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Niobium pentoxide as promoter in the mixed MgH_2/Nb_2O_5 system for hydrogen storage: a multitechnique investigation of the H_2 uptake

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Abstract Nb_2O_5 is known as good promoter for adsorption/desorption kinetics of hydrogen in magnesium hydride. In this article the interaction with hydrogen of bare Nb_2O_5, the oxidic component of the mixed MgH_2/Nb_2O_5 system, is investigated in various conditions (i.e. employing atomic, molecular and nascent hydrogen). The state of the hydrogen-Nb_2O_5 system was monitored using various techniques including: X-ray Diffraction, Electron Paramagnetic Resonance, Diffuse Reflectance UV-Vis Spectroscopy, Thermal Desorption Spectroscopy -Mass Spectrometry, Differential Scanning Calorimetry and Thermal Programmed Desorption. Niobium (V) oxide is not at all inert while interacting with hydrogen. This oxide is partially reduced by hydrogen, which is incorporated in the solid and released as both molecular hydrogen and water. This peculiar behaviour, reminiscent of some properties of the bronze family, suggests an active chemical role played by Nb_2O_5 in the mixed MgH_2/Nb_2O_5 system.

Introduction

A system based on hydrogen has been proposed as a possible issue in the search for new, environmental friendly energy technologies. Hydrogen in fact is the ideal fuel to reduce the emission of pollutants and of green-house gas in the atmosphere. The use of hydrogen, either in stationary or in mobile sources, opens however the problem of its production, transport and storage. The storage of hydrogen is particularly important for mobile sources, which require a system characterised by an high capacity and reasonable kinetics of absorption and desorption [1]. In this respect the hydrides of light metals, and in particular, magnesium hydride look rather promising in terms of storage capacity. In the case of MgH_2, for instance, the theoretical hydrogen storage capacity is 7.6 wt.% but the practical use of this system is limited by the slow rate of absorption-desorption phenomena. For this reason the attention of the research in the field has been focussed, in the recent past, to the increase of the kinetics performances of the system. In this respect, different attempts were made mixing the metal hydride with particular additives including non metals (graphite and organic compounds) [2–5], transition metal [6–9], transition metal fluorides [10–12] and oxides [13–18]. In the latter case, the best performance seems, to date, those shown by diniobium pentoxide (Nb_2O_5 or niobia) [19–21]. The intimate interaction between the additive, often called catalyst for the kinetic promotion exerted, and the metal hydride is obtained by prolonged ball milling of a mixture. A living debate is open on the nature of the mechanically activated mixture and on the nature and mechanism of the catalytic effect. While some Authors believe that the effect exerted by Niobium (V) oxide is purely mechanic (prevention of magnesium hydride sintering) [22, 23], other Authors have investigated the kinetics of the H_2–Nb_2O_5/Mg system indicating the enhanced hydrogen chemisorption induced by the oxide ‘‘catalyst’’ as the key factor of the improved performances of the mixed system [24, 25]. Friedrichs et al. for instance, proposed a ‘‘reactive pathway’’ mechanism [26]. In this model Nb_2O_5 generates hydrogen diffusion pathways,

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cracking the MgO overlayer and penetrating inside the MgH_2 grains.

The present work is focused to better understand the kinetic role of transition metal oxide addition to magnesium hydride. As mechanical milling produces a very complex and heterogeneous nanostructured system, the interaction of hydrogen with the bare diniobium pentoxide has been specifically investigated. Aim of this paper is to rationalize the features of the interaction of hydrogen with Nb_2O_5 in various conditions, in order to better understand the properties of the mixed system. The present paper therefore reports results concerning the interaction of Nb_2O_5 with (i) molecular hydrogen at temperature not too far from that used for the storage in MgH_2, (ii) atomic hydrogen in gas phase and (iii) the so called ''nascent'' hydrogen generated by metal-acid reaction in solution. As it will be shown in the following of the present paper, bare niobia is not at all an inert matrix with respect to hydrogen. This suggests that the special activity of this oxide as an additive for MgH_2 is not reducible, as elsewhere inferred, to a purely mechanical role but it is somehow related to its specific interaction with hydrogen.

