of bonding are different and allow ready distinction between the four modes. A summary of the differences in the vibrational spectra of the four bonding configurations of mononuclear borohydrides has been given by Marks and Kolb [2] and adapted by Parker [3].

The two most important vibrations for diagnosis of the bonding configuration are those that involve the terminal hydrogen-boron stretch (ν_{B-H_t}) and the bridging hydrogen-boron stretch (ν_{B-H_b}). These vibrations are relatively pure vibrations, in that they are not masked by other vibrations.

3.1.1. Alkali metal borohydrides

Lithium borohydride is a potential hydrogen storage material due to its theoretical maximum hydrogen capacity of 18.5 wt.%.

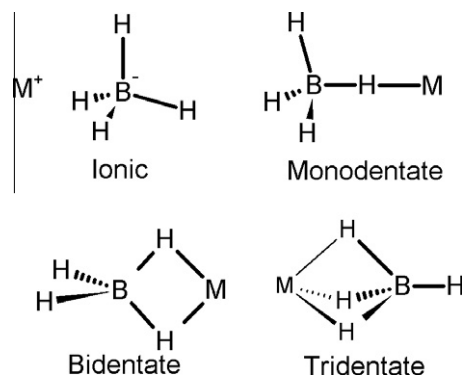


Fig. 1. Possible bonding configurations of the BH_4 ligand with a metal centre (M) [2].

It is, however, too stable with an enthalpy of formation of $\Delta H = -74\ kJ/mol\ H_2$ and only desorbs hydrogen at elevated temperatures above the melting point, with the onset of decomposition at $320\ ^\circ C$. Reversibility (i.e. rehydrogenation of $LiBH_4$ from the decomposed materials) has been reported after several hours at elevated temperatures of $600\ ^\circ C$ and pressures of 150 bar. The decomposition mechanism, and the various intermediates and products formed, are complex and not fully understood.

Lithium borohydride exists at room temperature as an orthorhombic structure ($Pnma$), $o-LiBH_4$. Upon heating to $108\ ^\circ C$, it undergoes a phase transition to a hexagonal phase ($P6_3mc$), $h-LiBH_4$. The $h-LiBH_4$ then melts at $270\ ^\circ C$ with no detectable change in mass to form liquid lithium borohydride $Li[BH_4]$, with the onset of thermal decomposition at $320\ ^\circ C$ yielding a total weight loss of 9 wt.% up to $600\ ^\circ C$ [15–19].

Racu et al. carried out a high resolution Raman study of the low temperature $o-LiBH_4$ phase between -268 and $25\ ^\circ C$ [20]. The work showed that there are 36 Raman active modes, 18 of which are external modes, with the other 18 being internal vibrations. Racu et al. were able to identify 14 further single modes, adding to the 13 single modes bands reported previously [21] assigning a total of 27 of the 36 vibrational modes using both $LiBH_4$ and $LiBD_4$ there are also four combination modes observed by both Racu et al. [20] and Gomes et al. [21]. The room temperature and $-190\ ^\circ C$ Raman spectra of $LiBH_4$ and $LiBD_4$ are shown in Fig. 2.

The spectrum of $LiBD_4$ in Fig. 2 shows the presence of residual B–H stretching, consistent with some remnant $LiBD_3H$ [22]. In the work by Gremaud et al. [22] they successfully demonstrate the isotopic exchange of D atoms of H atoms in isotopically pure $[BH_4]^-$ units of crystalline lithium borohydride. In addition, Borgschulte et al. [23,24] have shown evidence for the macroscopic diffusion of the $[BH_4]^-$ anions as well as exchange of hydrogen (and deuterium) between ions. The initial work focused on using Raman to observe the heating of $LiBH_4/LiBD_4$ in flowing D_2/H_2 and monitoring the exchange and diffusion for H/D at $250\ ^\circ C$ through the hexagonal phase [23]. Further work utilised spatially resolved Raman microscopy to probe a diffusion couple of $LiBH_4$ and $LiBD_4$, to measure the diffusion rates of deuterium in $LiBH_4$ and hydrogen in $LiBD_4$ purely as solid state reactions: the self diffusion rate of deuterium in $LiBH_4$ was determined to be $D \approx 7 \times 10^{-14}\ m^2\ s^{-1}$ at $300\ ^\circ C$.

Heating through the phase change was investigated using Raman [21,25] and XRD [26,27]. The $h-LiBH_4$ phase has significantly fewer vibrations compared to $o-LiBH_4$ leaving only two broad B–H stretch around $2300\ cm^{-1}$ and two B–H bend around $1300\ cm^{-1}$. There is also a significant shift in the ν_2 peak from around 1287 to $1302\ cm^{-1}$. The reason for a simplification in the Raman spectra is due to the increase in symmetry point group from

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