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IMPROVEMENTS OF HYDROGEN DESORPTION OF LITHIUM BOROHYDRIDE BY IMPREGNATION ONTO MSU-H CARBON REPLICA

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The hydrogen storage material lithium borohydride was infiltrated from solvent solution into the pores of the carbon replica of MSU-H mesoporous silica by the incipient wetness method. Different amounts of lithium borohydride up to 40 % from the weight of the high surface area carbonic material were used. By this method was achieved a good dispersion of the hydride into the carbonaceous support. The hydrogen desorption starts at temperatures as low as 150 ^{0}C for the sample with 8 wt% $LiBH_4$ dispersed onto the MSU-H carbon replica while pure $LiBH_4$ does not release hydrogen below 300 ^{0}C. After re-hydrogenation, a lower amount of hydrogen is desorbed due to the fact that increasing temperature up to 400 ^{0}C a part of hydride segregates outside the pores of the carbonaceous support.

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1. Introduction

One of the priorities of the mankind is the development of a “green” economy based on hydrogen. Therefore, an efficient storage method of H_2 becomes an important target. The drawbacks of the two classical alternatives to store hydrogen as liquid in cryogenic vessels or compressed hydrogen in pressurized gas cylinders are the costs of liquefaction / compression and the safety issues. The hydrogen storage materials are of high interest taking into account the large amount of hydrogen stored per unit volume (up to 150 kg of hydrogen stored in 1 m^3 of material) while liquid hydrogen contains only 71 kg hydrogen/m^3. Some metal hydrides can be loaded with hydrogen at pressures as low as 10 bars H_2, eliminating the compression costs and high pressure safety problems which occur for the pressurized gas cylinders filled with hydrogen. However, the problem raised by the metal hydrides is the low hydrogen content by weight which can be reversibly stored, below 2 wt% H_2 [1]. For this reason the search of hydrides with large mass content of hydrogen is imperative. Among the hydrogen storage materials, lithium borohydride ($LiBH_4$) is a material which contains one of the largest amounts of hydrogen, 13.8 wt% H_2 which is released according to reaction (1).

$$LiBH_4 \Rightarrow LiH + B + 3/2H_2 \tag{1}$$

Unfortunately $LiBH_4$ does not release hydrogen below 300 ^{0}C [2], above the melting temperature of $LiBH_4$, of 280 ^{0}C. Without the addition of any catalyst, the release of the total amount of 13.8 wt% H_2 occurs only at temperatures of 600 ^{0}C while the complete re-hydrogenation can be achieved under harsh conditions (600 ^{0}C, and 350 bars H_2) [2].

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$LiBH_4$ with the addition of $MgCl_2$ and $TiCl_3$ desorbed 5 wt% H_2 at 400 ^{0}C and re-absorbed 4.5 wt% at 600 ^{0}C and 70 bars H_2 [3]. The addition of SiO_2 proved to be useful to improve the hydrogen desorption of $LiBH_4$ by decreasing the starting desorption temperature, with almost 100 ^{0}C less than that of non–catalyzed $LiBH_4$ [4]. By ball milling of 75% $LiBH_4$ + 25% TiO_2 were formed composites which desorbed 9 wt% H_2 at temperatures below 600 ^{0}C and absorbed 8 wt% H_2 at 600 ^{0}C and 70 bars H_2 [5]. The addition of some halides seems useful to improve the desorption kinetics of lithium borohydride. The composites $LiBH_4$ - SiO_2 - TiF_3 desorbed 8.3 wt% H_2 at 500 ^{0}C and re-absorbed 4 wt% H_2 at the same temperature under 45 bars of hydrogen [6].

