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Synthesis and functional properties of Mg/MgH_2—FeNiCo (Raney type) composite

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Magnesium hydride (MgH_2) is considered a highly promising material for hydrogen storage and on-demand hydrogen generation due to its high hydrogen capacity, low cost, and environmental safety. However, its practical use, is limited by slow sorption—desorption kinetics and rapid passivation during hydrolysis caused by the formation of a poorly soluble $Mg(OH)_2$ layer. Mechanochemical hydrogenation is an effective method for producing nanocrystalline MgH_2 with improved reactivity, especially when catalytic additives are introduced to accelerate H_2 dissociation and diffusion. In this work, Mg/MgH_2—FeNiCo composites were synthesized by reactive ball milling in hydrogen with 10 wt. % FeNiCo (Raney type) additive. The FeNiCo catalyst was obtained by alkaline leaching of arc-melted Fe—Ni—Co—Al alloys. Structural analysis (XRD) confirmed the formation of α-MgH_2 and γ-MgH_2 phases, residual Mg and MgO. Microstructure observations showed heterogeneous particle morphology typical of high-energy milling. Hydrogen absorption experiments demonstrated that FeNiCo significantly accelerates magnesium hydrogenation: in 20 h the composite absorbed 5.52 wt. % H, whereas pure Mg reached only 2.43 wt. % under identical conditions. Thermal desorption studies showed that the main peak of hydrogen evolution for the composite occurs at a temperature of 280 °C. The composite was also evaluated as a material for hydrogen generation by hydrolysis. While MgH_2 milled for 20 h released only 3 % hydrogen in distilled water, the Mg/MgH_2—FeNiCo composite achieved 42 % conversion in 90 min. The use of $MgCl_2$ solutions further enhanced performance, increasing conversion up to 81 % at 0.1 mol · L^{-1}. These results confirm the catalytic efficiency of FeNiCo in both mechanochemical hydrogenation and hydrolysis, demonstrating its potential for efficient in situ hydrogen production.

Keywords: *composite materials, magnesium hydride, catalytic additives, Raney-type alloys, hydrogen, hydrolysis.*

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Introduction. Magnesium hydride (MgH_2) is a promising material for hydrogen storage and on-demand hydrogen generation due to its high hydrogen capacity, low cost, and environmental safety [1, 2]. However, its practical application is limited by slow sorption–desorption kinetics and the formation of a passivating $Mg(OH)_2$ layer during hydrolysis, which terminates the reaction at ~20 % conversion [3, 4]. Therefore, rapid and efficient synthesis of highly reactive MgH_2 remains an important challenge.

Mechanochemical hydrogenation offers a solution by enabling complete conversion of magnesium into nanocrystalline MgH_2 at room temperature. High-energy ball milling increases the surface area, reduces particle size, and creates numerous defects and grain boundaries, which accelerates hydrogen diffusion and hydride formation [5]. The reaction kinetics can be further improved with catalytic additives. Transition metals, their oxides, hydrides, and intermetallic compounds — especially Ti- and Zr-based — lower the activation barrier for H_2 dissociation and enhance desorption kinetics [6—8]. Sub-oxides such as $Ti_4Fe_2O_x$ and $Zr_3V_3O_x$ decrease the synthesis time of MgH_2 by a factor of four [9, 10], while graphite reduces particle agglomeration and improves cyclic stability [11, 12].

Hydrogen generation via MgH_2 hydrolysis is another promising application, particularly for portable systems [3, 4, 13]. However, the growth of $Mg(OH)_2$ on particle surfaces limits its efficiency. Various approaches have been explored to overcome passivation, including ball milling, alloying, acid or chloride-containing solutions, and catalytic additives [14—16]. Chloride salts are especially effective because they reduce pH and destabilize the hydroxide layer [17].

The purpose of this work was to investigate the effect of FeNiCo Raney-type additives on hydrogen sorption properties of a hydride composite obtained from magnesium and their hydrogen generation in the hydrolysis process.

