Two step mechanochemical synthesis of Nb doped MgO rock salt nanoparticles and its application for hydrogen storage in MgH$_2$

D. Pukazhselvan [a,*], Narendar Nasani [a], J. Pérez [a,b], Maria J. Hortigüela [a], Tao Yang [a], Igor Bdikin [a,c], Duncan Paul Fagg [a]

[a] Nanoengineering Research Group, Centre for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro, 3810-193 Aveiro, Portugal
[b] Center for Research in Ceramics and Composite Materials (CICECO), University of Aveiro, 3810-193 Aveiro, Portugal
[c] National Research University of Electronic Technology "MIET", Bld. 1, Shokin Square, 124498 Moscow, Russia

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ABSTRACT

In the present study, we demonstrate two mechanochemical approaches suitable for the bulk scale synthesis of catalytically active Nb doped MgO rock salt nanoparticles. In the first method, Nb$_2$O$_5$ initially was reduced to NbO$_2$ by MgH$_2$ and then transformed to Mg$_x$Nb$_y$O$_{x+y}$. In the second method, MgO and Nb$_2$O$_5$ were initially combined to make MgNb$_2$O$_6$ and then converted to Mg$_x$Nb$_y$O$_{x+y}$. The DSC-TG and Sievert's volumetric analysis suggest that the end product, Mg$_x$Nb$_y$O$_{x+y}$, is catalytically more active in comparison to all other oxide phases involved in the reaction, such as Nb$_2$O$_5$, NbO$_2$ and MgNb$_2$O$_6$.

Introduction

Hydrogen driven vehicles require high performance fuel tanks (T$_{dec}$/T$_{ab}$ = 85 °C) with an overall system hydrogen storage capacity of at least 5.5 wt.% [1,2]. Although, Magnesium hydride (material capacity: 7.6 wt.%) is considered as a potential storage material for tanks, greater than 300 °C is required for the liberation of hydrogen (ΔH of MgH$_2$ = −74 kJ/mol) [3]. Reports suggest that the ab/desorption performance of MgH$_2$ can be significantly improved by using metal oxide additives; most preferably Nb$_2$O$_5$ [4−9]. However, it has not yet been possible to explore the exact details regarding how Nb$_2$O$_5$ triggers the fast absorption/desorption of hydrogen in the MgH$_2$ system. In this respect, it is essential to understand the mechanism of

best additives because it renders the possibility of tailoring suitable additives for optimum system performance [10].

In the limited literature available on Nb/Nb_2O_5 dispersed MgH_2 systems, the existence of various Nb bearing phases, such as, pristine Nb_2O_5, Nb nanoparticles, unstable Nb hydrides, Nb/Mg containing monoxides and perovskites, etc, have been reported [11—16]. The theoretical cluster modeling studies suggest the existence of active species/spots in the system easing the mobility of hydrogen in/out of the system [17,18]. A thorough overview of published data in the literature suggests that, although the exact chemical nature of the Nb_2O_5 additive after mixing it with MgH_2 can not be concluded, it is generally now accepted that Nb_2O_5 does not remain unreacted with the MgH_2 particles. Recently, we have investigated the $MgH_2 - nNb_2O_5$ composite system for a series of n values ranging from 0.083 to 1.5 and provided evidence that a Nb dissolved MgO rock salt product forms over a wide range of n values. This is important, because, MgO is known as a hydrogen impermeable barrier layer for the MgH_2 system. This means that, when few Nb atoms substitute the Mg sites of MgO, a dramatic effect occurs to surmount the barrier effects. Inspired by these observations, we focus on the various possible ways of synthesizing Nb doped MgO rock salt nanoparticles that can be very useful for the catalysis of MgH_2.

In the present study, we follow two simple strategies through which catalytically active Nb dissolved MgO can be synthesized. The sequence of these two step strategies can, respectively, be written as $Nb_2O_5/MgH_2 \rightarrow NbO_2/MgH_2 \rightarrow Mg_xNb_yO_{x+y}$ and $Nb_2O_5/MgO \rightarrow MgNb_2O_6/MgH_2 \rightarrow Mg_xNb_yO_{x+y}$. We have also catalyzed MgH_2 samples by each of the oxide samples observed in the present study, i.e, two Nb dissolved MgO samples, $MgNb_2O_6$, NbO_2 and Nb_2O_5, and observed that the Nb dissolved MgO samples are far better additives than the remaining oxides.