Experimental

Nb_2O_5 (ex Aldrich, 99.99% pure) was used as received. Specific surface area measurements indicated a surface area of 4.7 m^2/g. All sample handlings were performed in air. Characterisation has been performed using different techniques. The structure was analysed by X-ray powder diffraction, performed using Cu–K_α radiation on Philips X'PERT PRO diffractometer. Rietveld refinement was used to analyse diffraction patterns by means of MAUD software [27]. TDA experiments were performed coupling a desorption manifold with a Mass Spectroscopy (MS) apparatus (Pfeiffer Vacuum Prisma). Parallel experiments were also performed by Differential Scanning Calorimetry (DSC) using a Perkin Elmer DSC7 machine equipped with a Thermal Conductivity gas analyser of the exhausted gas. EPR measurements were performed on a X band Bruker EMX spectrometer. Diffuse Reflectance UV-Vis. Spectroscopy was performed on a Cary 5 spectrometer.

The reactivity of niobia with hydrogen has been tested in three different types of experiment:

- Treatment in a molecular hydrogen atmosphere (200 mbar) at 673 K after outgassing niobium oxide at room temperature.
- Interaction with atomic hydrogen generated by glow discharge plasma (Microtron 200, Microwave Power Generator Mark 3, EMS). Plasma interaction with the solid was performed at least two times for each treatment, using a starting pressure of about 1 mbar of hydrogen and keeping the sample at room temperature. Before the treatment, niobium oxide was outgassed at room temperature.
- Interaction with ''nascent'' hydrogen generated in solution, adding a metal powder (Mg, Zn, Fe) to a suspension containing HCl and niobia under stirring.

Results

All the three standard treatments described above cause the colour of the oxide turn from white to blue. The samples treated with metal/HCl showed the deepest colour change. The blue colour is stable upon heating in oxygen up to about 573 K. The samples, coloured upon interaction with hydrogen, have been characterized by different experimental techniques. The main results are reported in the following. The results concerning hydrogen treated niobia are always compared with those obtained on the bare material. For the sake of brevity, however, we refrain to report, for all experiment, the effect of the three types of standard treatment and we will limit ourselves to the most relevant results.

XRD diffraction

X-ray diffraction has been performed on both the starting material and the sample after treatment with metallic zinc in hydrochloric acid. The two patterns, are very similar but, after performing a Rietveld refinement (Table 1, Fig. 1), it is possible to distinguish some modifications due to the treatment. Comparing structural parameters of untreated niobia with the ICSD [28] records for the high temperature polymorph of Nb_2O_5 [29, 30] it is possible to note a substantial coincidence of the crystalline structure. Small deviation may be justified by recording temperature effects. The comparison between the unit cell parameters of the treated and untreated samples shows that the interaction with nascent hydrogen brings about a small lattice constants modification for niobium (V) oxide. This behaviour is likely related with an intercalation of the hydrogen atom inside the structure of the oxide (vide infra). Another perceivable change regards coherent domain scattering dimension. In fact, the sample treated in hydrochloric acid with metallic zinc shows broader diffraction peaks with respect to as-received sample. This effect might be due to the intercalation of hydrogen, which stresses the structure and favours the cracking of the oxide, leading to a reduction of the coherent domain scattering.

Table 1 Rietveld refinement of experimental data and bibliographic cell parameters for bare and treated Nb_2O_5

	Coherent Domain Scattering Size (nm)	a(Å)	b(Å)	c(Å)	*β*	V(Å^3)	R%
''White''-bare Nb_2O_3	90	21.17(3)	3.824(6)	19.35(6)	119.82	1360	2.42
''Blue''-Nb_2O_5 treated with Zn/Hcl	54	21.18(6)	3.831(4)	19.40(3)	119.73	1368	1.73

