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SIZE-DEPENDENT EFFECTS

# Effects of nickel foam dimensions on catalytic activity of supported Co–Mn–B nanocomposites for hydrogen generation from stabilized borohydride solutions

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**Abstract** In the present work, the catalytic activity of electrodeposited Co–Mn–B nanocomposites towards controllable hydrolysis of sodium borohydride was studied. Deposition was performed on two types of Ni-foam (RECEMAT Int.) with different pore size, specific surface area and thickness. Higher deposit loading, as well as bigger real surface area, was obtained with foam samples possessing bigger pore size. The catalyst deposited on bigger pore foam promoted hydrogen generation with higher rates than the other one when contacted with a base-stabilized $NaBH_4$ solution. The same activation energy value, however, was determined for both supported catalysts. On the base of the obtained results, it may be concluded that the geometric factor plays predominant role for the catalytic activity of studied catalysts.

## Introduction

The successful use of hydrogen as an energy carrier for the future significantly depends on the conception of convenient and safe methods for its production, storage and transportation. Besides traditional methods [1, 2], complex hydrides as borohydrides ($M^IBH_4$) and alanates ($M^IAlH_4$) have attracted attention [3] for development of new safety systems for hydrogen storage and transportation.

Sodium borohydride ($NaBH_4$) is particularly attractive [4] in view of its various advantages. It has a higher hydrogen content (10.8 wt.%) and its equivalent energy density is nearly equal to that of diesel fuel. Relatively stable and non-flammable $NaBH_4$ aqueous solutions could be easily produced by addition of an alkaline base. On demand, such base-stabilized $NaBH_4$ solutions can be used for controllable hydrogen release promoted by a proper catalyst:

$$NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} 4H_2 + NaBO_2 \quad (1)$$

The reaction (1) is exothermic, and it does not require the addition of heat or application of high pressure to initiate. Sufficient amounts of hydrogen could be generated even at low temperatures (near 0°C). It is particularly efficient for hydrogen generation, since a half of $H_2$ molecules are supplied from sodium borohydride, and the water supplies the other half for a total of four $H_2$ molecules.

Presently, nanosized Ru and Pt particles are mainly used as catalysts for hydrolysis of $NaBH_4$ in alkaline solutions [5, 6]. Since the price of noble metals is too high, the development of alternative low-cost catalysts is very important. Lately, it was reported [7] that Co–B nanoparticles, produced by a borohydride reduction method, exhibit high catalytic activity towards sodium borohydride hydrolysis. Same nanoparticles, obtained

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in 3 different types of reactors, were previously studied by some of us [8–10] for other possible applications.

A non-conventional electrolytic growth of nanocomposite Co–Mn–B multilayers has been reported in our previous papers [11–13]. Compositional and structural similarities with some of the previously studied nanoparticles, produced by borohydride reduction [8–10], as well as the high hydrogen content of these electrodeposits [12] have attracted our attention to start investigations for their possible applications [14]. During polarization measurements with Co–Mn–B electrodes in base-stabilized sodium borohydride electrolytes, a significant hydrogen release was observed even at high anodic current densities [15]. Later observations motivated a separate investigation on catalytic activity of electrodeposited Co–Mn–B multilayers towards borohydride hydrolysis reaction.

In this paper, results from kinetic studies of sodium borohydride hydrolysis carried out on electrodeposited Co–Mn–B nanocomposites, used as catalysts, are presented. The catalyst layers have been deposited on two types of Ni-foam. The role of characteristic foam dimensions on the electrodeposit distribution, the resulting real surface area, as well as corresponding catalytic activity towards examined reaction is discussed. The obtained experimental results are compared with reference data and some conclusions on the possible application are also done.

## Experimental

Supported Co–Mn–B catalyst samples with a geometric area 1 $cm^2$ were produced by electrodeposition from complex sulphamate electrolyte containing 5 g $L^{-1}$ cobalt (II), 5 g $L^{-1}$ manganese (II) and 35 g $L^{-1}$ boric acid. Deposition was done upon two types of Ni-foam (RECEMAT Int.), which characteristics are shown in Table 1. Cobalt electrode was used as an anode. The electrolysis was carried out under potentiostatic conditions (–1.8 V vs. SCE) for 30 min at 40°C. For improvement of mechanical stability the button-shaped samples were pressed under pressure 200 kg $cm^{-2}$ at ambient conditions.

