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Comparison investigation of Co-based catalysts for the catalytic hydrolysis of sodium borohydride

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Catalyzed borohydride hydrolysis is a perspective method for hydrogen-on demand production. The produced hydrogen is with high purity, the process requires no energy and its kinetics can be easily controlled by proper catalysts. In this study, three Co-based nanocomposites (CoMnB, CoNiMnB and CoNiMoW) electrodeposited on nickel foam were investigated as catalysts for borohydride hydrolysis. Kinetics of the catalyzed reaction was investigated by water-displacement method at different temperatures from 16 ºC to 40 ºC. The highest hydrogen generation rates of 0,9 ml/min at 16 ºC and 2,1 ml/min at 40 ºC was obtained with CoNiMnB catalyst. At the same time, the process takes place with the lowest activation energy of 36,9 kJ/mol with this catalyst. The obtained results show that CoNiMnB-electrodeposits possess the highest catalytic activity among studied materials and can be used as a catalyst in hydrogen-on-demand generators for portable applications.

Key words: Hydrogen, borohydride, hydrolysis, hydrogen generator.

INTRODUCTION

Among all alternative power sources, hydrogen is claimed as the cleanest fuel of the future. Both in combustion engines and fuel cells its reaction with oxygen produces only water. In 1970's John Bockris first coined the term "hydrogen economy" as a concept for delivering energy using hydrogen. Nowadays, both the depletion of the fossil fuels and the environmental pollution drive to intensification of the R&D of the hydrogen technologies as an alternative to the current energy system.

Except the cost, hydrogen seems as a perfect fuel. The by-products of hydrogen combustion are electricity, water and heat. Although its low density makes efficient storage difficult, hydrogen has the highest energy of combustion per unit of mass. Energy conversion devices using hydrogen are highly efficient and produce very little or no harmful emissions. As an energy carrier, hydrogen can be produced safely and abundantly from diverse renewable resources such as hydroelectricity, solar and wind power. Since many of these are domestic sources, it can help decrease the dependence of nations on others for fuels eliminating the political polarizations that arise from cartel pricing, conflicting ideological and economic policies and hostilities among nations. For the same reasons, hydrogen is anticipated to join electricity as the foundation of a globally sustainable energy system using renewable energy [1, 2].

A wide range of technologies for hydrogen production has been developed. However, the steam methane reforming accounts for about 95 percent of the hydrogen produced today in the United States [3]. Another method, called partial oxidation, produces hydrogen by burning methane in air. Both processes produce a "synthesis gas", which is reacted with water to produce more hydrogen. Another attractive method is the renewable electrolysis, which uses an electric current to split water into hydrogen and oxygen. The electricity required can be generated using renewable energy technologies, such as wind, solar, geothermal, and hydroelectric power.

The wide use of hydrogen has several disadvantages. The production of hydrogen gas currently relies on fossil fuels, mainly natural gas, which results in huge CO_2 emissions and environmental pollution. The storage is tough, because hydrogen is a low-density gas. The distribution and infrastructure need to be refurbished to cope with hydrogen [4].

One of the promising methods for production of hydrogen-on-demand is the hydrolysis of alkaline borohydrides. Using sodium borohydride as a hydrogen carrier has several advantages. The

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produced hydrogen is quite pure. In some cases it is extremely important, because any waste may damage the proton-exchange membrane (PEM) in the fuel cells, for example. The borohydride hydrolysis reaction can be highly controllable – it stops if the catalyst is removed from the reactor. The reaction needs no energy and can operate at ambient temperature and pressure. According to the application, the amount of the released gas can be controlled by using proper catalyst. Among all catalysts studied, ruthenium catalysts possess the highest activity [5].

Low cost and effective transition metal catalysts are of interest for the development of on-board hydrogen generation systems for the fuel cell vehicles. With the aim of designing an efficient low-cost hydrogen generator for portable fuel cell applications, nickel–cobalt materials were reported to be promising catalysts [6-7]. The main method for their preparation is by a chemical reduction method [8].

In the present study, three types of Co-based composites were electrodeposited on Ni foam and investigated as catalysts for borohydride hydrolysis. The kinetics of the process was monitored through the volume of the evolved hydrogen at different temperatures. For each catalyst, the hydrogen evolution rate as well as the activation energy were estimated and compared.