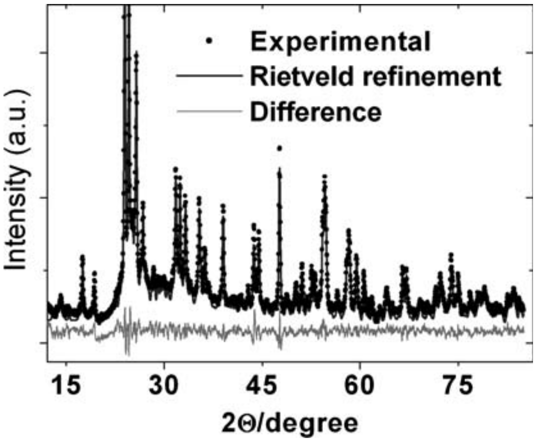

Fig. 1 XRD pattern and Rietveld refinement of a Nb_2O_5 sample treated in hydrochloric acid with metallic zinc

Electron paramagnetic resonance (EPR) and diffuse reflectance UV-vis spectroscopy

Bare Niobia, prior contact with hydrogen, does not display any EPR signal. After contact the changes occurred in the solid are witnessed by a serious difficulty in tuning the spectrometer. This phenomenon is due to a drop of the Quality (Q) Factor of the cavity caused by the interference of free electrons with the microwaves. The tuning has been possible only at 77 K and for samples contacted with a low amount of hydrogen. In such conditions an EPR signal, (Fig. 2) is observed. The signal is composed by two main features, namely a narrow and weak peak centred around $g = 2.003$ and a broad band in the region of g values lower than $g = 2.0023$. The latter one is likely due to aggregates of reduced niobium ion (Nb^{4+}). The absence of an hyperfine structure (^{93}Nb has a nuclear spin of 9/2) indicates the onset of dipolar interaction between vicinal niobium ions. The weak signal at $g = 2.003$ is typical of defects in the solid like trapped electron in oxygen vacancies. The whole EPR spectrum and the general behaviour of the sample after contact with hydrogen suggest that a certain reduction of the material has taken place due to the chemical action of hydrogen. Electrons released during reduction are either localized by Nb^{5+} ions, which reduce to Nb^{4+} or delocalized in the conduction band of the solid. The proposed picture is confirmed by optical absorption results. The UV-Vis spectra of Niobium pentoxide prior and after treatment in hydrogen are compared in Fig. 3. The initial spectrum shows the typical behaviour of many oxides with a valence to conduction band transition at about 400 nm (3.1 eV). The effect of hydrogen treatment is dramatic and it can be described in terms of the onset to the previous spectrum as a sort of wide absorption band, spanning from the UV to the Near Infrared regions. The maximum intensity of this absorption, that explains the color turning of the material from white to blue, is at about 750–800 nm. In this region, the absorption is associated with transitions from a Nb^{4+} to a Nb^{5+} centre (Inter Valence Charge Transfer) [31]. The drift of the absorption line beyond the band gap transition

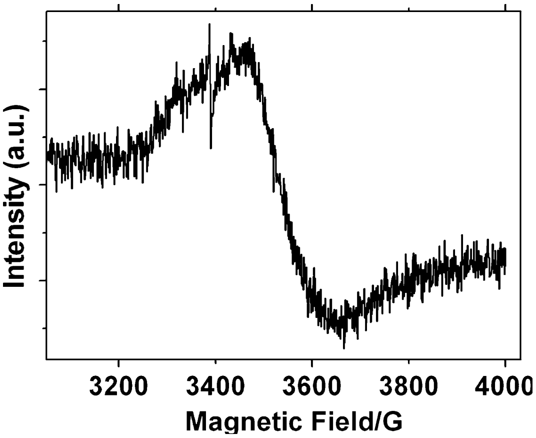

Fig. 2 EPR spectrum obtained after heating for one hour the Nb_2O_5 powder in molecular hydrogen atmosphere of about 200 mbar. Registered at 77 K with 1 G of modulation amplitude and 20 mW microwave power

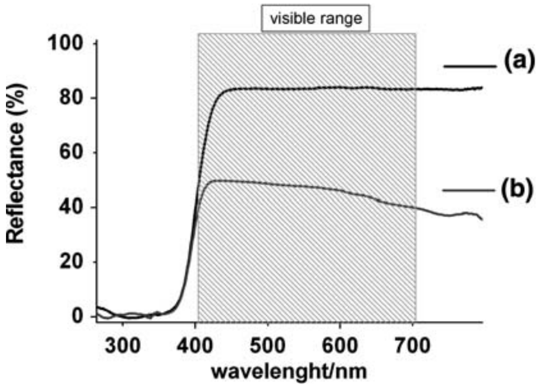

Fig. 3 Diffusion Reflectance spectra of Niobia before (curve a) and after (curve b) hydrogen treatment. Each hydrogen treatment gave the same results

indicates, once again, the presence of charge carriers (electrons) in the system.

