



HYDROGENATION AND HYDROLYSIS PROPERTIES OF MgH_2 COMPOSITES WITH ADDITIONS OF RMO_3 PEROVSKITES



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INTRODUCTION AND MOTIVATION

MgH_2 as a light metal hydride has the advantages of high weight capacity (7.6 wt.%), high volume density (110 kg/m³), environment friendly and a fairly low cost. In reaction with water (hydrolysis process) MgH_2 can generate 6.5 wt.% of hydrogen which can be used in fuel cells [1]. Unfortunately, the hydrolysis reaction rate is extremely slow. To increase the yield of hydrogen, solutions of acids and salts are used or the reaction temperature is increased. Another way to improve the kinetics of the reaction is the formation of nanocrystalline hydride. For this, magnesium hydride is synthesized by a high-energy ball milling with catalyst additives. In addition, the reaction area and concentration of defects increases, which allows to significantly reduce the reaction time. In our recent studies, it was shown that the use of $Zr_3V_3O_{0.6}$ suboxide and $Zr_3V_3O_{0.6}+C$ mixture as catalytic additives is an effective way to obtain composites based on MgH_2 with dual applications: for hydrogen gas storage and for hydrogen generation by hydrolysis [2]. Effective sorption/desorption properties when complex oxides with a perovskite structure were added to MgH_2 were demonstrated in [3]. In this work the effect of complex oxides $Dy_{0.5}Nd_{0.5}FeO_3$ and $TbFe_{0.5}Cr_{0.5}O_3$ with a perovskite structure on the hydrogenation of magnesium during milling and improvement of hydrogen sorption-desorption kinetics is shown. Also we tested the obtained MgH_2 -based composites for efficient hydrogen generation by hydrolysis.

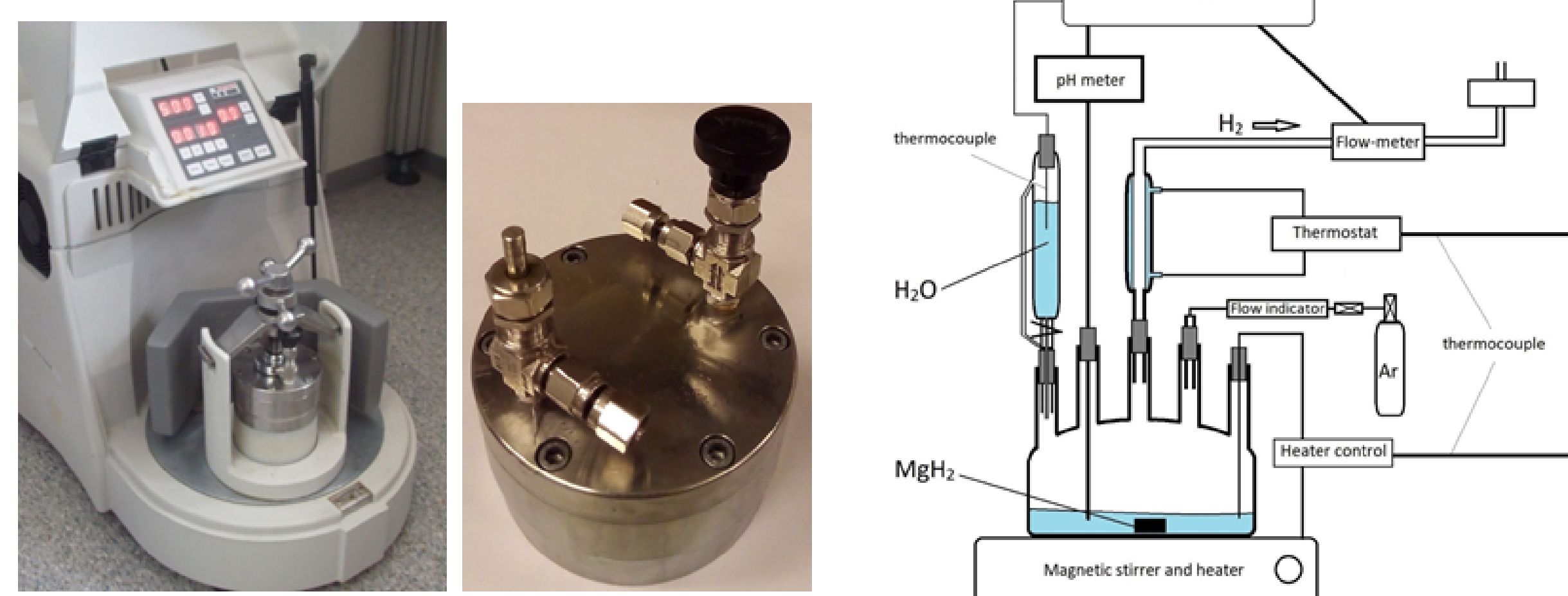
EXPERIMENTAL DETAILS

Materials: Mg (99.8 %, grit 50-150 mesh), graphite (Fluka, 99.9 %, $\leq 20 \mu m$) and RTO_3 ($Dy_{0.5}Nd_{0.5}FeO_3$ and $TbFe_{0.5}Cr_{0.5}O_3$) nanocrystalline powders prepared by low-temperature sol-gel method.