Another method used to improve the hydrogen desorption behaviour of the hydrides envisages their retention in dispersed form, at nanometric scale, during hydrogen absorption / desorbtion cycles. The reaction with hydrogen is facilitated by reduction of the diffusion paths in the grains of small dimension. By encapsulation of the hydride inside the nanopores of some compound with high surface area it is possible to block the increase of the hydride grain size during hydrogenation. Moreover, for pores approaching the 1 nm value it can be achieved not only an improvement of hydrogen desorption but also a thermodynamic destabilization of the hydride, i.e. an enhancement of the hydrogen desorption pressure, what is useful for a suitable hydrogen storage material. The ammonia borane infiltrated onto silica nanoporous support exhibited such thermodynamic improvement [7]. Previous studies proved that dehydrogenation kinetics of $LiBH_4$ can be improved by impregnation into mesoporous carbon aerogel [8,9].

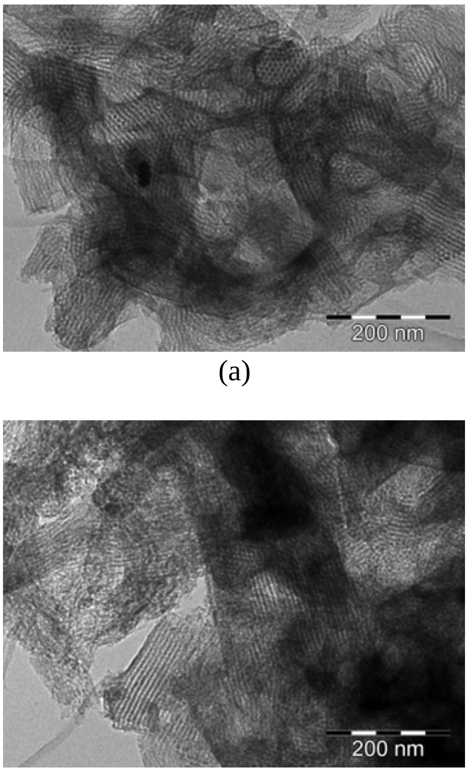
The aim of this paper is to study the hydrogen storage behaviour of $LiBH_4$ infiltrated by incipient wetness method into an ordered mesoporous carbon. The high surface area carbonaceous material is obtained by the template method starting from the mesoporous silica of MSU-H type. The present work shows the improvement of the desorption kinetics of $LiBH_4$ impregnated into the carbon replica of MSU-H compared with pure $LiBH_4$.

2. Experimental

The material of the initial silica mesoporous support was the commercially available MSU-H (purum, Sigma Aldrich). The carbon replica of MSU-H was obtained by a two steps procedure of impregnation with aqueous solution of sucrose (99.9 %, Sigma Aldrich) and a small amount of sulfuric acid. One gram of dehydrated MSU-H was impregnated in the first step with 1.25g sucrose, 0.14 g H_2SO_4 and 6 g H_2O. The resulted mixture was heated at 100 ^{0}C in air for 6 h and then at 155 ^{0}C in air for another 6h using a drying oven. During the second step, the caramelized mixture was impregnated with 0.75 g sucrose, 0.08 H_2SO_4 and 6 g H_2O. Once again the material was heated for 6h at 100 ^{0}C and 155 ^{0}C. The conversion of the caramelized sucrose to carbon was carried out by pyrolysis in nitrogen flow at 900 ^{0}C for 6h. The elimination of SiO_2 from the mixture silica-carbon was obtained by washing with 20% aqueous solution of hydrofluoric acid many times until obtaining neutral pH. The carbon replica of MSU-H (C-MSU-H) was then used for the impregnation of $LiBH_4$ by the incipient wetness method. In this respect a 0.1 M solution of $LiBH_4$ in tert–butyl–methyl-ether (TBME) was used for 10-40 steps of impregnation / heating at 80 ^{0}C under primary vacuum (10^{-3} mbars). The incipient wetness method was used in order to achieve the maximum loading with $LiBH_4$ of the carbonaceous support and in the same time avoiding as much as possible the segregation of the $LiBH_4$ outside the pores of C-MSUH. There were obtained samples with 8, 20 and 40wt% $LiBH_4$ impregnated into C-MSUH (further identified in the paper as x wt% $LiBH_4$-C-MSU-H where x=8, 20, 40). The samples processing was carried out into MBraun glove box under purified Argon (<1 ppm O_2, <1 ppm H_2O). X-Ray diffraction measurements were performed using a D-8 Advance Bruker diffractometer with Cu K-α radiation. TEM images were obtained with JEOL JEM 200CX analytical transmission electron microscope. A commercially available Sievert volumetric apparatus was used for hydrogen desorption measurements.

