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The interaction of hydrogen with oxidic promoters of hydrogen storage in magnesium hydride

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ABSTRACT

The present work is devoted to monitor the reactivity with hydrogen of various oxide systems (Nb_2O_5, WO_3 and a mixed Mg/Nb/O oxide) in the aim of understanding the role of oxides as promoters for hydrogen storage in MgH_2. The reactivity of the oxides has been tested using either molecular hydrogen or "nascent" hydrogen produced by reaction of zinc with hydrochloric acid. Thermal desorption-mass spectrometry experiments indicate that hydrogen adsorbed in Nb_2O_5 and Mg/Nb/O mixed oxides is, in part, reversibly released and, for a second fraction, released as water. By contrast, water is the only product desorbed by WO_3 after contact with hydrogen. This could explain the higher performances of Nb_2O_5 as kinetic promoter of hydrogen storage in comparison with WO_3.

1. Introduction

For the advent of a new technology based on the use of hydrogen as an environmental friendly fuel it is of vital importance to find materials suited for an efficient storage of this gas. An efficient storage is based on two main aspects, the former being the storage capacity and the second the sufficiently high rate of adsorption and desorption of the gas. In the case of MgH_2, for instance, the theoretical hydrogen storage capacity is rather interesting, but the practical use of this system is limited by the slow rate of adsorption–desorption phenomena. For this reason a great deal of work is devoted to increase the kinetics performances of the system. In this respect, different attempts were made mixing the magnesium hydride with particular additives including non-metals (graphite and organic compounds) [1,2], transition metals [3–5], transition metal fluorides [6,7] and oxides [8–14]. In the latter case, the best performance seems, to date, those shown by diniobium pentoxide (Nb_2O_5 or niobium (V) oxide) [15,16]. To observe a kinetic effect an intimate interaction between the metal hydride and the additive is needed, which is obtained by prolonged ball milling of a mixture of the two compounds. The nature of the mechanically activated mixture and the mechanism of the catalytic effect are still under discussion [17–19].

Mechanical milling, in fact, produces a very complex and heterogeneous nanostructured system. Recent work has shown that during cycling, in systems such as MgH_2/Nb_2O_5 [16] or MgH_2/Nb [20], prepared by ball milling, the additive undergoes a deep modification giving rise to new phases. In particular the work by Friedrichs et al. [16] has shown that in the ball milled MgH_2/Nb_2O_5 mixture, the oxide disappears, while MgO, metallic niobium and $Mg_3Nb_6O_{11}$ are formed. This mixed magnesium–niobium–oxygen phase, in particular, is known since the early 1970s [21], but a complete analysis of its interaction with hydrogen is still lacking.

The activity of our group is focused to investigate efficient light metal-based storage systems and, in particular, to better understand the role of transition metal oxide addition. Aim of our research is, at present, to understand the nature of the interaction of hydrogen with various oxides used as promoters (e.g. Nb_2O_5, WO_3) or formed during milling or cycling (e.g. $Mg_3Nb_6O_{11}$). This will allow a better understanding also of the properties of the whole mixed storage system.

The present paper reports results concerning the interaction of hydrogen with Nb_2O_5, WO_3 and a mixed Mg/Nb/O phase. The two binary oxides were treated using the so-called "nascent" hydrogen, generated by metal–acid reaction in solution. Though this method is far from those actually used in practical applications, the H_2-solid contact is very deep and the method results useful to understand the nature of the interaction and the potential performance of the solid in the real system. Results obtained with molecular and atomic hydrogen (whose experimental responses are less intense than those with "nascent" hydrogen) has been reported in another paper [22]. At variance, the mixed Nb–Mg–O phase has been treated, in two separate experiments, with both nascent and molecular hydrogen.

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2. Experimental

Nb_2O_5, WO_3, MgO and Nb (ex Aldrich) were used as received. The reactivity of pure and mixed oxides with hydrogen has been tested with "nascent" hydrogen generated in solution, adding metallic zinc to the suspension containing HCl (37%) and the solid and kept under stirring. In order to observe a significant interaction a good dispersion of the solid was needed.

Synthesis of the Mg/Nb/O mixed phase was performed following the procedure reported by Pagola et al. [23], with the only difference consisting in keeping the precursors (Nb_2O_5, Nb, MgO) at 1273 K for 32 h. X-ray diffraction (XRD) analysis of the solid phases was performed using a Philips X'PERT PRO (Cu Kα radiation). Rietveld refinement was used to analyse diffraction pattern by means of MAUD software [24]. Thermal desorption-mass spectroscopy (TD-MS) analysis was performed coupling an home-made thermal desorption apparatus to a quadrupolar mass spectrometer (Pfeiffer Vacuum Prisma).