Materials and methods. Hydride nanocomposites MgH_2—FeNiCo were prepared from magnesium powder (0.08—0.125 mm, Shanghai Synnad, 99.0 %) and Raney-type FeNiCo powder obtained by a leaching method. Compact metals Fe, Ni, Co, and Al (Alfa Aesar, 99.5 %) were used as starting materials FeNiCo synthesis; the corresponding aluminides were produced by arc melting. The resulting alloy (0.3 g) was mechanically ground in a mortar to obtain a fine powder with a particle size not exceeding 0.04—0.08 mm. The powder was treated with a 5 $mol \cdot L^{-1}$ NaOH solution at 20 °C. After the reaction was complete, the precipitate was washed three times with an alkaline solution at 70 °C using magnetic stirring at 220 rpm until gas evolution ceased completely. The obtained precipitate was subsequently washed five times with distilled water until neutral pH was achieved (verified using litmus paper) and then dried at room temperature.

Magnesium-based hydride composites (with 10 wt. % nanostructured additive) were prepared by reactive ball milling in a hydrogen atmosphere (up to 2 MPa) at a disk rotation speed of 400 rpm using a Fritsch Pulverisette-6 planetary mill. Stainless steel balls with a ball-to-powder mass ratio of 30 : 1 were employed as the milling media. The starting components were loaded in ambient air, whereas the synthesized composites were unloaded in an argon atmosphere and stored in sealed containers. The amount of hydrogen absorbed by the sample during milling was determined by a volumetric method based on the change in hydrogen pressure in a known volume.

Phase analysis of the samples was performed using powder X-ray diffraction patterns recorded on a DRON-3.0 diffractometer with Cu K_α radiation. The obtained data were analyzed by full-profile structural refinement using the Rietveld method. The microstructure of the synthesized

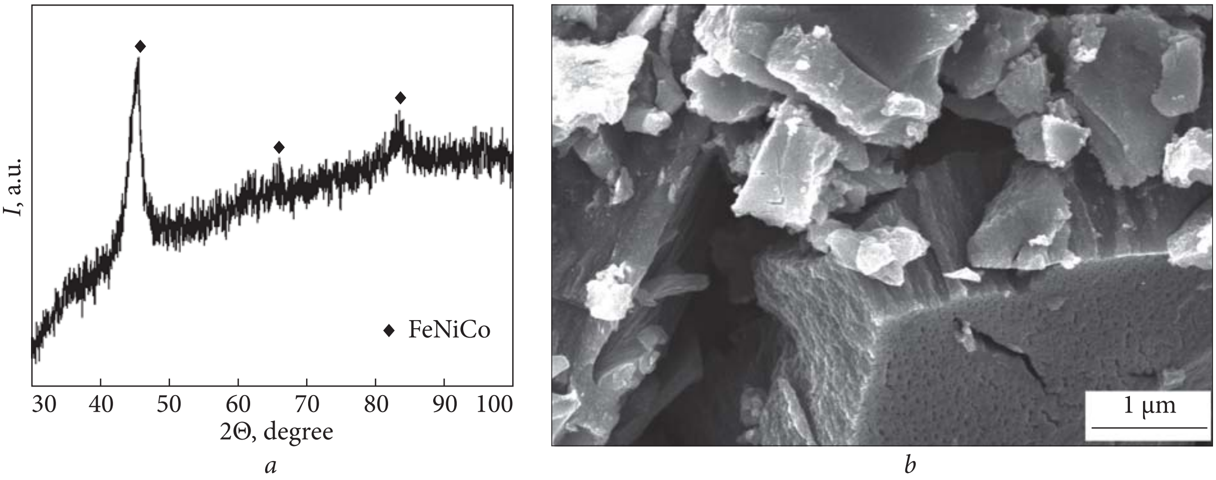


Fig. 1. X-ray diffraction pattern (*a*) and microstructural image (*b*) of FeNiCo-*R* powder

composites was examined by scanning electron microscopy (SEM) using an EVO 40XVP microscope equipped with an INCA Energy 350 spectrometer.

Hydrogen desorption from hydride composites was additionally investigated by thermal desorption spectroscopy (TDS). The samples were heated at a constant rate of 2 °C · min^{-1} under dynamic vacuum from room temperature to 450 °C. Sample with a mass 0.1 g was placed in an autoclave, and a vacuum was created in the system prior to heating. Sample temperature and pressure were continuously recorded; their changes indicated the progress of the dehydrogenation reaction. The hydrogen desorption temperature was determined from the sharp increase in the hydrogen flow.

Hydrogen generation by hydrolysis of MgH_2 was carried out under pseudo-isothermal conditions at 25 °C using the experimental setup described in [16]. Distilled water or aqueous magnesium chloride solutions (0.01—0.1 mol · L^{-1}) were employed as the reaction solutions. The total volume of the reaction mixture was 20 mL, and the mass of the tested sample was 0.2 g. The volume of the evolved hydrogen was determined by a volumetric method.