3. Results and discussions

TEM images obtained for the ordered mesoporous carbon replica of MSU-H are presented in Fig. 1a and 1b. It can be observed in transversal section the mesoporous structure with hexagonal pores. In Fig. 1b is shown a longitudinal section showing the long channels of the C-MSU-H grains. X-Ray diffraction measurements at grazing incidence depicted in Fig. 2 indicate a two-dimensional hexagonal structure (c >> a) with the lattice constant a = 11 nm as resulted from the positions of the (h k l) reflections given in the same figure. There is no evidence of any crystalline contribution at 2Theta above 2^0 in the XRD pattern of C-MSU-H. X-Ray diffraction patterns of the samples x wt% $LiBH_4$-C-MSU-H (x=8, 20, 40) obtained by the impregnation of the solution of 0.1 M $LiBH_4$ /TBME into C-MSU-H are presented in Fig. 3.



(a)

(b)

Fig.1. TEM images of the carbon replica of MSU-H. In (b) is evidenced the longitudinal section

In the same Fig. 3 it is shown for comparison also the XRD pattern of $LiBH_4$ dissolved into TBME and then re-crystallized by heating at 80 ^{0}C under vacuum conditions.

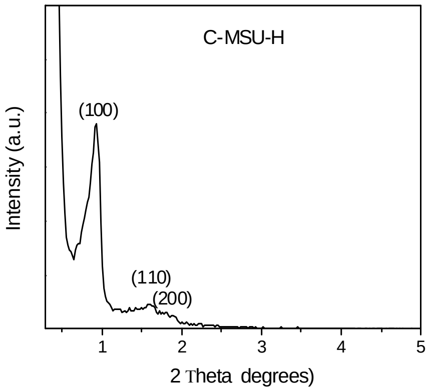


Fig. 2 Low angle X-Ray diffraction data of C-MSU-H

As shown in Fig. 3 the XRD pattern of the sample 8 wt% $LiBH_4$-CMSU-H does not evidence any crystalline contribution proving the complete dispersion of $LiBH_4$ inside the pores of C-MSU-H. The sample 20 wt% $LiBH_4$-CMSU-H exhibits an incipient precipitation of $LiBH_4$ outside the pores of C-MSU-H. This behaviour is more evidenced for the sample 40 wt% $LiBH_4$-CMSU-H, the segregation outside the C-MSU-H pores becoming more important at large amount of impregnated borohydride.

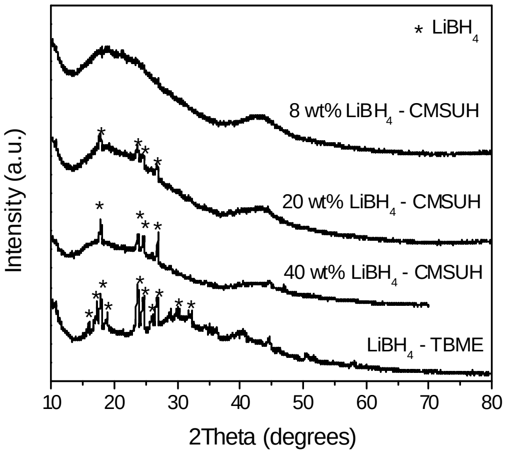


Fig. 3 X-Ray diffraction spectra of $LiBH_4$ impregnated into C-MSU-H and that of $LiBH_4$ dissolved into TBME and then re-crystallized