3. Results and discussion

The XRD diffraction pattern of the mixed phase (which appears as a black powder) obtained after synthesis is presented in Fig. 1, where the experimental and calculated data are reported. The agreement between the collected pattern and the Rietveld simulation is confirmed by the small difference between the experimental and the calculated profiles. The results of Rietveld refinement for the mixture of Mg/Nb/O phases are listed in Table 1. The abundance and the nature of the products differ considerably, in the present case, from those reported by Pagola et al. [23]. The major fraction of the sample is composed of mixed Mg/Nb/O phases: $Mg_3Nb_6O_{11}$ (22.7 wt%), $Mg_4Nb_2O_9$ (45.8 wt%) and $MgNb_2O_6$ (26.3 wt%). The remaining part of the material is constituted by NbO_2-Ht (1.2 wt%) and NbO (4.0 wt%). Moreover, in our mixture no presence of MgO was detectable. The mean size of the coherent scattering domain is around 300 nm for all phases except for NbO_2 whose dimension is around 50 nm. All cell parameters are quite close to those present in the ICSD database [25]. Both these features were expected due to the high temperature involved during the synthesis.

After the treatment with nascent hydrogen, the Nb_2O_5 sample turned from white to blue while the WO_3 sample turned from green-yellow to dark blue. Thermal desorption experiments performed on the two bare oxides (Nb_2O_5, WO_3) after contact with nascent hydrogen indicate that both hydrogen and water are released upon thermal desorption under vacuum. There is however a difference between the two oxides which is shown by the TD-MS plots reported in Fig. 2. In the case of niobium (V) oxide (Fig. 2a), comparable amounts of hydrogen and water are released at different temperatures, whereas water is practically the only desorbed product after hydrogen-WO_3 contact (Fig. 2b). In the case of Nb_2O_5, desorption of molecular hydrogen takes place in two distinct steps. The former occurs between 350 and 570 K while the latter occurs at around 650 K. To explain these findings, we have to consider the concepts of the intercalation chemistry of oxides, occurring when a lattice has sufficiently large channels to host small atoms. Both tungsten trioxide and diniobium pentoxide are in fact known for their ability to form "bronzes" with hydrogen and other light atoms. While the tungsten bronzes are very well known and widely investigated, the features of niobium bronzes are relatively less known [26]. Both hydrogen peaks observed by TD-MS, in the case of Nb_2O_5 are related to the interaction of hydrogen with the solid [27,28], and they might be associated to different intercalation sites for hydrogen inside the oxide. Two peaks due to water desorption ($m/z = 18$) centred at about 450 and 700 K are also observed for both WO_3 and Nb_2O_5. The lower temperature peak could be related to water weakly adsorbed in molecular form on the solid. By contrast, the higher temperature peak is due to the elimination of water which must be tightly bound to the structure, likely under the form of hydroxyl groups ($2OH^- \rightarrow O^{2-} + H_2O$). Summarizing, both niobium and tungsten oxides upon annealing decompose releasing different amounts of molecular hydrogen and water. In particular Nb_2O_5 desorbs comparable amounts of both molecules (H_2 and H_2O) whereas, in the case of WO_3, water is by far the most abundant one and the fraction of desorbed hydrogen is nearly negligible. This is likely related to the interplay between the formation enthalpy of the O–H bond in water and that of the O–H bond into the oxide forming the bronze [29]. Comparing the effect

Table 1
Phase abundance and structural parameters after synthesis of the Mg/Nb mixed oxide

	$Mg_3Nb_6O_{11}$	$Mg_4Nb_2O_9$	$MgNb_2O_6$	NbO	NbO_2-Ht
wt%	22.7	45.8	26.3	4.0	1.2
a (Å)	6.042 (1)	5.163 (8)	14.211 (7)	4.211 (9)	4.818 (8)
b (Å)	–	–	5.705 (6)	–	
c (Å)	7.468 (2)	14.028 (8)	5.038 (9)	–	3.022 (5)

Rw% equal to 2.25.

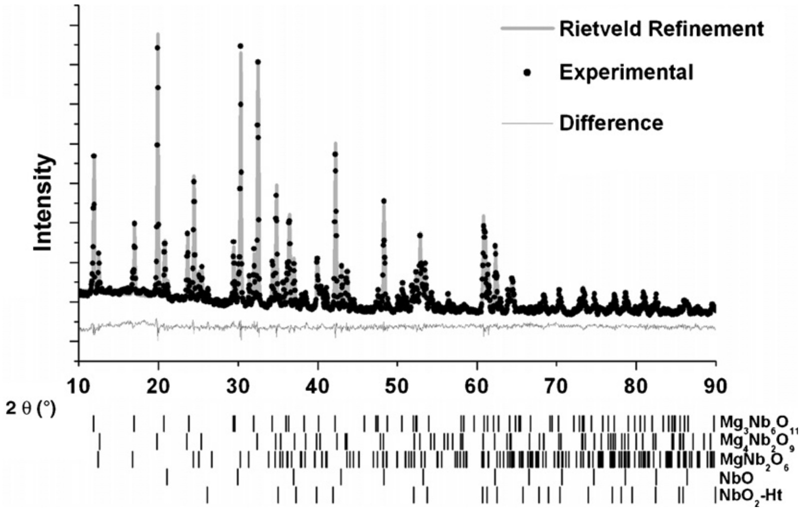

Fig. 1. XRD pattern and Rietveld refinement of Mg/Nb mixed oxide.