Results and discussion. The X-ray diffraction pattern and microstructural image of the leached powder (FeNiCo-*Raney* or FeNiCo-*R*) are shown in Fig. 1. X-ray phase analysis revealed that the obtained sample is single-phase, with a structural type (ST) corresponding to α-Fe (space group *Im-3m*), a lattice parameter a = 2.844 Å, and an average crystallite size of approximately 5 nm. Aluminum-containing phases were not detected by XRD; however, the presence of aluminum in minor amounts was confirmed by EDX analysis.

The hydride composites Mg/MgH_2—FeNiCo-*R* and Mg/MgH_2 were synthesized by a mechanochemical method. The hydrogen absorption curves for magnesium without additives and with the FeNiCo-*R* additive are shown in Fig. 2, *a*. The hydrogen content is expressed relative to the MgH_x hydride phase. During 20 h of synthesis, the Mg/MgH_2—FeNiCo-*R* composite absorbed 5.52 wt % H_2. For comparison, magnesium without additives absorbed only 2.43 wt % H_2 under identical conditions.

X-ray diffraction analysis of the composite (Fig. 2, *b*) revealed the formation of a mixture of two magnesium hydride polymorphs: α-MgH_2 (ST rutile-type TiO_2) and γ-MgH_2 (ST α-PbO_2-type). High deformation and the partially amorphous nature of the sample did not allow for ac-

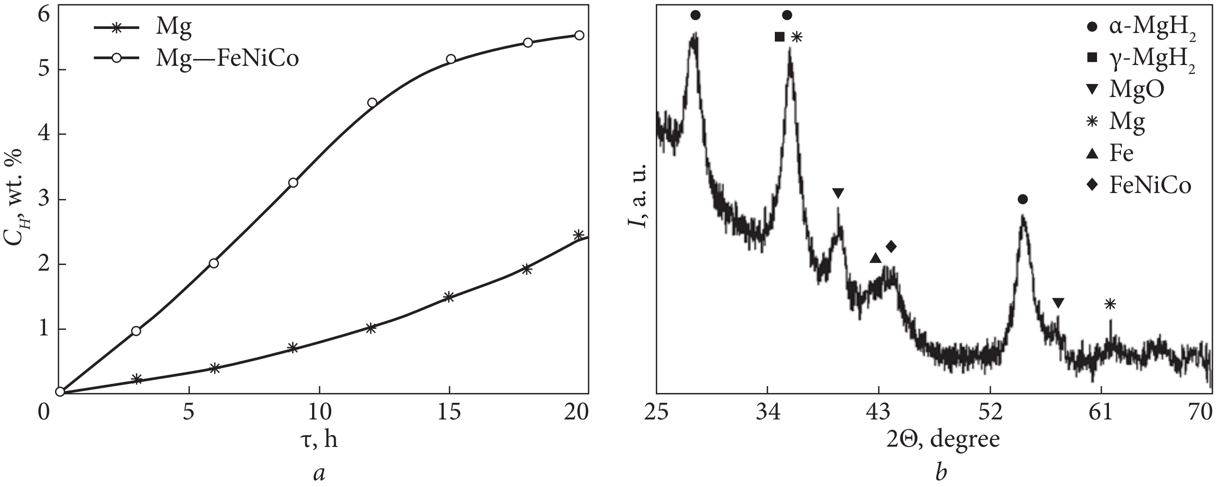
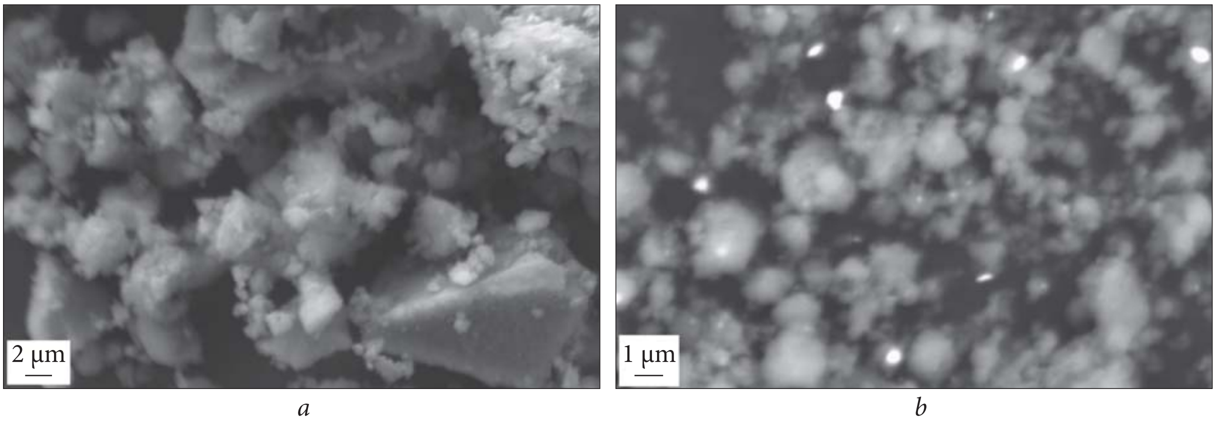
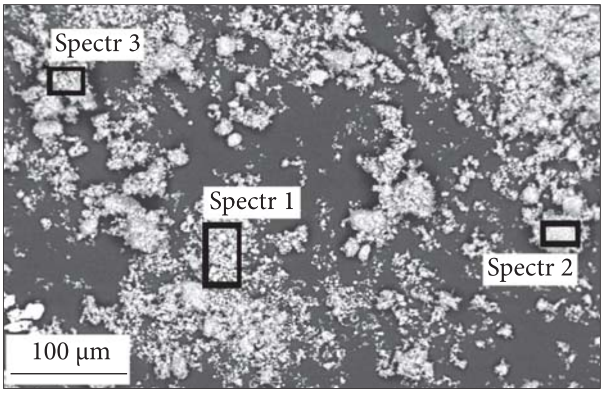


