Review

Spectroscopy and bonding in ternary metal hydride complexes—Potential hydrogen storage media

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Contents

A R T I C L E   I N F O

A B S T R A C T

Of the challenges that are still to be met to enable the widespread use of H_2 as a fuel for automotive applications, a safe, reliable and cheap method for its storage and transportation is paramount. This need has prompted a massive effort in the synthesis and characterisation of novel hydrides and a better understanding of existing materials. In this review the vibrational spectroscopy and the bonding of a wide range of ternary metal hydride complexes are discussed. The spectroscopic techniques used include transmission and photoacoustic infrared spectroscopy, Raman spectroscopy with excitation wavelengths ranging from 1064 to 515 nm, inelastic neutron scattering spectroscopy and nuclear resonant inelastic X-ray scattering spectroscopy. The systems studied are: the octahedral transition metal hydrides, other geometry's of transition metal hydrides, alkali metal, alkaline earth and aluminium compounds with the borohydride ion, the alkali metal and alkaline earth alanates and the alkali metal gallates. In all cases, while the central atom is the most important determinant of the properties, it has become increasingly clear that the counter-ion is much more than just a spectator; it often plays a key role in determining the stability of the material. As such, varying the counter-ion provides an important mechanism for optimising the desired properties and these are reflected in the spectra. In addition to its use in characterising materials, vibrational spectroscopy is used to investigate reactions and processes. The advantages of vibrational spectroscopy lie in its flexibility: it is not restricted to crystalline systems, amorphous or nanocrystalline materials are readily observable, it is amenable to *in situ* studies, it is democratic; infrared and Raman spectroscopy are not element specific and uniquely among probes they are able to follow a reaction across a change of state. Vibrational spectroscopy and *ab initio* calculations are a synergistic pairing. Comparison of computed and experimental spectra provides a stringent test of the calculation, while the calculation provides unambiguous assignments of the spectra. Generation of the inelastic neutron scattering spectrum provides the most reliable test since only the amplitude of motion of the atoms in each mode is required.

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1. Introduction

Of the challenges that are still to be met to enable the widespread use of H_2 as a fuel for automotive applications [1], a safe, reliable and cheap method for its transportation is paramount. The US Department of Energy (DOE) has set targets [2] for a number of parameters that must be met for a commercially viable storage material. These include: the wt% hydrogen, the reversibility of the system, the minimum temperature and H_2 pressure needed for absorption/desorption, the H_2 charging and discharging rate, the number of times the system can be cycled from one quarter full to completely full and the purity of the released H_2. All of these targets are important but the first that must be met is a material that contains sufficient hydrogen. For 2010 the target is 4.5 wt% hydrogen for the *complete* system, including tank, valves, regulators, piping, mounting brackets, insulation and any added cooling capacity. Thus the storage material needs to contain substantially more than 4.5 wt% hydrogen. For 2015 the target is 5.5 wt% hydrogen and the ultimate aim is 7.5 wt% hydrogen (in each case the other targets reversibility, *etc.* . . . . also become more stringent). The pressing need for new compounds that meet these criteria has initiated research worldwide in hydrogen storage materials.

A variety of methods have been proposed [3], which can be broadly divided into three categories: (i) storage as gaseous H_2 (ii) storage as liquid H_2 and (iii) storage in solid form. The last category can be divided into physisorption or adsorption in or on a porous material, where the interactions are largely Van der Waals forces, and absorption or chemisorption of H_2 leading to the reversible formation of a hydride, where there is chemical bonding between the hydrogen and other atoms.

Gaseous H_2 can be compressed to 800 bar [3,4] (a standard laboratory H_2 cylinder has a maximum pressure of 200 bar) in order to reach the gravimetric target for on-board utilization, although the containment systems developed to date are expensive. In addition, the very high pressure utilised leads to severe safety problems which are compounded by the safety problems of gaseous H_2 itself. Liquid H_2 requires cryogenic containment, with its concomitant weight penalty. A wide range of adsorbents are being investigated, these include carbon nanotubes and derivatives [5], clathrates [6] and metal organic framework (MOF) materials [7,8]. Most of these do not meet the DOE target, because a large amount of 'chemical scaffolding' is required in order to trap and retain the H_2 which leads to a low gravimetric capacity. Low temperature (77 K) and elevated pressure are also often needed to achieve even modest adsorption capacities.