Reactive ball milling: Fritsch 6 Pulverisette mill, milling conditions: 20 bar H_2 ; 400 rpm; milling time – 900 min.

Phase-structural analysis: powder XRD (Cu-K α), FULLPROF software.

All investigated specimens were subjected to **hydrolysis** at pseudo-isothermal conditions and temperature 25 °C. The hydrolysis setup consists of a glass vessel with a flat flanged lid and five necks placed on a magnetic stirrer allowing its heating. The reacting powder and water were added under inert conditions (in a flow of Ar gas).



RESULTS AND DISCUSSION

MgH_2 -based composites were prepared by reactive ball milling (RBM) in hydrogen gas @ 20 bar H_2 . We milled magnesium powder (Fluka, 99+%, a particle size of 0,1-0,3 mm) and 2 types of catalytic additives ($Dy_{0.5}Nd_{0.5}FeO_3$ and $TbFe_{0.5}Cr_{0.5}O_3$). XRD showed that mechanochemical hydrogenation leads to complete conversion of magnesium into a mixture of α - + γ - MgH_2 , and RMO_3 does not interact with H_2 (see Fig. 1).

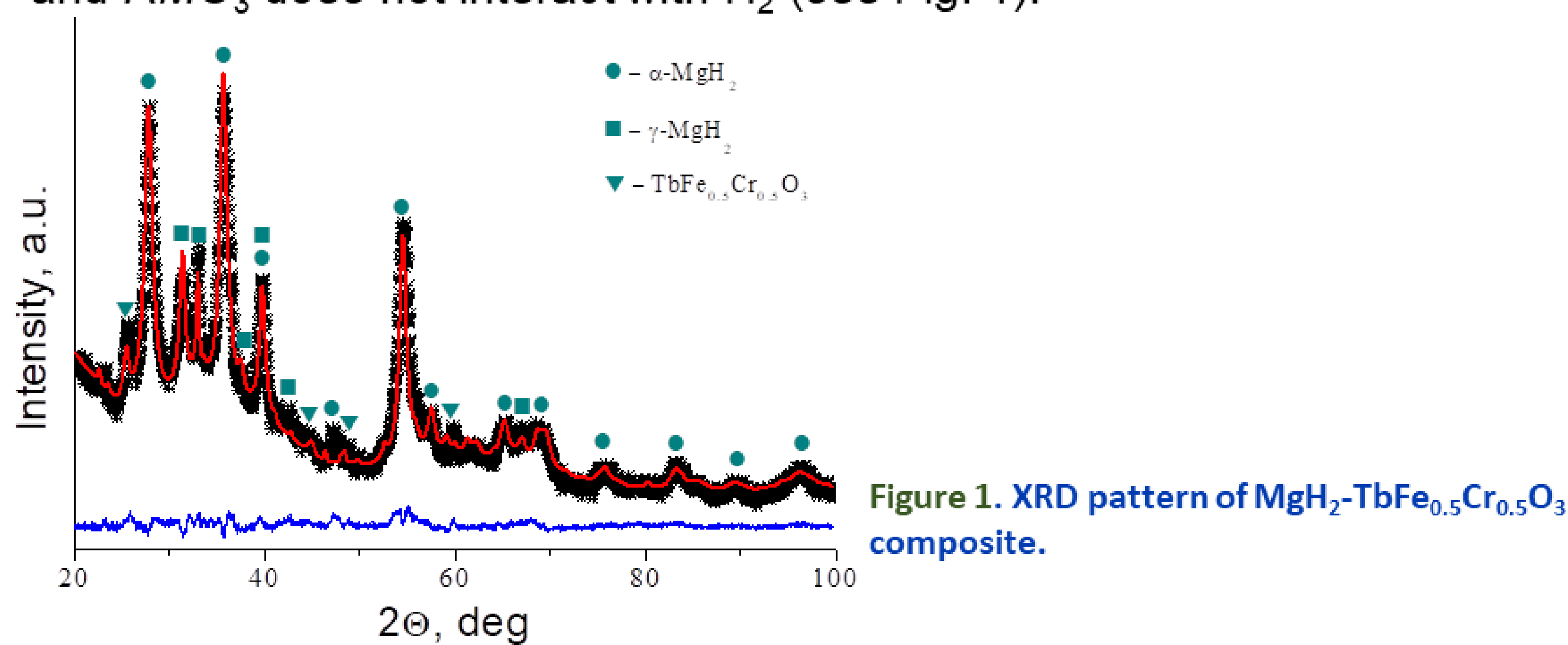


Figure 1. XRD pattern of MgH_2 - $TbFe_{0.5}Cr_{0.5}O_3$ composite.

