Ni-, Co- and Pt-based nanocatalysts for hydrogen generation via hydrolysis of $NaBH_4$

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Ni-, Co- and Pt-based nanostructures were prepared via different physical-chemical methods and tested as the catalysts of hydrolysis of $NaBH_4$. *Ni-Co bimetallic nanoparticles with different Ni/Co ratios were synthesized by the modified polyol method via the reduction of in situ precipitated slurries of Ni and Co hydroxides by hydrazine in ethylene glycol solutions. It was found that a Ni-Co nanoparticles with the equal Ni/Co content and mean size of 130 nm are a more active catalyst as compared to* $Ni_{75}Co_{25}$ *and* $Ni_{25}Co_{75}$ *nanopowders and provide a constant rate of hydrogen evolution up to the full conversion of* $NaBH_4$. *Zeolite supported Ni- and Co-based nanostructures (Ni-Z and Co-Z) as a convenient in use alternative to the metallic nanoparticles were synthesized via two-stage procedure consisted of adsorption of* Ni^{2+} *or* Co^{2+} *ions by zeolite from the aqueous solutions followed by the reduction of the adsorbed cations by* $NaBH_4$. *Using SEM and EDX it was found that such method of synthesis provide the uniform distribution of 50 – 100 nm metallic nanopaticles both on the surface and in the bulk of the carrier due to the high cation-exchange capacity of the aluminosilicates. It was found that Co-Z catalyst is more active compared to Ni-Z and in studied conditions provides the* H_2 *evolution rate close to 1450 mL/min per 1 g of precipitated metal. Various Pt-based nanocomposites were obtained by polyol synthesis and subsequently deposited on the carriers (carbon cloth or cordierite) as well as via a platinum electrodeposition on the titanium crump. It was found that the most efficient catalyst of the hydrolysis of* $NaBH_4$ *is a cordierite-supported nanodispersed Pt which is able to maintain operation of a 30 W battery of fuel cells for 9-10 hours when using for the hydrolysis 1.1 L of 10 % $NaBH_4$ solution.*

***Keywords**: $NaBH_4$ hydrolysis, nanocatalysts; Pt nanoparticles; Ni nanoparticles; Co nanoparticles; Zeolite.*

Introduction

Using hydrogen as an energy carrier allows to develop portable energy systems offering benefits of application in autonomous and compact energy sources. In such systems hydrogen is obtained directly at the place of its use, which eliminates the need for its storage and transportation. In recent years, special attention has been paid to the hydrides as a compact and efficient form of hydrogen storage [1]. Among them, sodium borohydride ($NaBH_4$) occupies a special place due to the high content of hydrogen (10.8 wt.% H), reasonable price, stability in alkaline solutions. Like many metal hydrides, it undergoes hydrolysis reaction in presence of water, releasing hydrogen and forming sodium metaborate $NaBO_2$ as a product. The use of catalysts maintains a controlled generation of hydrogen at room temperature.

Several reviews were devoted to a description of different classes of catalysts where their feasibility and conditions of use was systematically analyzed [2-7]. The largest group of catalysts is heterogeneous catalysts containing transition metals. Transition metals include more than 20 elements, among which a significant attention is paid to cobalt, nickel, ruthenium and platinum. Elementary catalysts are the most studied ones; binary and ternary catalysts have become increasingly in focus of the research in recent years. Among them, Al, Ag, Ca, Cr, Cs, In, La, Mg, Mn, Mo, Sb, Sn, W, Zr are the alloying additives. Catalysts with boron and phosphorus (for example, Co-B, Ni-B, Co-P systems, etc.) can be separated into an individual group. These catalysts can be synthesized “in situ” by addition of the metal salts directly in the working solution of $NaBH_4$. When considering efficiency and convenience of use, the catalysts, immobilized on the carriers, are frequently used. They can be in a form of metal films, foams or nanoparticles deposited on the surface of activated carbon, carbon nanotubes, graphene, oxides ($LiCoO_2$, TiO_2, Al_2O_3, etc.), clays, polymers, rubber, etc. From the point of view of practical use, special attention is paid to the different alumosilicates, both synthetic and of a natural origin as carriers for catalysts [8,9]. They are chemically and thermally stable and capable of ion exchange involving *d*-metal ions. Such cation exchange reactions allow obtaining nanostructured catalysts with uniformly distributed catalytic elements both on the surface of the granules (or powders) and in the bulk while using such specific type of the carrier leads to the increased resistance to the oxidation of the supported *d*-elements.