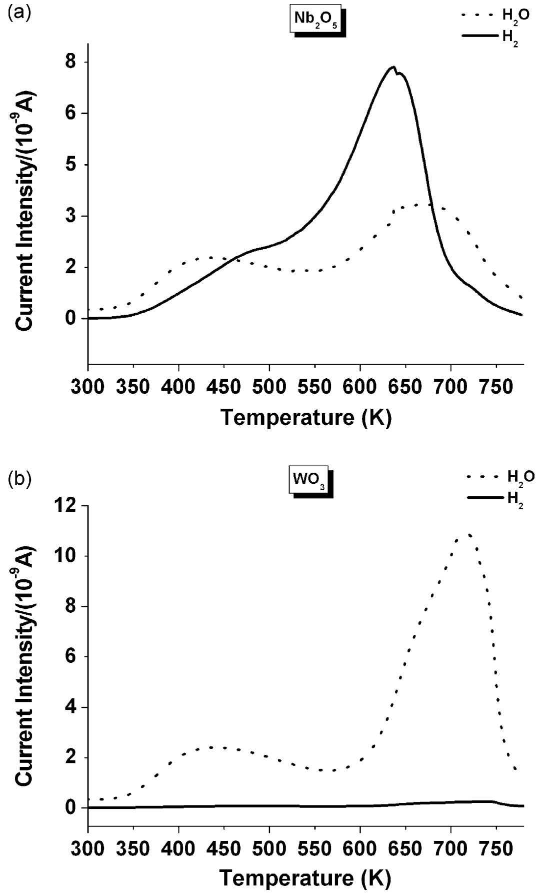

Fig. 2. TD-MS spectra for bare oxides after contact with nascent hydrogen. Mass/charge ratios of 2 (hydrogen) and 18 (water) have been monitored. (a) Nb_2O_5 and (b) WO_3.

of Nb_2O_5 and WO_3 milled with MgH_2 as promoters for hydrogen storage, a remarkable difference in adsorption–desorption kinetics was observed; being the niobium (V) oxide additive the one with the stronger positive influence [11]. This result may be explained in terms of the different decomposition behaviour of niobium hydrogen-bronzes with respect to tungsten hydrogen-bronzes, as evidenced by the data shown in Fig. 2.

A series of thermal desorption experiments, similar to those described above, has been performed on the mixed Mg/Nb/O samples (Table 1). The reactivity of the mixed oxides with hydrogen, in terms of uptake and desorption of molecular hydrogen, is higher than that of the bare Nb_2O_5 oxide [22]. The as prepared mixture releases molecular hydrogen already after synthesis without any contact with hydrogen (Fig. 3a, line 1). This fact can be explained considering that molecular hydrogen is present during synthesis inside the quartz vessel (as confirmed by mass spectrometry analysis). This residual hydrogen is likely produced by redox interaction at high temperature of metal niobium with traces of water desorbed by MgO and Nb_2O_5 surfaces and, once formed, it interacts with the mixed oxide phases. A second thermal annealing in vacuo, in fact, does not origin any further hydrogen release (Fig. 3a, line 2). After treatment of the powder at 673 K with molecular hydrogen (60 min) desorption of hydrogen is again observed (Fig. 3a, line 3). The amount of H_2 desorbed in such a case is definitely higher than that desorbed, in the same experimental conditions, by Nb_2O_5 [22]. In fact the signal recorded by the mass spectrometer is rather intense and it is centred at about 725 K. The mixed Mg/Nb/O phases show therefore a high capability of uptaking molecular hydrogen with respect to bare Nb_2O_5.