EXPERIMENTAL

Catalyst preparation

CoMnB, CoNiMnB and CoNiMoW coatings were produced by electrodeposition from on Ni-foam. Complex electrolytes consisted of 5 g/l Co^{2+}, 5 g/l Mn^{2+}, 0-5 g/l Ni^{2+} and 35 g/l H_3BO_3 were used to produce CoMnB- and CoNiMnB-electrodeposits. The electrolysis was carried out at 40 ^{o}C for 30 min. Cobalt was used as an anode and the supported material (Ni-foam) was connected as a cathode. The electrolyte for CoNiMoW preparation consisted of sodium citrate – 72 g/l, $Na_2WO_4.2H_2O$ – 24 g/l, Na_2MoO_4 – 6g/l, $Ni(SO_3NH_2)_2$ – 16 g/l, $Co(SO_3NH_2)_2$ – 16 g/l. The pH of the obtained solution was adjusted to pH = 10 with NH_4OH. The morphology of the developed materials was analyzed by scanning electron microscopy (SEM) using Leo 1455VP microscope.

Experimental setup

The experimental setup used in this investigation is presented on Fig. 1. 10,0 ml alkaline solution of sodium borohydride (5% $NaBH_4$/6M KOH) was placed in the reactor (2). The temperature of the reactor was controlled by a thermostat (1). The investigated catalyst (5) was placed in the borohydride solution and the reactor was closed hermetically with rubber stopper with a gas outlet (3). The produced hydrogen was measured by water displacement method. The hydrogen generation rate was estimated as a volume of the produced hydrogen per unit of time. Series experiments were carried out for each catalyst at different temperatures in the range from 16 ^{o}C to 45 ^{o}C. Using the obtained kinetic data, the activation energy was calculated.

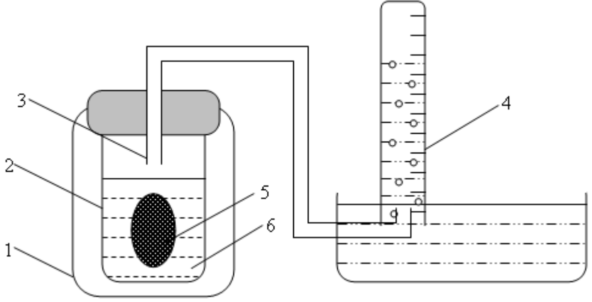

Fig. 1. Experimental setup: 1 – Thermostat; 2 – Reactor; 3 – Outlet for the generated gases; 4 – Cylinder; 5 – Catalyst; 6 – 5 % $NaBH_4$/6M KOH solution.

RESULTS AND DISCUSSION

All produced electrodeposits have similar dendrite structure. The coatings cover almost the whole surface of the supported material (Ni-foam), following its porous structure - Fig. 2.

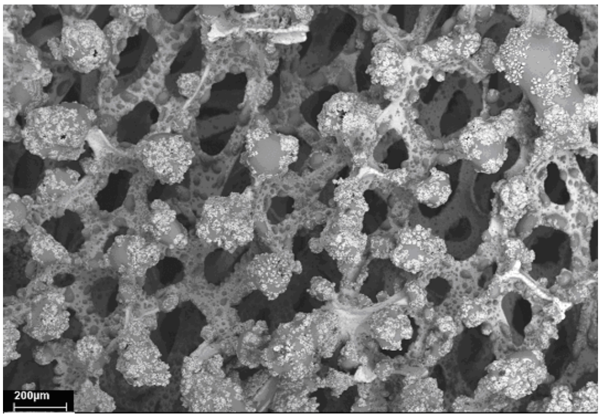

Fig. 2. SEM image of CoMnB electrodeposit on Ni-foam.

The kinetics of the borihydride hydrolysis by using studied catalysts is presented on Fig. 3. As seen from the graphs, the hydrogen evolution begins right after the catalyst contacts with the borohydride solution and linear dependences of the quantity of generated hydrogen with time are observed for all investigated materials. The values of the reaction rate obtained with the electrodeposited catalysts, however, are higher than that with the bare Ni-foam.