Experimental

The samples, MgH_2, Nb_2O_5 and MgO were purchased from Alfa Aeser Chemicals Ltd. The reactants in their required proportions were loaded in a stainless steel milling vial (ball to powder ratio 1:75) under inert atmosphere. Milling operation was performed by using a PM200 mechanical miller at the speed of 350 rpm for 30 h reaction time. The phase-structural features of the products were monitored by using a Siemens X-ray diffractometer working with CuK_α radiation, $\lambda = 1.541$ Å. In order to check the catalytic activity of the synthesized samples, 3 wt.% of each sample (see the sample codes in Table 1) was mixed with magnesium hydride for 5 h under an inert atmosphere. Hydrogen storage measurements were performed using a Sievert's type metal-gas reaction analyzer built in our laboratory. The DSC-TGA measurements were performed by a NETZSCH STA 449 F3 thermal analyzer using Ar as a carrier gas where Alumina was the reference sample. The microstructural analysis was characterized by SU70 Hitachi ultra high resolution field emission scanning electron microscope. The crystallite size of the samples was calculated by using Scherrer method. The surface chemical analysis was performed by XPS instrument

equipped with a hemispherical electron energy analyzer (SPECS Phoibos 150). High resolution spectra were recorded for the in-situ 175 °C heat treated samples by scanning the surface at the normal take-off angle with a pass energy of 20 eV.

Results and discussion

Two step synthesis of Nb doped MgO

Method − 1: Initially, the reactants MgH_2 and Nb_2O_5 were taken in a 1:1 M ratio and milled under nitrogen atmosphere for 10 h. This reaction leads to the reduction of Nb_2O_5 to NbO_2 following the reaction (1)

$$MgH_2 + Nb_2O_5 \rightarrow 2NbO_2 + MgO + \tfrac{1}{2} H_2 \qquad (1)$$
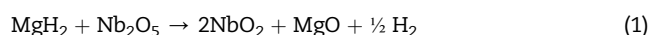
The obtained product is denoted as S_1 in Table 1 and the corresponding XRD profile (a_1) is illustrated in Fig. 1. As seen, the dominant presence of NbO_2 peaks suggests that the Nb_2O_5 has reduced to NbO_2 due to its reaction with MgH_2. However, it is surprising that the Mg bearing product(s) can not be seen in the XRD. The lattice parameter values of the obtained NbO_2 show noticeable change as compared to the standard values (see S_1 in Table 1). This may be due to the dissolution of Mg atoms in the NbO_2 lattice. However, it is also likely that Mg exists in a XRD indiscernible Mg bearing phase (amorphous or highly dispersed nanocrystals).

In the second step of the reaction, the products of the reaction (1), i.e. S_1 was mixed with MgH_2 in a 1:5 M ratio and the mechanochemical reaction was performed for 30 h. The obtained product is denoted as S_2 in Table 1 and the corresponding XRD pattern is given as a_2 in Fig. 1. As seen in the XRD, a product $Mg_xNb_yO_{x+y}$ resembling to MgO can be obtained (compare with the pattern "c" in Fig. 1).

Method − 2: In this case, MgO and Nb_2O_5 were taken in 1:1 M ratio and ball milled for 30 h (sample S_3). The XRD of this sample "b_1" suggests that the following reaction has occurred,

$$MgO + Nb_2O_5 \rightarrow MgNb_2O_6 \qquad (2)$$

In the second step of the reaction, the product of reaction (2), i.e. $MgNb_2O_6$ was taken along with MgH_2 in a 1:5 M ratio and ball milled for 30 h. The XRD of the obtained product (S_4) shown as pattern "b_2" in Fig. 1 confirms the formation of $Mg_xNb_yO_{x+y}$ in this sample. Note that, in both the cases of S_2 and S_4, one can see the presence of significant amount of Fe impurity. This is because the Nb doped MgO is a hard, corrosive rock salt powder that erodes the steel milling vials. However, we have also achieved the synthesis of Fe free $Mg_xNb_yO_{x+y}$ by using zirconia based vials, and the results are being reported in another communication.

The structural and microstructural details of samples $S_1 - S_5$ are summarized in Table 1. The crystallite size of NbO_2 and $MgNb_2O_6$, respectively, ~15 and ~16 nm, but the size of the end product $Mg_xNb_yO_{x+y}$ is 7–8 nm. The morphology associated to the gross particle size changes of samples S_1, S_2, S_3 and S_4 are