**Table 1** Characteristics of Ni-foam types [16], used as a catalyst support (provided by the RECEMAT International)

| Ni-foam type | Average pore diameter [mm] | Specific surface area [$m^2/m^3$] | Thickness [mm] |
|---|---|---|---|
| RCM-Ni-4753.016 | 0.4 | 5,400 | 1.6 |
| RCM-Ni-2733.03 | 0.6 | 2,800 | 3.0 |

The catalyst morphology as well as cross-section distribution in the foam was observed by means of scanning electron microscopy (SEM) with a Leo 1455VP microscope. The real surface area of catalyst samples was estimated by a cyclic voltammetry method, described elsewhere [14].

The kinetic studies with electrodeposited Co–Mn–B catalysts were carried out into a sealed reactor, which temperature was maintained by a thermostat. The supported catalyst was put into the reaction chamber, and then the reactor was closed tightly by a lid with an inlet for the reaction solution and an outlet for the gaseous products. The reaction solutions were prepared by dissolving pre-determined amount of $NaBH_4$ (Fluka, reagent grade) into 5 wt% NaOH aqueous solution. Equal volumes of stabilized $NaBH_4$ aqueous solutions were injected through the lid inlet into the reaction chamber. Continuously homogenizing of reaction solution was applied by a magnetic stirrer. The volume of hydrogen, released as a product of reaction (1), was detected by a water displacement method.

## Results and discussion

### Catalyst characterization

As previously reported [11–13], Co–Mn–B electrodeposits obtained on Cu-foil, possess a very attractive multilayered structure built-up of succeeding each other bright and dark layers. It was established [12] that the bright layers contain large amounts of cobalt (up to 80 at.%) and oxygen, while the dark ones consist of boron (<30 at.%), manganese (<15 at.%) and oxygen. A large hydrogen content (up to 9 at.%) is also determined in these systems [12].

Both types of Ni-foam, used in this study, are produced by electrodeposition metallization of open cell polyurethane foams [16, 17]. The material is very open and has a tight pore size distribution. The morphology of Co–Mn–B deposit on such Ni-foam is shown in Fig. 1.

Independently on the substrate, the typical ‘‘cauliflower’’ shape [11–13] of the multilayered Co–Mn–B dendrite is kept, where successive growth fronts are observed, the light ones being rich of cobalt, and the dark ones—rich of manganese and oxygen. However, some peculiarities connected with the use of Ni-foam as a support should be pointed out. Although the foam pores are not filled and blocked entirely, the layers are deposited mainly on the outer surface of the support—Fig. 2.

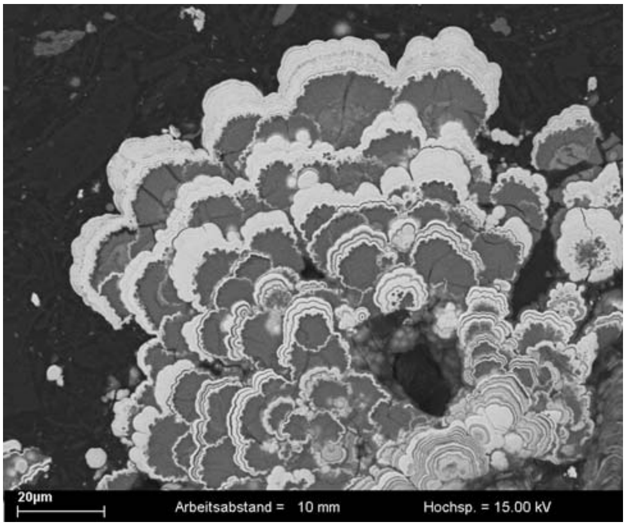

**Fig. 1** Morphology of Co–Mn–B deposit on RCM-Ni-4753.016 foam

It is also seen from the cross-section presented in Fig. 3 that the amounts of deposit decrease in the depth of the foam. This resulting distribution of the deposit is probably due to diffusion limitations for feeding the inner parts of foam with an electrolyte.

After pressing, however, the deposits lose their characteristic dendrite morphology as the distances between separate branches decreased or disappeared.