Fig. 2. Curves of mechanochemical hydrogenation of Mg and Mg—FeNiCo-*R* (*a*) and X-ray diffraction pattern of the hydride composite Mg/MgH$_2$—FeNiCo-*R* (*b*)





Element	Spectr 1		Spectr 2		Spectr 3	
	wt.%	at.%	wt.%	at.%	wt.%	at.%
Mg	93.57	97.19	82.35	79.24	81.93	79.30
O	–	–	12.87	18.81	12.54	18.45
Fe	2.27	1.03	1.98	0.83	1.85	0.78
Ni	2.18	0.94	1.42	0.57	1.61	0.64
Co	1.98	0.85	1.38	0.55	2.08	0.83

c

Fig. 3. Microstructure of Mg/MgH$_2$ (*a*), Mg/MgH$_2$—FeNiCo-*R* (*b*) composites powder with a milling time of 20 h, and element distribution for Mg/MgH$_2$—FeNiCo-*R* (*c*)

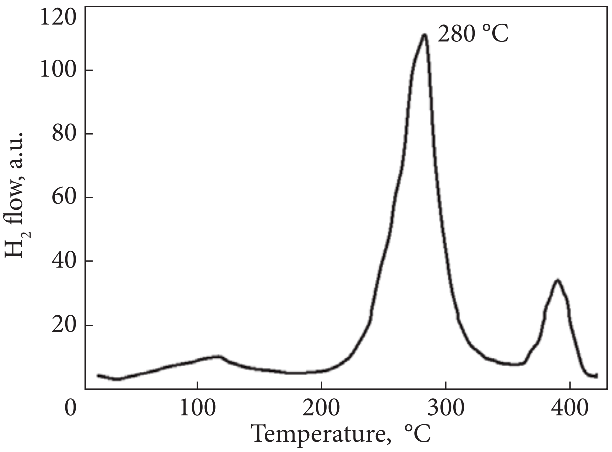
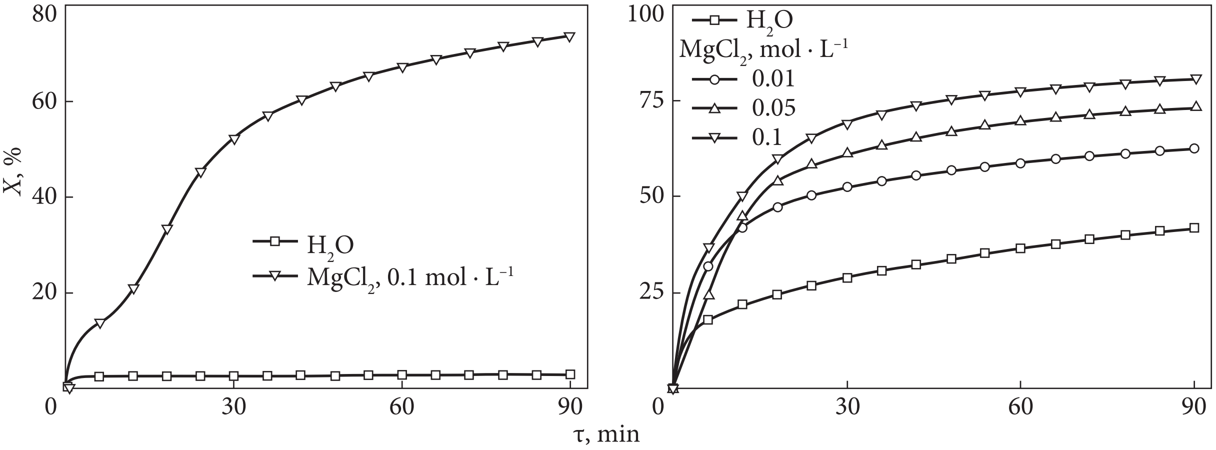


