

# SOPHISTICATED ELECTROCATALYSTS FOR ECONOMICAL PRODUCTION OF HYDROGEN PART A: STRUCTURAL CHARACTERIZATION

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## Abstract:

*An original procedure was applied in order to prepare composite electrocatalysts for hydrogen evolution reaction (HER), containing Ni, Co and CoNi as a hyper d-electronic phase and TiO<sub>2</sub> as a hypo-phase deposited on conductive carbon substrate Vulcan XC-72. The catalyst's support (TiO<sub>2</sub> and carbon) was thermally treated on 250 and 480°C in the atmosphere of H<sub>2</sub> and N<sub>2</sub>. XRD and SEM methods were employed in order to elucidate the influence of temperature on the structural characteristics of catalysts.*

*XRD analysis has shown that all catalysts contain hyper d- metallic phase of crystalline structure, the size of grains being 10-20 nm, except the Co-phase that showed to be amorphous (grain size < 2 nm). TiO<sub>2</sub> calcinated on 480°C has shown typical anatase structure, while no crystalline state was observed for that calcinated on 250°C.*

*For all types of catalysts, an aggregation of grains in clusters of a size of typically 100 nm was observed by SEM analysis. Also, a presence of empty space, that improves material's porosity and specific surface area respectively, has been shown. Further improvements of the non-platinum hypo-hyper d- catalysts are in course.*

**Keywords:** *hypo-hyper d- catalyst, hydrogen evolution reaction (HER), Co, CoNi, Ni, anatase*

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## 1. INTRODUCTION

The electrochemical technologies for hydrogen production (water electrolysis, chlor-alkaly industry) and fuel cells become more and more significant in the field of alternative sources of energy. The use of electrochemically generated hydrogen, either in fuel cells or for heat generation, is characterized by advantages of both high content of energy and avoidance of environmental pollution.

Electrode materials for hydrogen evolution have to satisfy some criterions from different aspects. By the technical point of view, the electrode material has to be stable (no corrosion, no passivation etc.) and to catalyses the hydrogen evolution reaction (high current density at lower overpotential). Economical reasons favor cheaper material, while environmental concern is in favor of usage of nonpolluting materials. So, the choice of electrode material is very difficult due to the conflict of technical and economical issues. Platinum was found to be electrode on top of which hydrogen evolves with minimum overpotential [1]. But Pt and other precious metals don't satisfy economical reason, because they are expensive, while

cheaper substituents using non-precious metals as Ni, Co etc. suffer of corrosion, passivation and similar problems.

There are two basic approaches how to find more active, stable and cheaper electrode material: *i*) developing of real surface area of the electrode (using of porous electrodes) and *ii*) developing of multicomponent catalysts.

Based on Brewer's theory of bonding in metals and intermetallic phases<sup>[2]</sup>, Jak{i} and his group successfully alloyed non-precious dual combination of Mo and Co and produced materials with electrocatalytic activity even superior to that of individual metals of platinum group. Jak{i} has extended Brewer valence-bond theory giving an explanation of alloying effect on the rate of hydrogen evolution on electrodes based on transition metals<sup>[3]</sup>. According to his consideration, the mutual combination of the metals on the right side of transition series, which are good individual electrocatalysts (hyper *d*- electronic phase) and the metals of the left side, which are poor electrocatalysts (hypo *d*- electronic phase), shows pronounced synergetic effect. As a result, composite hypo-hyper *d*- electrocatalysts become subject of scientific and technical interest, so a "new era" of electrocatalysis was opened.

Hypo and hyper *d*- electronic phases can be in elemental or in valence state, so that many combinations are possible, for example, metal-metal, metal-metal sulfide, metal-metal oxide etc<sup>[4]</sup>.

The subject of study in this paper is preparation and structural characterization of nanostructured composite catalysts with hyper *d*- metallic phase (Ni, Co, CoNi) and hypo *d*- oxide phase (TiO<sub>2</sub>).

## 2. EXPERIMENTAL

A modified sol-gel procedure<sup>[5]</sup> was applied to prepare composite hypo-hyper *d*- electrocatalysts for hydrogen evolution. Firstly, the hypo *d*- electronic oxide phase was deposited on carbon substrate. Ti-isopropoxide (Aldrich, 97%) was added into dispersed Vulcan XC-72 (Cabot Corp. Boston Mass.) in anhydrous ethanol (Merck, p.a.). To provide hydrolyzation of Ti-isopropoxide to Ti(OH)<sub>4</sub>, small amount of 1M HNO<sub>3</sub> (Merck, p.a.) in the ratio 10:1 was added. This mixture was evaporated at 60°C with intensive stirring until fine nano-structured powder of catalyst support was obtained. Further, the metallic hyper *d*-phase was grafted on the catalyst support. An individual or mixed Me-2,4-pentaedionate (Alfa Aesar, Johnson Matthey, GmbH) was dissolved in absolute ethanol or acetone. This solution was added into dispersed catalyst support in anhydrous ethanol. Evaporation was carried out under the same conditions as above. The obtained catalyst powder consists of Ti(OH)<sub>4</sub> with respective amount of 18% TiO<sub>2</sub>, 10% Me or composite metallic phase and the rest is carbon. To decompose Ti(OH)<sub>4</sub> to TiO<sub>2</sub> and the rest amount of organometallics, the powder was calcinated at 250°C in the atmosphere of H<sub>2</sub> and N<sub>2</sub>. Three different types of catalysts were prepared, e.g.: 18% TiO<sub>2</sub> + 10% Ni + Carbon, 18% TiO<sub>2</sub> + 10% CoNi + Carbon and 18% TiO<sub>2</sub> + 10% Co + Carbon.