The described effects become more pronounced with increasing the time of contact with hydrogen or moving towards less mild conditions. The spectrum reported in Fig. 3b corresponds to the early stages of the interaction but allows distinguishing both the described effects.

Summarizing, EPR and DR-UV-Vis spectroscopy converge in indicating that the modifications of the electronic structure of the solid following the interaction with hydrogen are remarkable and they are due to the effective reduction of the system with formation of both reduced centres and mobile electrons in the solid.

Thermal desorption spectroscopy-mass spectrometry (TDS-MS)

The effects of hydrogen interaction with Niobia have been also tested by coupling analysis by MS with thermal desorption. The temperature of the system was raised under vacuo at constant rate (28 K/min.) and the desorbed products were analyzed (Fig. 4). The solid samples after interaction with hydrogen, following the different approaches illustrated in the experimental section, have a point in common, i.e. they desorb water and molecular hydrogen in the range between 370 K and 770 K. The samples differ one from the other in terms of the desorbed amount. In particular, the oxide treated with ''nascent'' hydrogen in hydrochloric acid solution is much more effective in trapping (hence in desorbing) hydrogen and water. Desorption of molecular hydrogen takes place in two distinct steps. The former occurs between 470 K and 570 K while the latter at around 670 K and is clearly visible in the case of nascent hydrogen treatment only, while, in all the other cases, this type of desorption is less defined or under the detection limit. Two steps in the desorption of water are also observed with peaks centered around 450 K and 720 K, respectively. The confirmation that hydrogen gas is indeed released by the oxide without any interference of desorption from the glass walls of the cell was achieved by an ''ad-hoc'' experiment based on transferring, before mass spectroscopy analysis, the niobium pentoxide sample from the cell in which it underwent atomic hydrogen treatment, to another cell not previously exposed to hydrogen. The results of the thermal desorption did not show appreciable variations in comparison with the previous experiments confirming that the released hydrogen is actually connected to niobia desorption. A peak at the same temperature of that corresponding to hydrogen desorption at low temperature (Fig. 4b) has already been observed in an hydrogen-TPD experiment from a Pt/Nb_2O_5 catalyst [32]. Summarizing, both hydrogen peaks observed by MS-TDS are related to the interaction of hydrogen with the solid, and they have to be associated to different forms of hydrogen inside the oxide.

Two peaks due to water release are also observed for all samples. The lower temperature peak could be related to water weakly adsorbed in molecular form on the solid. By contrast the higher temperature peak must be due to the elimination of water, which must be tightly bound to the structure, likely under the form of hydroxyl groups ($2\ OH^- \rightarrow O^{2-} + H_2O$).

The formation of hydroxyls group is another consequence of the interaction hydrogen with niobium pentoxide as discussed below.

Differential scanning calorimetry-thermal programmed desorption (DSC-TPD)

Coupled DSC-TPD desorption experiments (Fig. 5) have been carried out heating at 20 K/min, the blue powder obtained by treatment with metallic zinc and hydrochloric acid. A clear correspondence between the DSC and TPD signal is observed. The picture provided by MS-TDS results is confirmed by DSC-TPD results. The endothermic DSC signal appears very intense because the hydrogen desorption in the calorimetric cell containing the sample modifies significantly the thermal conductance of the