Hydrogen-in-metal systems (where the hydrogen atom occupies an interstitial site in the metal lattice and is not bonded to a particular atom) [9] such as PdH [10] or $LaNi_5H_6$ [11] are attractive because they are stable and readily reversible, unfortunately, they do not meet the DOE target because of the mass of metal. In a ternary metal hydride, $A_x[TH_y]$ or $A_x(MH_y)$ (A = alkali or alkaline earth metal, T = transition metal, M = B, Al or Ga) the use of a lighter Group I or II element increases the gravimetric density, this can be further increased by the use of B or Al as the atom to which hydrogen is bonded. Most metallic hydrides absorb hydrogen up to a hydrogen-to-metal ratio of 2. Compounds with a hydrogen to metal ratio of >2 (up to 4.5 in $Ba[ReH_9]$ is known) are all ionic or covalent complex hydrides, as opposed to hydrogen-in-metal systems. This has prompted an intense effort in the synthesis and characterisation of novel ternary hydrides [12–15]. The hydrides offer ways of tailoring the properties of the material by changing either (or both) the central metal atom or the counter-ion. The current view [16] is that the best candidates for hydrogen storage materials are the borohydrides and alanates. The most important reasons are illustrated in Fig. 1 that compares the volumetric and gravimetric H_2 density for a variety of systems and methods. The highest

volumetric hydrogen density known today is 150 kg m^{-3} found in $Mg_2[FeH_6]$ and $Al(BH_4)_3$, which is more than double that of liquid hydrogen, while $Li(BH_4)$ has the highest gravimetric hydrogen density of 18 wt%. Other benefits of the use of metal hydride complexes include the absence of elements, such as halides, that can lead to undesirable side reactions that both reduce the amount of H_2 available to use and may be corrosive or toxic; the formation of ammonia from amides or imides is a case in point (although borohydrides can give diborane as a highly undesirable by-product).

Another reason for interest in these materials is the possibility of new chemistry with the compounds as exemplified by the large number of derivatives of the $[ReH_9]^{2-}$ ion [17] and the extensive use of $Li(AlH_4)$ and $Na(BH_4)$ as reducing agents in organic chemistry [18].

The syntheses and structures of the compounds have been extensively reviewed [12–15]. The focus of this review is the vibrational spectroscopy of the materials. In this review we will first consider the vibrational spectroscopy of the $A_2[TH_6]$ complexes, since these form the most extensively studied hydrides and show the effect of varying both the alkali or alkaline earth metal, A, and the transition metal, T. Transition metal complexes of other stoichiometries will then be considered. The spectroscopy of the ternary borohydrides, alanates and gallates is then discussed.

2. Survey of ternary metal hydride complexes

Fig. 2 shows the transition elements for which ternary metal hydrides are known (coloured red or blue). For some elements, several complexes are known, thus ruthenium forms octahedral complexes $A_2[RuH_6]$ where A = Ca, Sr, Ba, Eu, Yb as well as quaternary complexes $CaEu[RuH_6]$ [19–21]. Palladium forms complexes with different formal oxidation states and structures: $A_2[PdH_2]$ (A = Li, Na) with linear $[PdH_2]^{2-}$ ions [22,23], $BaNa[PdH_3]$ with trigonal planar $[PdH_3]^{3-}$ ions [24] and $Ba_2[PdH_4]$ with tetrahedral $[PdH_4]^{4-}$ ions [25], which are all contain formally zero valent Pd, in addition there are $A_2[PdH_4]$ complexes [26,27] (A = Na, K, Rb) with square planar $[PdH_4]^{2-}$ ions, which contain formally divalent Pd. Those elements for which at least one complex has been studied by vibrational spectroscopy are shown in red.

What is striking about Fig. 2 is the apparent dividing line at the (Mn, Tc, Re) triad. Transition elements to the left do not form complexes, instead hydrogen-in-metal systems are found, while elements to the right form an extensive array of complexes of different stoichiometries, geometries and oxidation states. This division may be artificial; recent work [28] has produced evidence that a $Mg_3[CrH_6]$ complex is formed at 8 GPa, although the hydrides were not located. Many of the elements to the right of the (Mn, Tc, Re) triad form hydrogen-in-metal compounds depending on the hydrogen to metal ratio. Thus Mg_2Ni initially reacts with H_2 to give $Mg_2NiH_{0.3}$ while it forms $Mg_2[NiH_4]$ with excess H_2 [29]. Similarly, YMn_2 forms a series of solid solutions [30] YMn_2H_x ($0.1 \leq x \leq 0.43$) at a few bar H_2 pressure at room temperature but forms $(YMn)[MnH_6]$ at 0.2 GPa and 473 K [31]. Together, these observations suggest that compound formation to the left of (Mn, Tc, Re) may be possible but that it requires much more forcing conditions than for the elements to the right of, and including (Mn, Tc, Re).

3. Vibrational spectroscopy and *ab initio* methods

A variety of vibrational spectroscopies have been used to study the compounds. These include infrared, Raman, inelastic neutron scattering (INS) and nuclear resonant inelastic X-ray scattering (NRIXS) spectroscopies. Infrared spectra are usually obtained from mulls or KBr discs, although special precautions to exclude air