It was shown by SEM that the obtained composites have a polydisperse morphology and their particle size distributions (PSD) may be fitted by Log-Normal function. The mean size of the particles of MgH_2 - RMO_3 -C composite is smaller as compared to that of MgH_2 - RMO_3 . SEM-images and PSD histograms for $RMO_3=Nd_{0.5}Dy_{0.5}FeO_3$ are shown in Fig. 2.

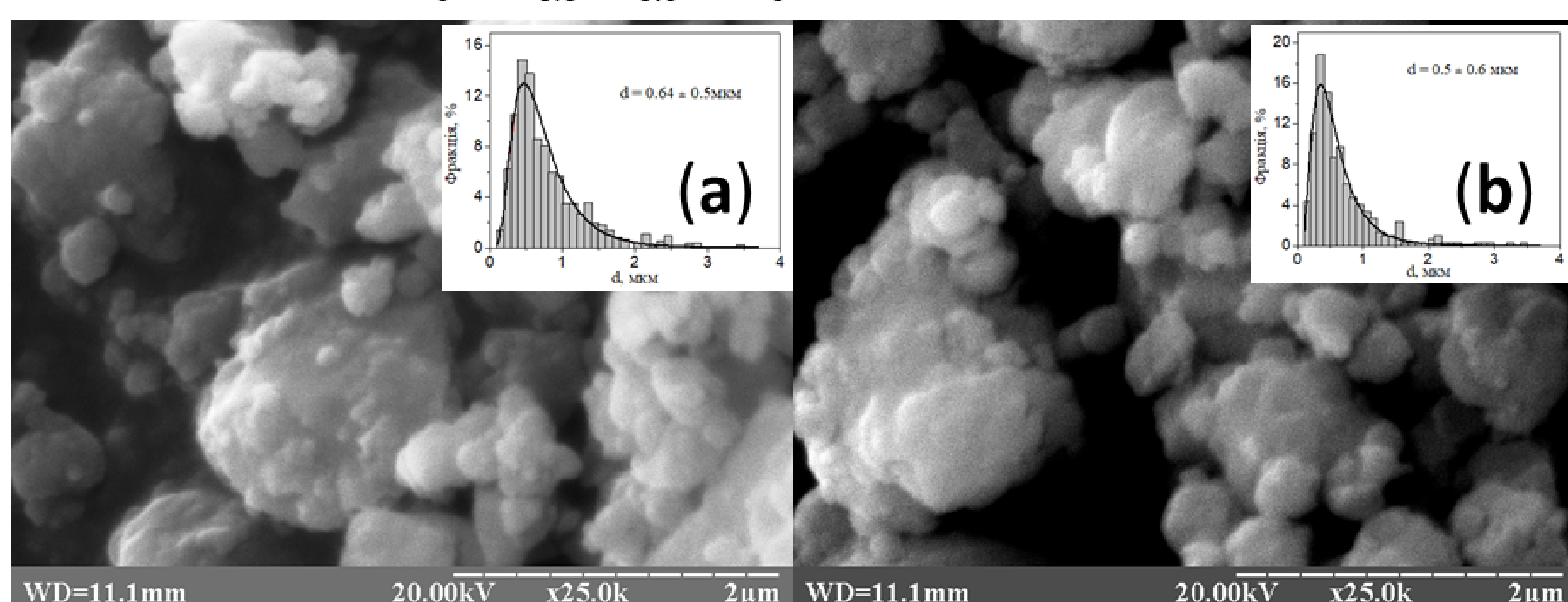


Figure 2. SEM-images of MgH_2 - $Nd_{0.5}Dy_{0.5}FeO_3$ (a) and MgH_2 - $Nd_{0.5}Dy_{0.5}FeO_3$ -C (b) composites. Insertions are the corresponding PSD histograms.