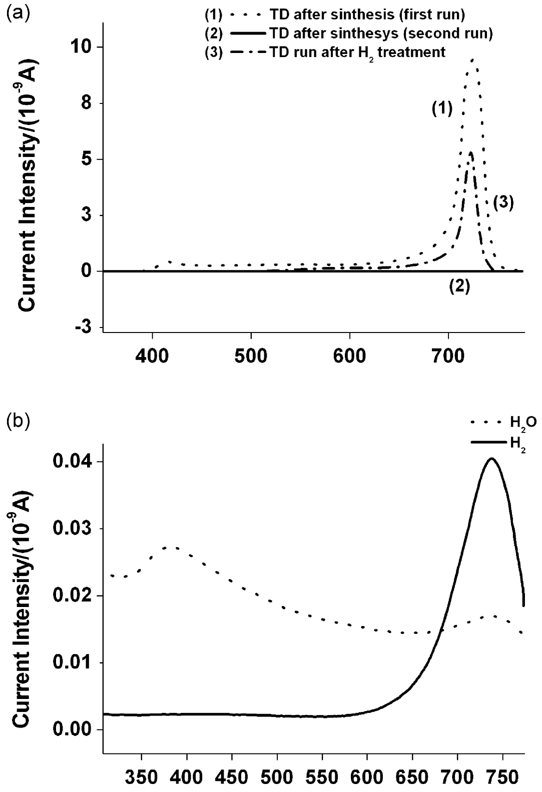

Fig. 3. TD-MS spectra for the Mg/Nb/O mixture. (a) After contact with molecular hydrogen at 673 K. Water signal ($m/z = 18$) is not reported due to its weak intensity if compared to hydrogen ($m/z = 2$). (b) Water ($m/z = 18$) and hydrogen ($m/z = 2$) signals after contact with nascent hydrogen.

Hydrogen release, by the way, is observed also after contact of the mixed oxide with nascent hydrogen in aqueous medium (Fig. 3b). In this case water is also present, beside H_2, in the desorbed fraction. As it can be deduced by the intensity scale in Fig. 3b the hydrogen peak centred at around 725 K is rather weak, nevertheless its presence is irrefutable.

Explaining the peculiar reactivity shown by the synthesised Mg/Nb/O mixture is not a straightforward task. A preliminary remark involves the absence of metallic niobium in the obtained phase mixture which means that the hydrogen uptake is indeed due to an oxidic phase. NbO and $Mg_3Nb_6O_{11}$ phases are, very likely, the compounds responsible for the observed reactivity of the mixture. In fact the two compounds have some similarities being characterised by the presence of octahedral niobium clusters in their structure and by a metallic or quasi-metallic behaviour [30].

The data reported in the present paper point to an active role of the oxide phases as promoters of the hydrogen storage in Mg–MgH_2 which goes beyond a simple mechanical action, consisting in the separation of very small crystallites of the hydride. Even though much work has still to be done in order to obtain a thorough picture of this system, our data suggest that oxides with good capability of bronze formation, can act as an "active-reservoir" of hydrogen in the system. In other words, we think that, in real Nb_2O_5–Mg/MgH_2 systems, the oxidic phase plays a twofold role, being simultaneously an hydrogen activator (hydrogen is split in atoms upon contact with the oxide surface) and an hydrogen carrier (hydrogen diffuse into the oxide). We have shown, in fact, that hydrogen is absorbed in niobium oxidic phases (at least in Nb_2O_5 and, most likely, $Mg_2Nb_6O_{11}$) in dissociated, weakly bound form. For this reason it is desorbed mainly as molecular hydrogen (Figs. 2a and 3a). As the oxidic layer partially covers the Mg grains in the milled system [16], the contact of the latter with an active, dissociated form of hydrogen should favor its incorporation in the lattice. These results are in agreement with those obtained for thin films of Nb_2O_5 which have a “catalytic” ability in splitting and transporting the hydrogen molecule [31] and confirm the results of Barkhordarian et al. [32] who suggested that a high affinity between the transition metal oxide additive and hydrogen is one of the conditions for an efficient hydrogen incorporation in Mg.

The mixed Mg/Nb/O phases show an even more pronounced action in splitting and releasing molecular hydrogen rather than simple Nb_2O_5. Their synthesis, which is difficult if performed via thermal reaction, may be relatively easily achieved with the high energies of a milling system, which contains a strong reducing component such as magnesium hydride. The action of Nb_2O_5 and Mg/Nb mixed oxides is somewhat peculiar and another oxide such as WO_3, which shows a strong capability in forming hydrogen bronzes, is not similarly efficient in promoting the kinetics of hydrogen uptake [11]. This fact can be related to the property of WO_3, which releases mainly water after contact with hydrogen, while Nb_2O_5-based materials desorb a relevant fraction of molecular hydrogen after the uptake. Further work is needed to better understand the role of each oxide phase component in the real MgH_2/Nb_2O_5 system prepared by mechanical milling.

4. Conclusions

Interaction of hydrogen with bare Nb_2O_5, WO_3 and an oxidic mixture (containing mixed Mg/Nb/O phases) has been investigated by means of thermal desorption analysis. Bare Nb_2O_5 is able to release molecular hydrogen if previously reacted with nascent hydrogen. The Mg/Nb/O multi-phases mixture also shows a certain reversible uptake of nascent hydrogen, but performs a stronger uptake if reacted with molecular hydrogen.

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