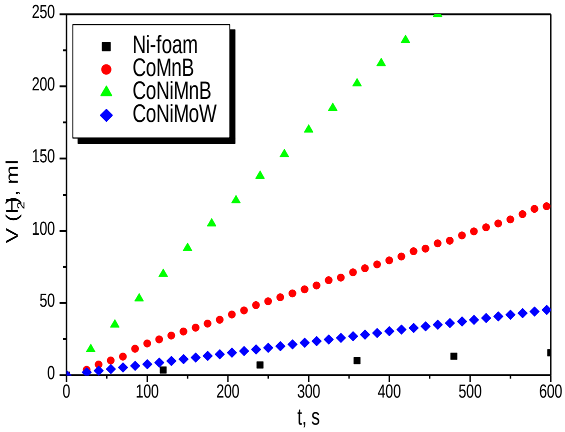

Fig. 3. Hydrogen generation during sodium borohydride hydrolysis process, catalyzed by Ni-foam, CoMnB, CoNiMnB and CoNiMoW at 25 °C.

The values of the hydrogen generation rate obtained with the catalysts at different temperatures as well as the activation energy, estimated from the Arrhenius plots, are summarized in Table 1. The highest rate values, exceeding with an order of magnitude those with the other materials, were achieved with the CoNiMnB catalyst. The lowest activation energy of 36,9 kJ/mol, which is even lower than the values reported for the ruthenium catalyst (E_a = 56 kJ/mol) [9], was also obtained with this catalyst. Besides the similar composition and close activation energy with that of CoNiMnB, the lowest reaction rates were achieved with CoNiMoW catalysts, which reveals their potentials as anodic electrocatalysts for direct borohydride electrooxidation.

Table 1. Hydrogen generation rate (ml/s) and activation energy (kJ/mol) of the sodium borohydride hydrolysis, catalyzed by the investigated materials.

Material	Hydrogen generation rate (ml/s)				E_a
	16 °C	25 °C	30 °C	40 °C	(kJ/mol)
CoMnB	0,061	0,162	0,277	0,501	54,9
CoNiMnB	0,901	1,300	1,402	2,101	36,9
CoNiMoW	0,063	0,076	0,115	0,252	37,8

CONCLUSION

The results from the present study show that the CoNiMnB electrodeposits possess the highest catalytic activity towards borohydride hydrolysis among investigated materials. Although the achieved hydrogen generation rates are lower than those with other reported catalysts, these materials can be used in hydrogen-on-demand generators for portable applications. The low catalytic activity of the other two catalysts (CoMnB and CoNiMoW) makes them proper candidates as anode electrocatalysts for Direct Borohydride Fuel Cells, where the hydrolysis is a competitive process to the direct borohydride electrooxidation.

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СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА Co-СЪДЪРЖАЩИ КАТАЛИЗАТОРИ ЗА ХИДРОЛИЗА НА НАТРИЕВ БОРХИДРИД

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(Резюме)

Каталитичната хидролиза на борхидриди е перспективен метод за производство на водород. Получаваният водород е с висока чистота, процесът не изисква внасяне на енергия и кинетиката му може лесно да се контролира чрез подходящи катализатори. В настоящата разработка, три Co-съдържащи нанокомпозита (CoMnB, CoNiMnB и CoNiMoW), електроотложени върху пенообразен никел, са изследвани като катализатори на хидролизата на натриев борхидрид. Скоростта на процеса бе определяна чрез измерване на обема вода, изместен от генерирания водород за единица време. Кинетиката на реакцията бе проследявана при различни температури в интервала от 16 °C до 40 °C. Най-големи скорости на получаване на водород от 0,9 ml/min при 16 °C и 2,1 ml/min при 40 °C бе получена с CoNiMnB катализатор. В същото време, с този катализатор реакцията протича и с най-ниска активираща енаргия от 36,9 kJ/mol. Получените резултати показват, че електроотложените CoNiMnB нанокомпозити притежават най-висока каталитична активност от изследваните материали и може да бъдат използвани като катализатори в генератори на водород за портативни мобилни приложения.