Hydrogen production rate during hydrolysis of MgH_2 -based nanocomposites

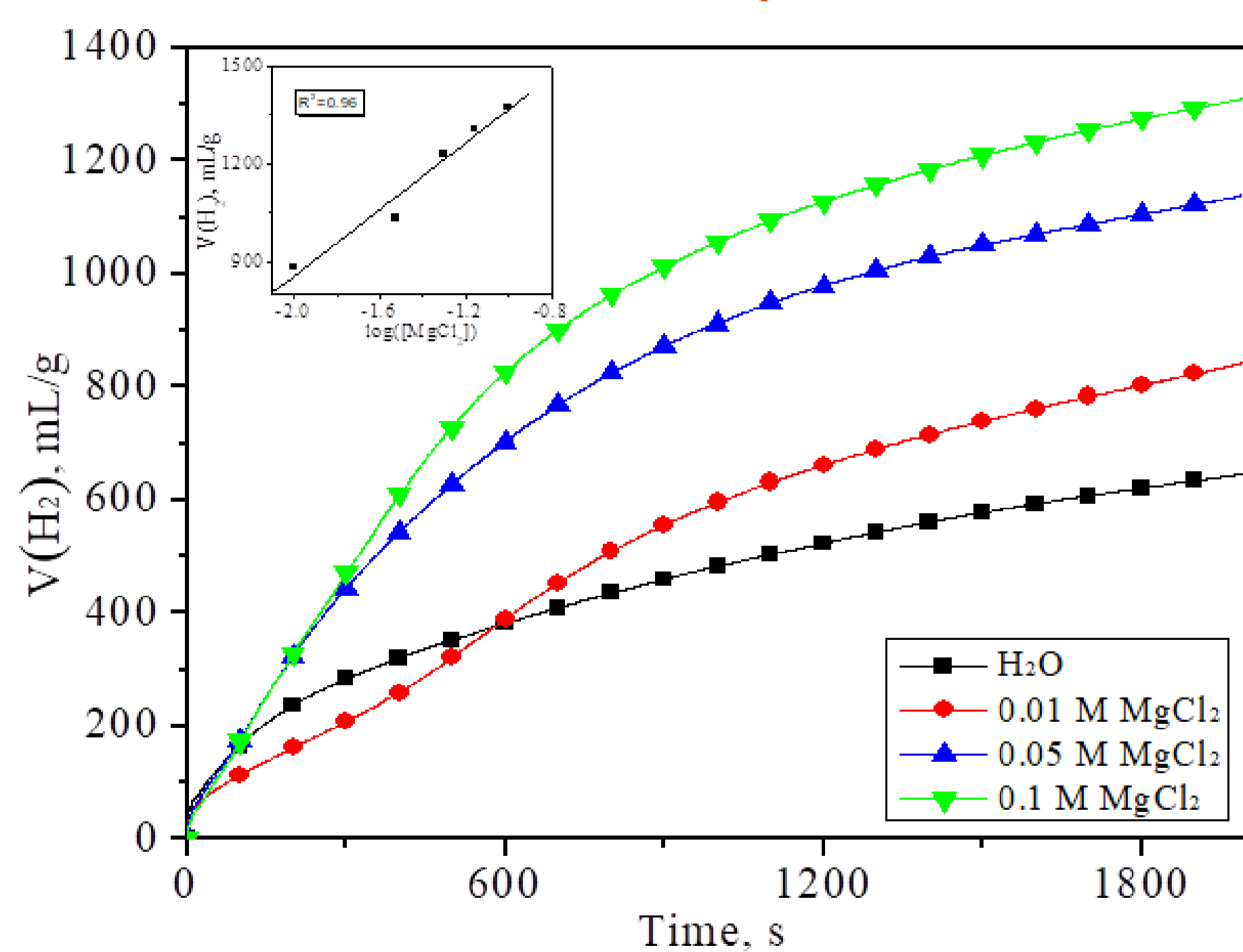


Figure 3. Hydrogen generation from MgH_2 - $TbFe_{0.5}Cr_{0.5}O_3$ -C composites in $MgCl_2$ solutions. Insert shows a dependence of the volume of H_2 released for 2000 s on the log of $MgCl_2$ concentration.