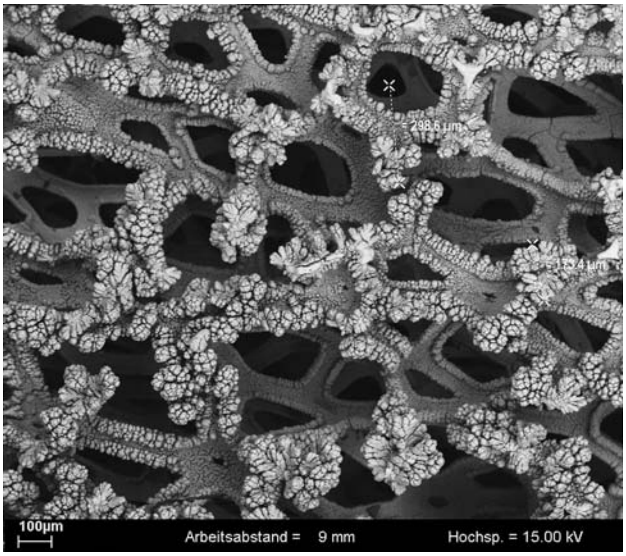

**Fig. 2** SEM image of Co–Mn–B deposit on RCM-Ni-4753.016 foam

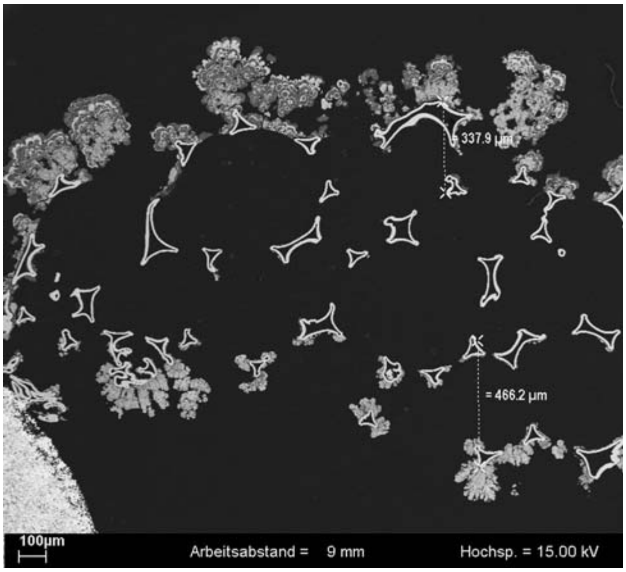

**Fig. 3** Cross-section of Co–Mn–B deposit on RCM-Ni-4753.016 foam

Real surface area of produced catalysts was determined from reproducible cyclic voltammograms, obtained with samples in alkaline solution [14]. The integrated areas under the single well-shaped anodic and cathodic peaks, corresponding to the formation and reduction of $Co(OH)_2$, respectively:

$$Co(OH)_2 + 2e^- \leftrightarrow Co + 2OH^-, \qquad (2)$$

were compared with those obtained with a fresh polished Co-plate electrode, having determined geometric area. The estimations show that investigated samples possess from 40 to 70 times higher real active area than their geometric area. Typically, the catalysts deposited on bigger pore Ni-foam has to about 50% larger real surface area than those supported on small pore foam. Referring to the data in Table 1, it becomes obvious that pore size of used type metal foam has a predominant role for formation of rougher surface during electrodeposition than its specific surface area and thickness. As reported [17], permeability of RECEMAT metal foam samples are correlated with the foam pore diameters, while it is not affected by the sample thickness.

## Hydrogen generation kinetics

Kinetic studies of catalyzed borohydride hydrolysis were carried out with catalysts deposited on the both types of Ni-foam. Typically, a linear dependence of generated hydrogen volume with time is observed at given conditions, as seen in Fig. 4.

The reaction starts immediately after the borohydride solution contacts with the catalysts and it goes on with a constant rate for the whole experimental window. An activation period is not observed with this

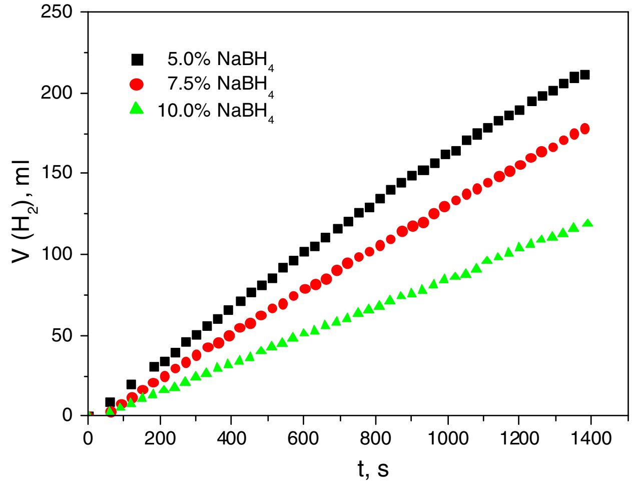

**Fig. 4** Kinetic curves for hydrogen generation by hydrolysis of *x* wt% NaBH$_4$ + 5 wt% NaOH solution (*x* = 5÷10) at 20°C using Co–Mn–B/RCM-Ni-4753.016 foam catalyst

type of catalysts, in a contrast to the previously studied Co–B catalysts [7].