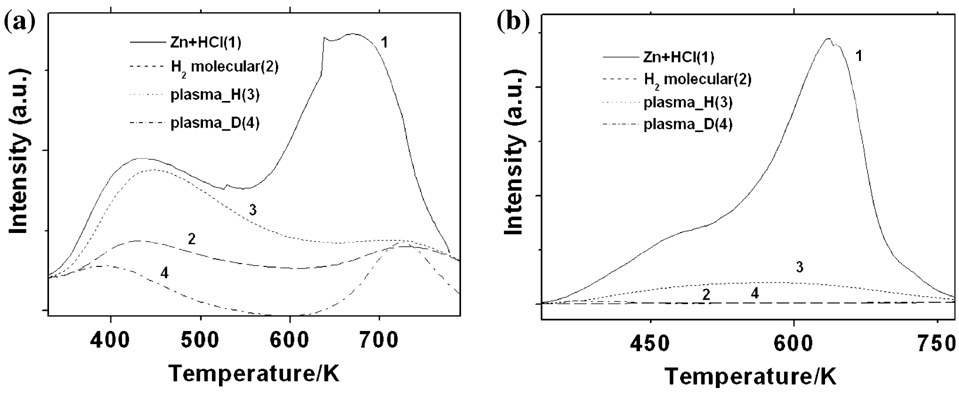

Fig. 4 Mass Spectroscopy response during heating of bare and hydrogen treated (plasma, heating with molecular hydrogen, HCl/Zn) Nb_2O_5. (**a**) desorption of water (m/q = 18), (**b**) desorption of hydrogen (m/q = 2)

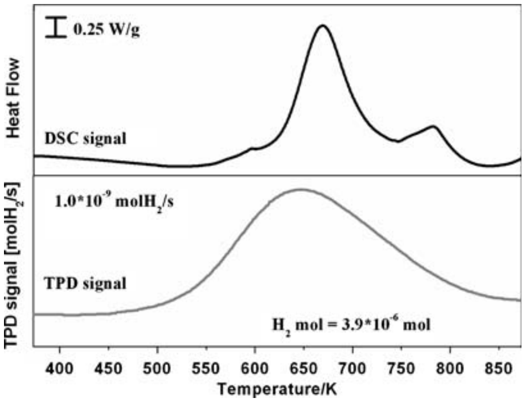

Fig. 5 DSC-TP signals for a Nb_2O_5 sample treated in hydrochloric acid with metallic zinc. The TPD signal is associated with a thermal conductance in the carrier gas due to hydrogen desorption from the sample

flowing argon gas [33, 34] (not so for water desorption), so that the heat of desorption cannot been measured accurately. In the DSC experiment (Fig. 5) the heat flow clearly indicates the occurrence of three distinct desorption processes; the correspondence with the hydrogen desorption monitored by TPD is not so well defined, but an analysis of the signal shape evidences an asymmetric profile, due to the overlapping of different peaks. The structure of the three signals recorded by DSC-TPD is somehow comparable with what observed by MS-TDS analysis (Fig. 4b) and it is probably related to desorption of hydrogen located in distinct sites present in the structure. The temperature shift observed for corresponding peaks is due to a kinetic effect, amenable to the different heating rates used in the DSC and MS-TDS experiments, respectively. From the integration of the TPD signal, the amount of hydrogen desorbed was 3.9×10^{-6} mol for 8.13×10^{-5} mol of niobium oxide, which roughly corresponds to a stoichiometry formula of $H_{0.1}Nb_2O_5$. No similar signals were obtained using bare niobia powder in a blank experiment.

Discussion

The experimental results illustrated above, converge in indicating two facts: (a) the effect of hydrogen treatment in various ways is a reduction of the solid accompanied by a change of the colour and a delocalisation of charge carriers in the conduction band; (b) hydrogen and water are released when the solid is annealed under vacuo.

To explain this behaviour, the concepts of the intercalation chemistry of oxides, occurring when a lattice has sufficiently large channels to host small atoms, have to be considerated. Similarly to the case of Tungsten trioxide (WO_3), Niobium (V) oxide is in fact known for its ability to form ‘‘bronzes’’ with hydrogen and other light atoms. A bronze forms by dissolving an atom in the crystal lattice of the oxide. Ionisation of the dissolved atom dramatically modifies the physical properties of the oxide, inducing colouring and metal lustre appearance together with a strong increase of electric conductivity, which can reach values close to those of metals. Niobium bronzes have been less investigated in comparison with tungsten bronzes. While several reports are available on lithium containing niobium bronzes, as they are used in electrochromic devices, the features of hydrogen containing ones are relatively less known [35–38].