Fig. 4. Hydrogen TDS curve in vacuum for composite Mg/MgH_2—FeNiCo-*R*



a *b*

Fig. 5. Dependence of hydrogen yield (*X*) on time for Mg/MgH_2 (*a*) and Mg/MgH_2—FeNiCo-*R* (*b*)

Degree of conversion (hydrogen yield) and volume of hydrogen released from Mg/MgH_2 and Mg/MgH_2—FeNiCo-*R* (20 h of milling) during 90 min of hydrolysis

C($MgCl_2$), mol · L^{-1}	Mg/MgH_2		Mg/MgH_2—FeNiCo-*R*	
	X, %	*V*, ml · g^{-1}	*X*, %	*V*, ml · g^{-1}
0	3	35	41.8	621
0.01	—	—	62.4	929
0.05	—	—	73.3	1090
0.1	73.7	934	80.8	1202

curate identification of the phases and their quantitative content. Nevertheless, the presence of the main reflections of additional phases allowed for the identification of unreacted magnesium and magnesium oxide. The selected milling duration was insufficient to achieve complete transformation of magnesium to magnesium hydride. The presence of residual metallic magnesium in the composites correlates with the results of hydrogen uptake measurements. The detection of MgO is attributed to slight oxidation of the material during X-ray data collection in air. No additional phases indicating chemical interaction between Mg (or its hydride) and the additives during reactive milling in hydrogen were detected.

Powder morphology evaluation showed that the average particle size of Mg/MgH_2 was 1.42 μm after 20 h of milling, while for Mg/MgH_2—FeNiCo-*R* composite was 1.0 μm (Fig. 3, *a* and *b*, respectively). EDX analysis confirmed a uniform distribution of the additive within the Mg/MgH_2—FeNiCo-*R* hydride composite (Fig. 3, *c*). The average particle size of Mg/MgH_2 milled for 72 h decreased to 0.64 μm, indicating the significant influence of milling duration as an experimental parameter.

TDS (heating rate 2 $°C \cdot min^{-1}$) of the Mg/MgH_2—FeNiCo-*R* composite showed that the main peak of hydrogen desorption temperature is 280 °C (Fig. 4). However, an additional hydrogen release from the composite was also observed at 388 °C. This separation of the desorption profile will be clarified in further studies.

Comminution of magnesium hydride during milling significantly increases the hydrogen yield in the hydrolysis reaction. The optimal milling duration depends on several factors, including the type of catalytic additives, milling speed and energy, and the purity and dispersity of the initial magnesium [18]. During hydrolysis in distilled water, the conversion yield of MgH_2 milled for 20 h was only 3 % (Fig. 5, *a*). Prolonging the milling time to 72 h increased the reaction yield to 49 %. Thus, the milling duration (and, accordingly, enhanced dispersity and increased particle surface area) accounts for the nearly comparable hydrogen release from pure magnesium hydride and the Mg/MgH_2—FeNiCo-*R* composite. The dispersion of magnesium hydride and its composites also has a pronounced effect on their functional explosive characteristics [19]. Thus, mechanochemical synthesis is also a promising approach to the production of magnesium hydride as an energy-containing material for specialized applications.