In few cases, a small delay of the reaction rate at the end of experiment has been detected. These observations may be attributed to a partial blockage of the catalyst surface by produced low-soluble metaborates.

An interesting result is that the rate of hydrogen release decreases with increasing sodium borohydride concentration. Similar influence of borohydride concentration has been reported for other catalysts [5–7]. Amendola et al. supposed that greater H$_2$ generation rates at lower NaBH$_4$ concentration are possibly due to reduced solution viscosity, which allows more NaBH$_4$ and H$_2$O to contact catalyst surfaces [5].

To examine the role of dimensions of Ni-foam on the activity of supported Co–Mn–B catalysts for reaction (1), kinetic studies at various temperatures (16–36°C) were carried out. Taking into account the observed influence of borohydride concentration on the hydrogen generation rate, this set of experiments were carried out using 5 wt% NaBH$_4$ + 5 wt% NaOH solution. To compare the amounts of hydrogen generated at different temperatures, all measured volumes were recalculated to values corresponding to the standard temperature ($T_o$ = 273 K). The obtained kinetic curves are presented in Fig. 5.

According to the theory prediction, generally the reaction rate increases with the solution temperature for both catalyst types. For comparison of catalysts activities, hydrogen generation rates $k$ (mol min$^{-1}$ g$^{-1}$) were estimated from the data in Fig. 5. Following the Arrhenius equation

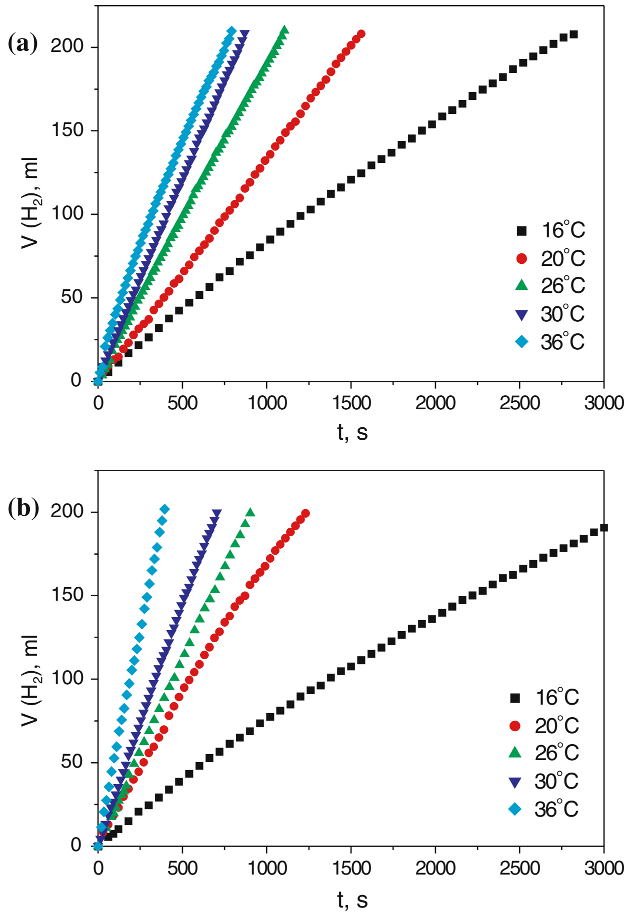

**Fig. 5** Kinetic curves for hydrogen generation by hydrolysis of 5 wt% NaBH$_4$ + 5 wt% NaOH solution obtained at different temperatures with: (**a**) Co–Mn–B/RCM-Ni-4753.016 catalyst; (**b**) Co–Mn–B/RCM-Ni-2733.03 catalyst

$$\ln k = \ln k_0 - (E_a/RT), \tag{3}$$

where $k_0$ is the rate constant (mol min$^{-1}$ g$^{-1}$), $E_a$—the activation energy (kJ mol$^{-1}$), $R$—the gas constant (8.3143 kJ mol$^{-1}$ K$^{-1}$), and $T$—the reaction temperature (K), dependences of ln $k$ versus 1/$T$ were plotted in Fig. 6.

As seen, at same temperatures higher reaction rates were obtained with the catalysts supported on Ni-foam with bigger pores (RCM-Ni-2733.03). However, practically equal values of activation energy were estimated from the slopes of Arrhenius plots in Fig. 6. This is an indication for the same reaction mechanism with the both catalysts used. On the basis of these determinations, we proposed that the different reaction rates obtained with the both catalysts result from differences in their real surface areas, and therefore different number of active sites per unit of geometric area.