In this study we present the data of the studies of the kinetics of hydrolysis of $NaBH_4$ catalyzed by amorphous Ni-B and Co-B catalysts, the method of synthesis of zeolite-supported Ni and Co catalysts as well as a comparison of the catalytic activity of the amorphous and zeolite-supported nanocatalysts in the hydrogen generation process.

Decomposition of an aqueous solution of sodium borohydride is one of the most productive methods of hydrogen production by hydrolysis. In alkaline solutions, the interaction of $NaBH_4$ with water practically does not occur, which makes it possible to store such solutions for a long time. However, when more than catalysts of various types are used (300 homogeneous and heterogeneous catalyzers are known), sodium borohydride becomes able to react with water at ambient temperature. The most active catalysts of this reaction are rhodium, ruthenium and platinum [3,4,7,10]. In our studies, we used nanodispersed platinum immobilized on various substrates as a catalyst for $NaBH_4$ hydrolysis. Flat and cylindrical flow reactors were designed and manufactured. Furthermore, we have developed and tested Ni- and Co-based catalysts of the process.

Materials and Experimental details

For the preparation of Ni and Co based catalysts, acetates $Ni(CH_3COO)_2{\cdot}4H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$ and zeolite Na-A were used. As a reducing agent for the Ni-Co-NPs preparation N_2H_4 was used. All used reagents were purchased from Sfera Sim (Lviv, Ukraine, 99+% grade). For the regulation of the pH of the working solutions, NaOH (titrant, Kharkovreachem, Ukraine) was used.

The XRD patterns of the samples were measured at a diffractometer DRON-3.0 using Fe-Kα radiation. Investigations of the morphology, quantitative elemental analysis and elemental mapping of the obtained catalysts were performed by using EVO-40 XVP (Carl Zeiss) scanning electron microscope equipped with Inca Energy 350 (Oxford Instruments) microprobe analysis system. Ion exchange capacity of zeolite as related to Ni^{2+} and Co^{2+} ions was evaluated by photocolorimetry by using Shimadzu Uvmini spectrophotometer.

Kinetics of hydrolysis of $NaBH_4$ in the presence of Ni- and Co-based catalysts was investigated at 20 °C when applying pseudo-isothermal conditions in a setup similar to the one described in [11] and consisting of a two-neck glass vessel immersed into a water bath equipped with a magnetic stirrer and injector of the solutions of $NaBH_4$ (5 mL, 1M) The generated hydrogen was released through an Allihn-type fluid-cooled condenser which was connected to a filled with water bottle. Then, H_2 was collected at room temperatures by replacing the water in a beaker.

The Pt catalyst, used in the flat flow reactor, consisted of nanodispersed platinum (up to 40 wt.%) deposited on carbon black (XC-72), which, in turn, was immobilized on the surface of carbon cloth (1-2 mg/cm^2).

For the cylindrical reactor, platinum catalysts were prepared by their deposition on various substrates:

1) 100 mg of the platinum catalyst (40 %) on carbon black XC-72 was applied on a carbon cloth (50 cm^2) which was then rolled with a 4 mesh polyamide net and packed into a reactor;

2) 150 mg of platinum was applied on the 2 g of activated granular carbon AG-3 by polyol-synthesis with reduction with $NaBH_4$ and placed in a reactor;

3) Platinum was electrochemically deposited on porous defatted and pickled titanium crump from the electrolyte 25 g/l of K_2PtCl_6, 100 g/l of $NaNO_2$ and 20 ml/l of ammonia solution (0.915 g/cm^3) at a temperature of 70°C and a cathode current density of 20 mA/cm^2. Under these conditions, the yield of platinum was about 30 %. The weight of precipitated platinum was monitored gravimetrically. The surface density of platinum was 1-4 mg/cm^2.