Magnesium chloride solution is the most promising and extensively studied medium for the hydrolysis reaction [16]. Owing to its low molecular weight, it enables a high conversion of magnesium hydride with only a minor increase in the overall mass of the composition. The use of $MgCl_2$ solutions significantly enhances both the hydrogen evolution rate and the degree of conversion (Table). In particular, for Mg/MgH_2 milled for 20 h, the conversion increased from 3 % in distilled water to 74 % in a 0.1 $mol \cdot L^{-1}$ $MgCl_2$ solution.

For the Mg/MgH_2—FeNiCo-*R* composite, the degree of conversion increased by a factor of two compared with the reaction in distilled water (Fig. 5). These values are slightly lower than the previously reported conversion degrees for composites containing binary additives FeCo-*R* [20]. This difference may be attributed to variations in the amount of oxide phases present in the synthesized nanoadditives. At the same time, a comparative analysis of these compositionally similar materials indicates that the composite with the ternary nanoadditive exhibits somewhat improved hydrogen uptake kinetics.

Conclusions. Thus, this study demonstrates the effect of the FeNiCo catalytic additive on the hydrogenation rate of magnesium during reactive ball milling. The hydrogenation time of magne-

sium with additives is, on average, approximately three times shorter than that of pure magnesium. The structure of the resulting composites was analyzed and characterized using X-ray diffraction and scanning electron microscopy. X-ray phase analysis of the diffraction patterns revealed the presence of hydride phases MgH_2 (α-MgH_2 and γ-MgH_2), magnesium oxide, and residual magnesium that did not react with hydrogen within the composite. The obtained TDS spectrum showed that the synthesized composite exhibits main hydrogen desorption peak at 280 °C. The material was also tested as a hydrogen-generating material by means of hydrolysis. The results indicated that within 90 min the degree of conversion in distilled water reached 42 % and increased significantly upon the addition of $MgCl_2$ ($0.1 \text{ mol} \cdot L^{-1}$), reaching 81 %. The synthesized composites may also be considered as energy-containing materials for specialized applications.

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СИНТЕЗ ТА ФУНКЦІОНАЛЬНІ ВЛАСТИВОСТІ КОМПОЗИТА Mg/MgH_2—FeNiCo (ТИПУ РЕНЕЯ)

Гідрид магнію (MgH_2) вважається перспективним матеріалом для зберігання водню та його генерації за потреби. Однак його практичне використання обмежене через повільну кінетику сорбції—десорбції та швидку пасивацію під час гідролізу внаслідок утворення погано розчинного шару $Mg(OH)_2$. Механохімічне гідрування є ефективним методом отримання нанокристалічного MgH_2 з покращеною реакційною здатністю, особливо у разі введення каталітичних добавок для прискорення дисоціації та дифузії H_2. У дослідженні композити Mg/MgH_2—FeNiCo було синтезовано методом реактивного кульового помелу у водні з 10 мас. % добавкою FeNiCo (типу Ренея). Каталізатор FeNiCo отримано шляхом лужного вилуговування дугово-розплавлених сплавів Fe—Ni—Co—Al. Структурний аналіз (XRD) підтвердив утворення фаз α-MgH_2 та γ-MgH_2, залишкових Mg та MgO. За допомогою сканувальної електронної мікроскопії (SEM) визначено гетерогенну морфологію частинок, типову для високоенергетичного помелу. Експерименти з поглинання водню показали, що FeNiCo значно прискорює гідрування магнію: протягом 20 год композит поглинув 5,52 мас. % H, тоді як чистий Mg — лише 2,43 мас.% за ідентичних умов. Згідно з результатами дослідження термодесорбції, основний пік виділення водню для композита відбувається за температури 280 °C. Композит також був оцінений як матеріал для отримання водню шляхом гідролізу. Тоді як MgH_2, подрібнений протягом 20 год, вивільнив лише 3 % водню в дистильованій воді, композит Mg/MgH_2—FeNiCo досяг 42 % конверсії за 90 хв. Використання розчинів $MgCl_2$ ще більше покращило продуктивність, збільшивши конверсію до 81 % за концентрації 0,1 моль/л. Отримані результати підтверджують каталітичну ефективність FeNiCo як у механохімічному гідруванні, так і в гідролізі, демонструючи його потенціал для ефективного виробництва водню.

Ключові слова: *композитні матеріали, гідрид магнію, каталітичні добавки, сплави типу Ренея, водень, гідроліз.*