



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9

Title: PHYSICAL CHEMISTRY 2014 (Proceedings)

Editors: Ž. Čupić and S. Anić

Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia

Publisher: Society of Physical Chemists of Serbia

For Publisher: S. Anić, President of Society of Physical Chemists of Serbia

Printed by: “Jovan” Printing and Publishing Company; 200 Copies;

Number of pages: 6+ 441; **Format:** B5; Printing finished in September 2014.

Text and Layout: “Jovan”

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*12th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Organized by
The Society of Physical Chemists of
Serbia*

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REMARKABLE SORPTION PROPERTIES OF MgH₂-VO₂ NANOCOMPOSITES

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ABSTRACT

Composite of MgH₂□VO₂ has been synthesized by high-energy mechanical milling. The sorption properties of composites were examined by differential scanning calorimetry and sorption analysis. It has been shown that at relatively low temperature sorption reaction is notably enhanced. Complete desorption of pure MgH₂ at 380°C finishes after 30 minutes while composite material fully desorbs in less than 2 minutes even at lower temperatures.

INTRODUCTION

Much effort has been devoted on studies of metal hydrides for hydrogen storage. Metallic magnesium and magnesium based compounds are considered as promising candidates, since magnesium is an abundant, cheap and light metal with a high hydrogen sorption capacity (7.6 wt.%). Anyhow the problem of sluggish kinetics is main drawback of this material. It has been shown that high energy ball milling of magnesium hydride with various additives (oxide, non-oxide ceramics, amines etc.) improves the hydrogen sorption properties [1–3]. In contrast to bulk hydride, the form of fine powder has many advantages such large surface-to volume ratio which enhances hydrogen diffusion and nucleation of MgH₂. Regarding additives, metal oxide are both catalysts and very efficient milling agents that can create defects in magnesium hydride [4]. A wide range of different metal oxide was used to improve the properties of MgH₂ [5–7]. *Bobet et al.* reported the beneficial effect CeO₂ on MgH₂ sorption kinetics. *Bormann et al.* proposed that oxide interfaces attached to the oxide catalysts might locally destabilize the magnesium hydride phase [6]. *Oelerich et al.* investigated the influence of metal oxides on the sorption behaviour of nanocrystalline Mg-based systems [5]. The highest desorption rates are achieved with V₂O₅ and Fe₃O₄. Metal oxides, compared to the

MgH₂/transition metals composites, are dispersed homogeneously due to the brittleness. Oxides improves desorption kinetics even in very small doses. The fast sorption kinetics of composite may originate from a very high defect density, introduced at the surface of the metal oxide particles during high-energy ball milling [8].

On the other hand the catalytic nature of oxides originate from their vacant structure, therefore in this paper we have used VO₂(B) to enhance sorption properties of MgH₂

EXPERIMENTAL

Composite material was synthesized by high-energy ball milling using Spex 8000M mixer mill. 85 mass% of commercial of MgH₂ (Alpha Aesar 98%) and 15 mass % of hydrothermally synthesized VO₂(B) (from V₂O₅, Merck) was used as a precursors. Composite was milled for 2h using ball to powder ratio (BPR) 10:1. All samples were kept and handled in Ar atmosphere in a glove box. DSC measurements were performed in temperature range from 80 to 500°C, using 10K/min step. Desorption/absorption cycles were performed at different temperatures and corresponding pressures to determine the dependence of H₂ sorption concentration and temperature of activation using Hydrogen Sorption Analyser (HSA)

RESULTS AND DISCUSSION

HSA was used to examine the volume of hydrogen released from samples in a pre-set time period and temperature. In commercial MgH₂, at desorption temperature of 380°C, HSA curve reaches a plateau (maximum capacity of 5.7wt.%) after 30 min (see Fig. 1). At lower temperature (350°C) desorption begins only after 30 minutes, and after 100 minutes does not reach maximum desorption (reached ~4.5wt.%) even in a repeated cycle.

Also, capacity in absorption mode was significantly lower (~4.7wt.%) compared to absorption capacity at 380°C.