Very promising for catalytic hydrolysis of $NaBH_4$ is the nanodispersed platinum catalyst immobilized on cordierite of honeycomb structure with surface, previously modified by alumina. We used the synthetic cordierite (general formula $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) with a square canal density of 400 canals per square inch and canal cross-sectional area of 1 mm^2. After the modification of cordierite surface by Al_2O_3 sol, the carrier was impregnated with the H_2PtCl_6 solution. Reduction of platinum was carried out by a 10 % solution of sodium borohydride. Content of platinum in the prepared composite catalyst was 27.9 mg/g. Such monolithic catalyst was placed into the flat or cylindrical flow reactors for the testing.

Results and Discussion

Catalytic Activity of Ni-Co NPs for hydrolysis of $NaBH_4$.

Ni-Co-NPs were synthesized via the reduction of the mixtures of Ni^{2+} and Co^{2+} by hydrazine in alkaline water/ethylene glycol solutions. Obtained precipitates were washed by deionized water and studied using XRD and SEM. It was found that 1) the samples do not contain any unreacted hydroxides (Fig. 1) and their composition is equal to the ratio of Ni/Co in the reaction mixture; 2) the mean size of Ni-Co-NPs slightly decreased with the decrease of Ni content increasing up to 50 % (Fig. 2).

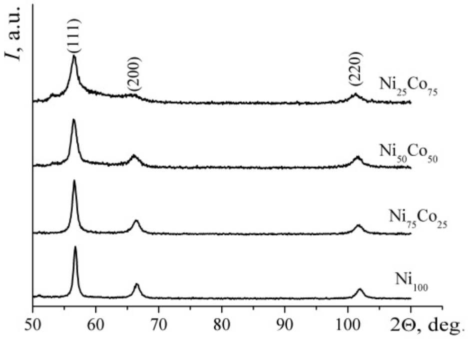

Fig. 1. XRD-patterns of Ni-Co-NPs (Fe-K_α).

Obtained Ni-Co-NPs were tested as catalysts of the hydrolysis of alkaline (pH = 9) solution of $NaBH_4$. It was found that 1) Ni-Co-NPs provide a constant rate of hydrogen evolution up to the full conversion of $NaBH_4$ (see Fig. 3); 2) $Ni_{50}Co_{50}$ nanoparticles show the best catalytic activity providing the H_2 evolution rate close to 300 mL/min per 1 g of catalyst; 3) the increase of Co content in the Ni-Co-NPs up to 25 % leads to a sharp decrease of the rate of H_2 evolution. The decreasing rate of $NaBH_4$ hydrolysis observed for $Ni_{25}Co_{75}$ may be caused by the morphological peculiarities of the obtained samples.

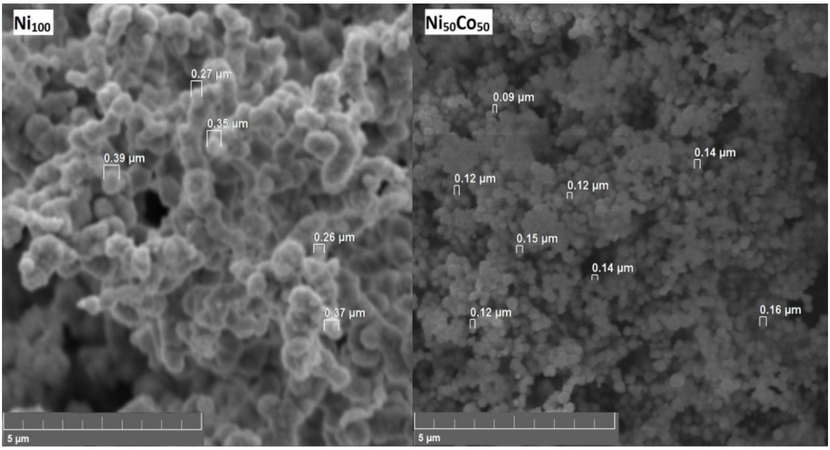

Fig. 2. SEM-images of Ni_{100} and $Ni_{50}Co_{50}$ samples.

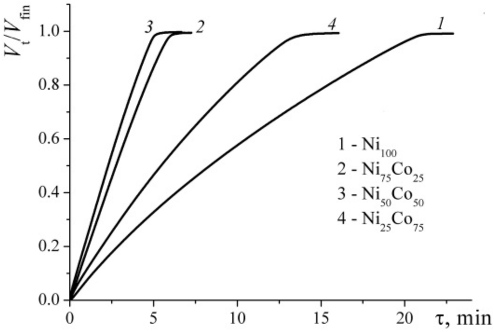

Fig. 3. The kinetic curves of H_2 evolution catalyzed by Ni-Co-NPs.