There are two possible reaction pathways, which describe the interaction of hydrogen with niobium oxide accounting for the colouring, the metallic behaviour of the solid and the thermal desorption evidence.

$$\mathrm{Nb}_2^{(5+)}\mathrm{O}_5 + x\mathrm{H}^+ + x\mathrm{e}^- \rightarrow \mathrm{H}_x\mathrm{Nb}_x^{(4+)}\mathrm{Nb}_{2-x}^{(5+)}\mathrm{O}_5 \qquad (1)$$

$$\mathrm{Nb}_2^{(5+)}\mathrm{O}_5 + x\mathrm{H}^+ + x\mathrm{e}^- \rightarrow \mathrm{Nb}_x^{(4+)}\mathrm{Nb}_{2-x}^{(5+)}\mathrm{O}_5(\mathrm{OH})_x \qquad (2)$$

The two processes are similar as in both reactions ionisation of the incoming hydrogen occurs with release of electrons which can either delocalize into the conduction band of the solid or be localized on a niobium ion which changes its oxidation state. For the sake of simplicity, this latter case is considered in reactions 1 and 2. In the case of reaction 2, the protons formed upon ionisation bind to a lattice oxide ion, forming a stable hydroxyl group. In the former case (reaction 1) they are less tightly bound to the lattice. Also in this case, however, the H atom likely binds with the oxygen but, in a less stable form [39]. Upon annealing two possible reactive channels can be followed leading respectively to hydrogen and water desorption.

$$\mathrm{H}_x\mathrm{Nb}_x^{(4+)}\mathrm{Nb}_{2-x}^{(5+)}\mathrm{O}_5 \rightarrow \mathrm{Nb}_2^{(5+)}\mathrm{O}_5 + x/2\mathrm{H}_2 \qquad (3)$$

$$\mathrm{Nb}_x^{(4+)}\ \mathrm{Nb}_{2-x}^{(5+)}\mathrm{O}_{5-x}(\mathrm{OH})_x \rightarrow \mathrm{Nb}_x^{(4+)}\mathrm{Nb}_{2-x}^{(5+)}\mathrm{O}_{5-x/2} + x/2\mathrm{H}_2\mathrm{O} \qquad (4)$$

Reaction 3 tends to restore the initial oxidation state of the material while, with reaction 4, the solid is left in a partially reduced state. The proposed reaction paths are not only in agreement with our experimental observations but also with what reported for most members of the ‘‘hydrogen bronze’’ family, which tend to release mainly water after small uptakes of hydrogen. This is due to differences in the enthalpies of the OH bond in water and in bronze and the enthalpy of formation of the oxide bronze [39].

Conclusions

Considering the data illustrated in this paper, we can examine the results for the mixed system MgH_2/Nb_2O_5 available in the literature under a new light. Even though much work has still to be done in order to obtain a thorough picture of this system, our data confirm that Nb_2O_5 can act as an ''active-reservoir'' of hydrogen and that it has a potential role in the kinetic activation of hydrogen uptake in the mixed system. It has been shown that thin films of Nb_2O_5 have a ''catalytic'' ability in splitting and transporting the hydrogen molecule [40]. This ''catalytic'' process may be not the only one. The chemistry of the intercalation compounds (called bronzes) and the experimental results above illustrated indicate that Nb_2O_5 may also act as reservoir loading a certain amount of ''splitted'' hydrogen in its structure. The activity of splitted hydrogen at the interface with magnesium particles may thus be increased with respect to the actual pressure the sample is exposed to. Future work is in progress in our laboratory to prepare mixed Mg–Nb–O phases (which are known to form upon mechanical treatment and hydrogen cycling of Nb_2O_5/MgH_2) and characterise their behaviour in the interaction with hydrogen.

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