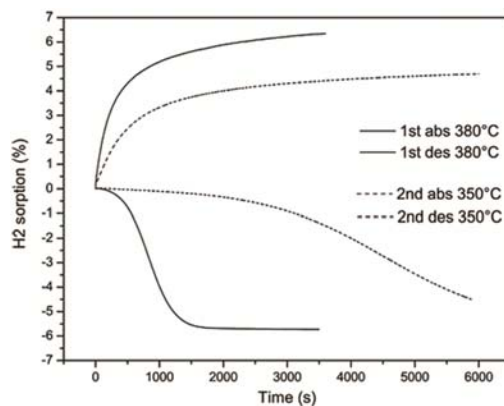


Figure 1. Sorption curves of commercial MgH₂

Milled composite material, with the addition of 15 mass% $\text{VO}_2(\text{B})$, shows significant acceleration of hydrogen desorption: at temperature of 360°C maximum capacity of 3.6 wt.% is reached after ~ 80 seconds. At 350°C , maximum desorption capacity of 3.6 wt.% is reached after ~ 95 seconds, and at temperature of 340°C capacity increases to 3.8wt.% and this value is reached after ~ 125 seconds (see Fig. 2).

DSC curves of commercial MgH_2 and composite material are shown in Figure 3. It can be see that temperature decreased from 454°C to 401°C with temperature onset at 385°C . Since the area under the peak is directly proportional to the change in enthalpy, by integration of DSC peaks it is obtained 1382J/g for commercial MgH_2 , and 1025J/g for synthesized composite. Decrease in enthalpy corresponds to decrease in hydrogen capacity which is in accordance with the results of hydrogen sorption measurements.

CONCLUSION

$\text{MgH}_2\text{-VO}_2$ composites were synthesized by mechanical milling. The sorption reaction was followed by differential scanning calorimetry and sorption analysis. Results indicate excellent catalytic activity of $\text{VO}_2(\text{B})$ in both adsorption and desorption process. The temperature onset for desorption is significantly decreased. The main fact is that composite demonstrate excellent reversibility in sorption reaction. The maximum capacity of hydrogen is released in less than 2 minutes from synthesized composites, representing a dramatic speed-up of kinetics performances comparing to the unprocessed MgH_2 .

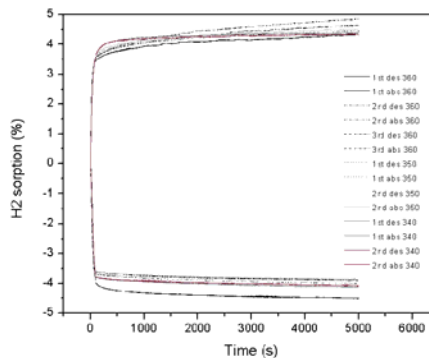


Figure 2. Cycling curves of composite material at 360°C

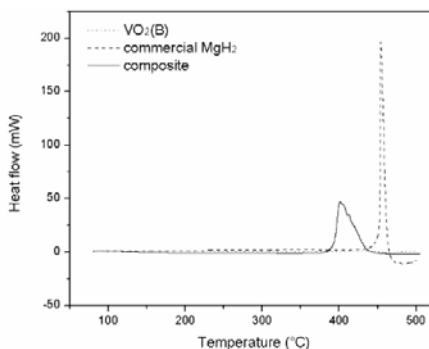


Figure 3. DSC curves of commercial MgH_2 and composite material

ACKNOWLEDGEMENT

This research was financially supported by Ministry of Education, Science and Technological Development of the Republic of Serbia under grant III 45012. The authors express their gratitude to COST Action MP1103 “Nanostructured Materials for Solid-State Hydrogen Storage”.

REFERENCES

- [1] L. Schlapbach, A. Zuttel, *Nature* 2001, 414, 353 – 358.
- [2] A. Zuttel, *Mater. Today*, 2003, 6, 24 – 33.
- [3] A. Bassetti, E. Bonetti, L. Pasquini, A. Montone, J. Grbovic, Vittori Antisari *Eur Phys J B* 2005, 43, 19 – 27.
- [4] *Hydrogen Fuel-production, transport and storage*, Taylor and Francis, 2008.
- [5] W. Oelerich, T. Klassen, R. Bormann, *J. Alloys Compd.* 2001, 315, 237 – 242.
- [6] J. L. Bobet, S. Desmoulins-Krawiec, E. Grigorova, F. Cansell, B. Chevalier, *J. Alloys Compd.* 2003, 351, 217 – 221.
- [7] A. Borgschulte, U. Bosenberg, G. Barkhordarian, M. Dornheim, R. Bormann. *Catal Today* 2007, 120, 262 – 269.
- [8] A. Borgschulte, M. Biemann, A. Zuttel, G. Barkhordarian, M. Dornheim, R. Bormann. *Appl. Surf Sci* 2008, 254, 2377 – 2384.