Zeolite-supported Ni/Co catalysts for hydrolysis of $NaBH_4$.

Ni-Co-NPs appear to be efficient catalysts of the hydrolysis of $NaBH_4$. At the same time, the usability of such types of catalysts is insufficient for their use in the systems for hydrogen generation due to their low stability to oxidation by atmospheric oxygen at ambient conditions.

That is why the complex nanostructured catalysts based on zeolite and Ni and Co were studied. As it was mentioned in the Introduction, alumosilicates in general and zeolites in particular show the ability to participate in the process of cation exchange and this feature was used to synthesize nanostructured catalysts. The synthesis procedure included two stages, namely adsorption of Ni^{2+} or Co^{2+} by zeolite from an aqueous solution followed by a reduction of the adsorbed cations by $NaBH_4$. It was found that cation exchange capacities of zeolite for Ni^{2+} and Co^{2+} are high and equal to 2.6 and 2.4 % by weight respectively. Obtained catalysts were studied using SEM and it was found that metals are evenly distributed on the surface of the zeolite granules (Fig. 4).

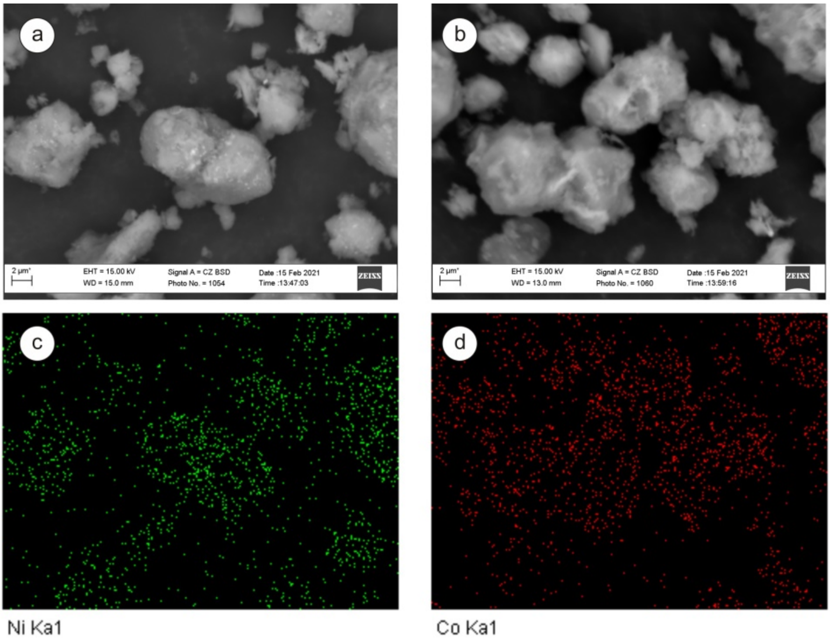

Fig. 4. SEM images of Ni-Z (a) and Co-Z (b) and the distribution of Ni (c) and Co (d).

Synthesized samples were tested as catalysts of the hydrolysis of $NaBH_4$. For the hydrolysis experiment 0.5 g of catalyst and 5 mL of 1 mol/L $NaBH_4$ solution (5 wt. % NaOH) were used. As it was expected, catalytic activity of Co-Z is higher than that for the Ni-Z (Fig. 5) and promotes the H_2 evolution with a rate close to 1450 mL/min per 1 g of the precipitated metal.

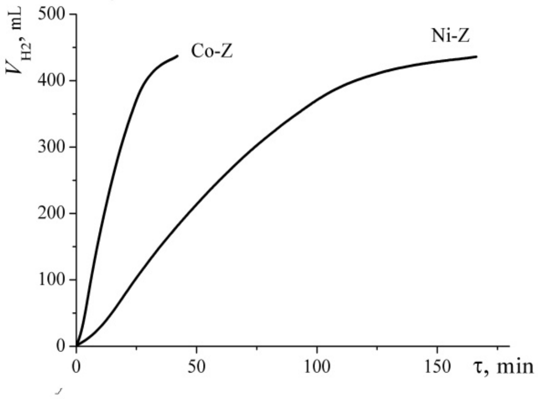

Fig. 5. Kinetic curves of H_2 evolution catalyzed by Ni-Z and Co-Z.