Hydrogen desorption measurements with temperature ramp of 2^0C/min were performed for the as-prepared $LiBH_4$–C-MSU-H samples up to temperatures of 400 ^{0}C as shown in Fig. 4. The fastest desorption occurs for the sample with 8 wt% $LiBH_4$, when the borohydride is most dispersed into the mesoporous support as was already proved by the XRD data shown in Fig. 3. For this sample the hydrogen desorption starts at temperatures as low as 150 ^{0}C while for the other two samples with 20 wt% $LiBH_4$ and 40 wt% $LiBH_4$ the desorption begins at about 170 ^{0}C and 200 ^{0}C, respectively.

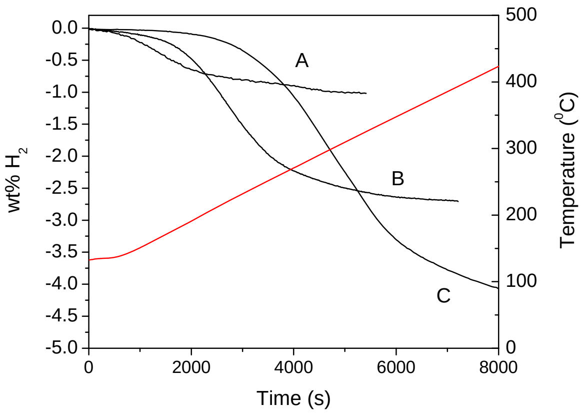


Fig. 4 Hydrogen desorption kinetics with temperature ramp of 2 ^{0}C/min for the as prepared samples: A) 8wt%$LiBH_4$-CMSUH, B) 20wt%$LiBH_4$-CMSUH and C) 40wt%$LiBH_4$-CMSUH

One must recall that pure $LiBH_4$ can release a maximum of 13.8 wt% H_2 when the temperature is raised up to 600 ^{0}C. Therefore, the sample obtained by impregnation of 8 wt% $LiBH_4$ into C-MSU-H cannot release more than the theoretical amount of 1.1 wt% H_2. From Fig. 4 it can be seen that 1.01 wt% of hydrogen is released below 325 ^{0}C by the sample 8 wt% $LiBH_4$ – C-MSU-H. The sample with 20 wt% $LiBH_4$ desorbs 2.7 wt% H_2 below 375 ^{0}C while its theoretical hydrogen content is 2.8 wt% H_2. The sample 40 wt% $LiBH_4$ –C-MSU-H releases 4.1 wt% H_2 below 400 ^{0}C and its theoretical amount of hydrogen is 5.5 wt%. It can be seen in the case of the sample with 40 wt% $LiBH_4$ a substantial deterioration of desorption kinetics compared with the other two samples explained by the borohydride segregation outside the pores of C-MSU-H (confirmed also by the XRD data from Fig. 3). The increase of $LiBH_4$ grains hinders the hydrogen diffusion and in consequence worsens the desorption kinetics.

After re-hydrogenation of the desorbed samples at 400 ^{0}C and 100 bars of H_2, were performed again hydrogen desorption measurements with temperature ramp of 2 ^{0}C/ min up to 400 ^{0}C as shown in Fig. 5. The reason to make desorption measurements also for the re-hydrogenated samples was to study the reversible storage capacity of $LiBH_4$-C-MSU-H composites.