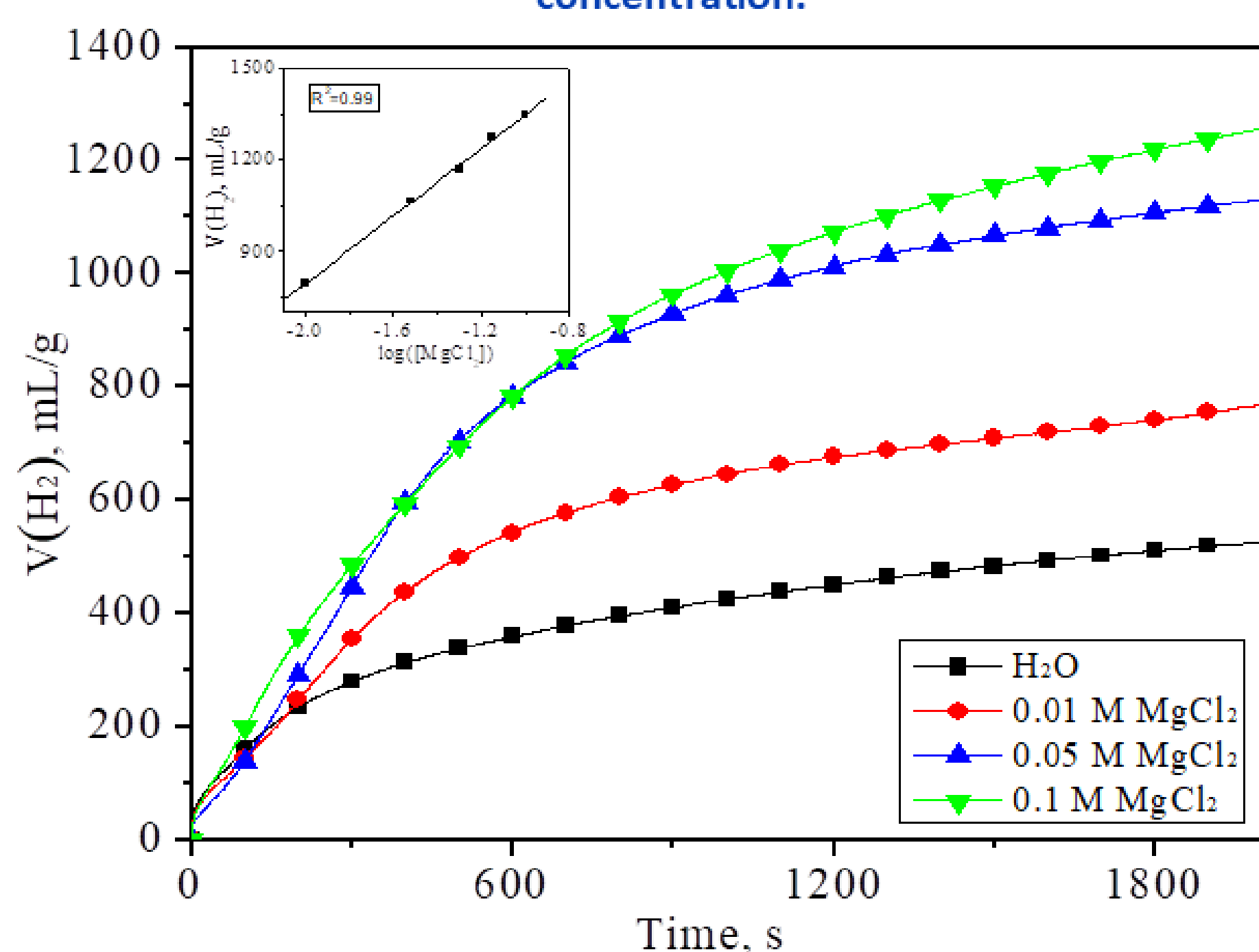


Figure 4. Hydrogen generation from MgH_2 - $Nd_{0.5}Dy_{0.5}FeO_3$ -C composites in $MgCl_2$ solutions. Insert shows a dependence of the volume of H_2 released for 2000 s on the log of $MgCl_2$ concentration.

CONCLUSIONS

Mg - RMO_3 and Mg - RMO_3 -C ($RMO_3 = Dy_{0.5}Nd_{0.5}FeO_3$ and $TbFe_{0.5}Cr_{0.5}O_3$) were synthesized by ball milling in a hydrogen atmosphere (20 bar). The formation of α - and γ - MgH_2 was shown by XRD studies. We observed also that the compounds with a perovskite structure do not interact with hydrogen during milling. Thermal desorption studies allowed to estimate the desorption activation energy: 123 kJ/mol for Mg - $TbFe_{0.5}Cr_{0.5}O_3$ and 147 kJ/mol for Mg - $Dy_{0.5}Nd_{0.5}FeO_3$ composites. Microstructural studies demonstrated that the addition of graphite results in a more dispersed morphology. The obtained materials demonstrate effective H_2 generation by hydrolysis in $MgCl_2$ solutions. A strong dependence of the conversion rate from the $MgCl_2$ concentration was observed. Highest conversion rate reached 82-88% (1200-1300 mL/g) for 30 min of hydrolysis in 0.1 M $MgCl_2$ solution for MgH_2 - RMO_3 -C composites.

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