Thus, a high catalytic activity of the synthesized zeolite-supported Ni and Co nanocatalysts, as well as their stability at ambient conditions make such catalysts attractive from the point of view of their practical application for promoting an efficient generation of hydrogen gas.

Hydrogen generation by hydrolysis of $NaBH_4$ using supported Pt catalysts.

At 24 °C, the measured rate of hydrogen evolution during the hydrolysis of 10 % $NaBH_4$ + 5 % NaOH solution in a flat flow reactor with nanodispersed Pt catalyst immobilized on the carbon cloth was directly proportional to the solution pumping rate and reached 400 ml/min. at a flow rate of sodium borohydride solution of 7.8 ml/min. This is sufficient for a stable supply by hydrogen fuel of a 30 W hydrogen-oxygen fuel cell. The decomposition degree of sodium borohydride decreases with increasing rate of pumping the solution through the generator.

It was shown that the platinized titanium is less active than the catalyst obtained by the polyol method. During the formation of a roll from the carbon cloth with applied platinum catalyst, the latter peeled off. That is why its activity was lower than that for the flat reactor.

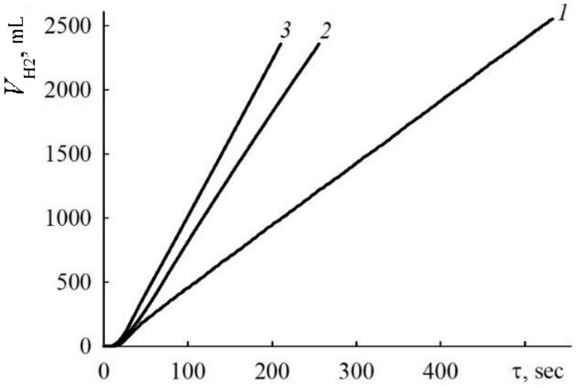

Fig. 6. Time dependencies of the volumes of the evolved hydrogen during the hydrolysis of 10 mL of the 10 % $NaBH_4$ + 5 % NaOH solution in the 5 mL cylindrical flow reactor with Pt/Al_2O_3/cordierite catalyst at the following rates of the solution flow (mL/min): 1.1 (*1*), 2.4 (*2*) and 2.75 (*3*)

According to the Fig. 6, the rate of hydrogen evolution from the alkaline 10 % $NaBH_4$ solution during its hydrolysis when using Pt catalyst immobilized on cordierite superficially modified by Al_2O_3 is practically constant if the rate of solution flow and $NaBH_4$ concentration are constant. When the rate of the solution flow increased, the hydrogen evolution accelerated. As it follows from Fig. 6, the hydrolysis of 1.1 liters of such a solution will ensure the operation of a 30 W battery of fuel cells for 9-10 hours. This catalyst provides a high and stable rate of hydrogen generation at a moderate $NaBH_4$ solution temperature of 60 ± 5°C.

Conclusions

Ni-Co-NPs with different Ni/Co ratios were synthesized via the reduction of the mixtures of Ni^{2+} and Co^{2+} precursors by hydrazine in alkaline water/ethylene glycol solutions and tested as the catalysts of the hydrolysis of alkaline solutions of $NaBH_4$. It was found that the rate of the hydrolysis reaction non-monotonically changes as related to the Co content in the Ni-Co-NPs, while the highest H_2 evolution rate was observed for $Ni_{50}Co_{50}$. A simple and reproducible method of synthesis of the stable zeolite-based nanostructured Ni and Co containing catalysts of the hydrolysis of $NaBH_4$ was developed. The optimized catalyst provides high (1450 mL/min per 1 g of the precipitated metal at maximum) H_2 evolution rate. Different chemical and electrochemical techniques of the preparation of Pt-based nanocomposite catalysts were tested. It was established that the most efficient catalytic system is PtNPs immobilized on a superficially modified cordierite with honeycomb structure. When 1.1 L of $NaBH_4$ solution is subjected to the hydrolysis process, an application of the mentioned catalyst in a cylindrical flow reactor generates a sufficient amount of hydrogen gas allowing to operate a 30 W battery of the fuel cells for 9-10 hours.

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