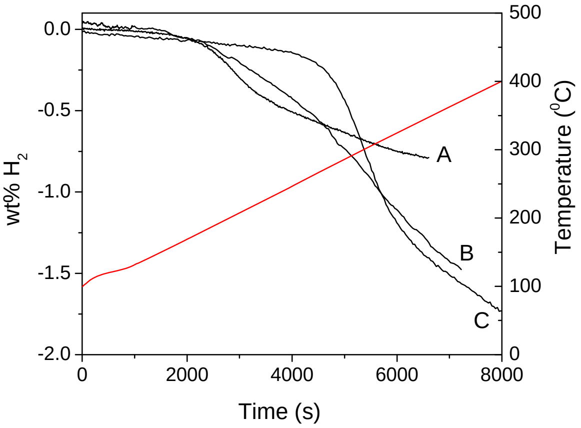


Fig. 5 Hydrogen desorption kinetics with temperature ramp of 2 ^{0}C/min for the re-hydrogenated samples: A) 8wt%$LiBH_4$-CMSUH, B) 20wt%$LiBH_4$-CMSUH and C) 40wt%$LiBH_4$-CMSUH

The re-hydrogenation of the samples was performed under mild conditions, suitable for practical applications (400 ^{0}C and 100 bars H_2) for only 2 hours. The recovering of the total amount of desorbed hydrogen for pristine $LiBH_4$ was previously achieved [2] under harsh conditions (600 ^{0}C and 350 bars H_2) in much longer time. The complete re-hydrogenation cannot be achieved at the temperatures and hydrogen pressures used in the present work. However, these cautions are necessary to avoid the massive segregation of $LiBH_4$ outside the pores of the mesoporous carbon.

The sample 8 wt% $LiBH_4$–C-MSU-H desorbs 0.79 wt% of hydrogen after re-hydrogenation (78% from the amount of H_2 desorbed by the as-prepared sample).The re-hydrogenated sample with 20 wt% $LiBH_4$ infiltrated into the mesoporous support releases 1.48 wt% H_2 (55% from the hydrogen quantity desorbed by the pristine sample) while the last sample (with 40 wt% $LiBH_4$) desorbs only 1.75 wt% of hydrogen.

Hydrogen desorption from the re-hydrogenated samples with 8 wt% $LiBH_4$ and 20 wt% $LiBH_4$ starts at about 200 ^{0}C while for the pristine samples the desorption begins at lower temperatures, 150 ^{0}C and 170 ^{0}C, respectively. The hydrogen release from the re-hydrogenated 40 wt% $LiBH_4$ –C-MSU-H sample begins at about 280 ^{0}C (the melting temperature of $LiBH_4$) with 80 ^{0}C higher than for the pristine sample.

The kinetics of hydrogen desorption for the re-hydrogenated samples displayed in Fig. 5 is worsened compared with the pristine samples (see Fig. 4) for all the compositions, both from the point of view of the initial desorption temperature and that of the amount of stored hydrogen. The explanation of this behaviour is the segregation of $LiBH_4$ outside the pores of C-MSU-H during heating up to 400 ^{0}C (one must recall that the melting temperature of $LiBH_4$ is about 280 ^{0}C).

Compared with pure lithium borohydride, which does not release hydrogen below 300 ^{0}C, the re-hydrogenated composites with 8 and 20 wt% $LiBH_4$ impregnated into C-MSU-H desorbs H_2 even at 200 ^{0}C. Moreover, the hydrogen reversibly stored by these composites reaches between one half and two-thirds of the maximum theoretically allowed amount.

3. Conclusions

The carbon replica of MSU-H was successfully synthesized by a reverse template method. Lithium borohydride was impregnated into the MSU-H carbon replica (C-MSUH) from a solution of TBME using the incipient wetness method. The amount of hydrogen released by the as-prepared $LiBH_4$-C-MSUH composites for the compositions with 8 and 20 wt% $LiBH_4$ approaches the maximum theoretically allowed limit. The hydrogen desorption starts at temperatures as low as 150 ^{0}C for the sample with 8 wt% $LiBH_4$ dispersed onto the MSU-H carbon replica while pure $LiBH_4$ does not release hydrogen below 300 ^{0}C. After re-hydrogenation, only between one half and two-thirds of the maximum theoretically allowed amount is desorbed due to the fact that increasing the temperature up to 400 ^{0}C a part of hydride segregates outside the pores of the high surface area carbonaceous support.

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