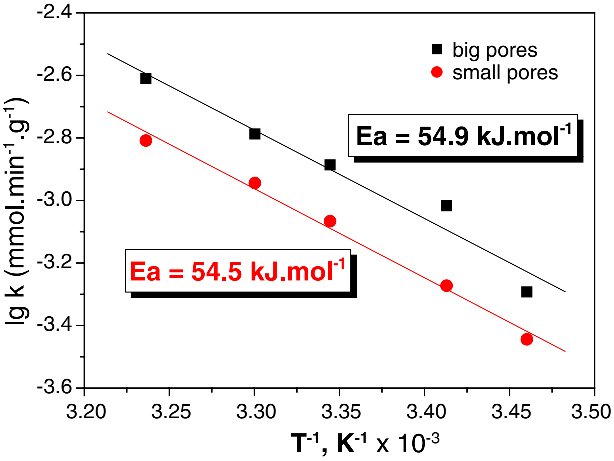

**Fig. 6** Arrhenius plots for catalyzed hydrolysis of 5 wt% $NaBH_4$ + 5 wt% NaOH solution using Co–Mn–B/RCM-Ni-4753.016 (small pores) and Co–Mn–B/RCM-Ni-2733.03 (big pores) catalyst

To confirm this proposal, we estimated values of reaction rates $k_1$ (mol min$^{-1}$ g$^{-1}$ cm$^{-2}$) by using data from Fig. 6 and those ones obtained for real catalyst surfaces. Plots of ln $k_1$ versus $1/T$ are presented in Fig. 7.

From observed Arrhenius plots in Fig. 7, it may be firmly concluded that both catalysts possess the same intrinsic activity and therefore, the geometric factor plays predominant role for the performance of these supported catalysts.

It is worth noting, that the estimated value of activation energy (~55 kJ mol$^{-1}$) for tested catalysts is lower than the reported one for Co–B (~65 kJ mol$^{-1}$) [7] and close to that reported for Ru-catalyst (56 kJ mol$^{-1}$) [5]. The lower reaction rates determined with catalysts tested in this study in comparison with those obtained with Co–B [7] may be probably referred to the different state, in which catalysts were used. However, the determined amounts of generated hydrogen are suitable to supply some portable devices, for example micro power fuel cells. Constant rate of hydrogen release at definite conditions and the possibility to vary this rate by controlling temperature in moderate range are additional advantages of this catalyst type. Further optimization of catalyst preparation, as well as hydrogen generation conditions is going to be performed.

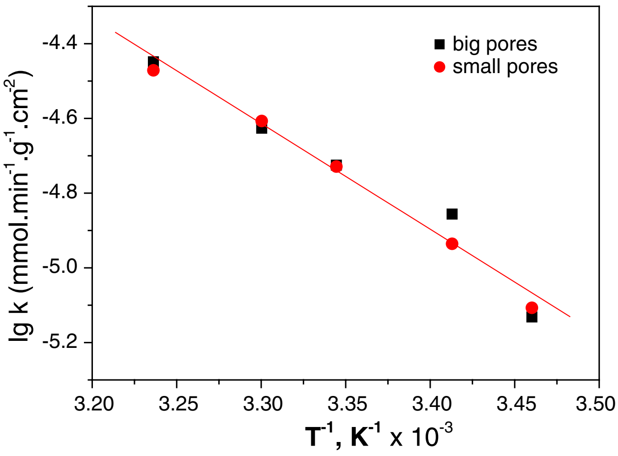

**Fig. 7** Arrhenius plots for catalyzed hydrolysis of base-stabilized $NaBH_4$ solution, taking into account the real surface area of catalysts, estimated by cyclic voltammetry method

## Conclusions

Nanocomposite Co–Mn–B multilayers, produced by electrodeposition on two types of Ni-foam, were examined as catalysts for hydrogen generation by controllable hydrolysis of base-stabilized sodium borohydride solution. The catalysts, deposited on the foam with bigger pores, show higher hydrogen generation rates at equal temperatures and sodium borohydride concentrations. An identical reaction mechanism and a same intrinsic activity for both tested catalysts may be concluded from the almost equal values of activation energy (~55 kJ mol$^{-1}$), determined from Arrhenius plots.

Taking into account that the geometric factor plays predominant role for the total activity of this type of catalysts, further investigations, aiming increase of real catalyst surface, optimization of catalyst loading as well as solution concentration, temperature and hydrodynamic conditions should be carried out.

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