To obtain anatase structure of TiO<sub>2</sub>, the catalyst support was thermally treated at 480°C and after that dispersed into ethanol in order to graft the hyper *d*-metallic phase. Finally the catalyst was calcinated at 250°C. The composition of these catalysts was the same as the previous ones. The only difference was the structure of TiO<sub>2</sub>.

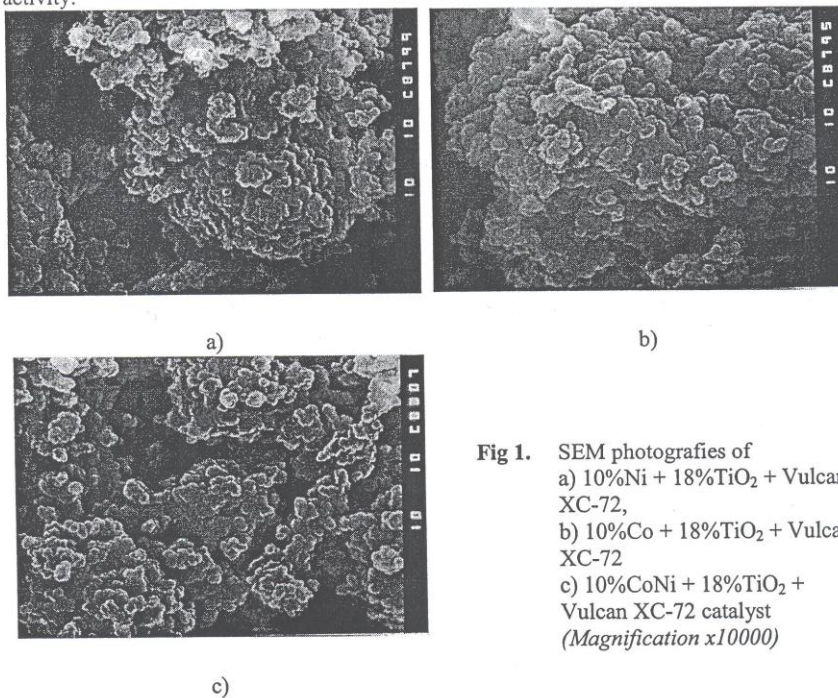
For visual observation of the sample's structure, Scanning Electronic Microscope (SEM) was employed (JEOL, model JEM 200 CX).

X-ray diffraction method was used to determine the structural characteristics of the obtained catalysts. XRD measurements were carried out on XRD diffractometer Philips APD 15,  $\text{CuK}\alpha$  radiation.

The BET-method was used to determine and compare the specific surface area ( $ssa$ ) of the catalysts. The measurements were performed by AREA-METER "STROHLEIN" instrumentation.

### 3. RESULTS AND DISCUSSION

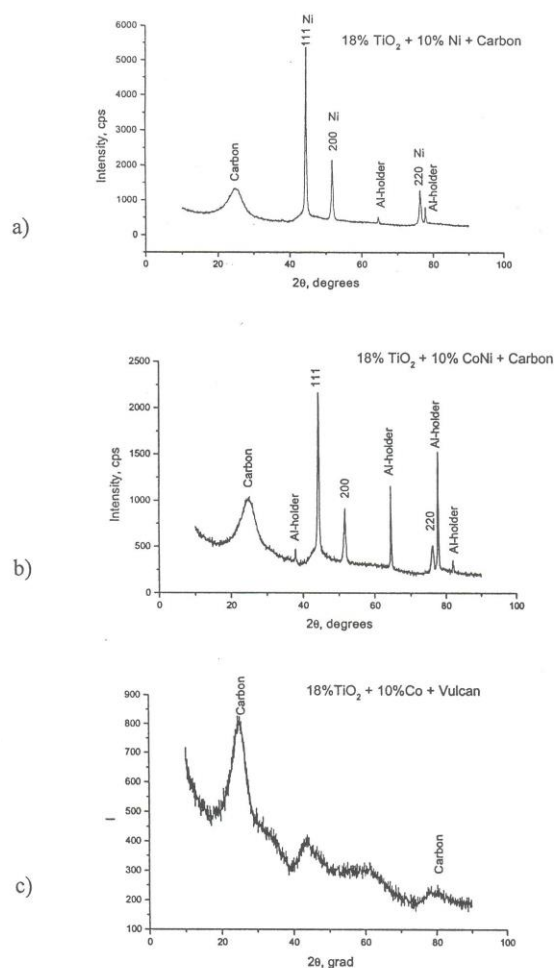
Microphotographies from the SEM observation are shown in the Fig 1. As one can be seen, the catalyst's particles deposited on Vulcan are of a spherical shape. There is a grouping of the particles in clusters sized of 100-200 nm, whereat good adherence between particles is achieved. Presence of a numbers of holes between the aggregates is evident, thus contributing to the higher specific surface area, and consequently to a higher electrocatalytic activity.



**Fig 1.** SEM fotografies of  
a) 10%Ni + 18%TiO<sub>2</sub> + Vulcan XC-72,  
b) 10%Co + 18%TiO<sub>2</sub> + Vulcan XC-72  
c) 10%CoNi + 18%TiO<sub>2</sub> + Vulcan XC-72 catalyst  
(Magnification  $\times 10000$ )

Further information about the structure of the catalysts was obtained by XRD analysis. XRD spectra for the catalysts thermally treated on 250°C are shown in the Fig. 2. The first XRD pattern (Fig. 2a) corresponds to pure Ni of crystalline f.c.c structure with cell parameter  $a=3,524 \text{ \AA}$  and particles size of 10-20 nm. XRD- spectra of Co based catalyst shows very wide range of peaks, corresponding to particles of size less than 2 nm (Fig. 2b). Co is almost amorphous and phase identification is impossible. For the third catalyst (Fig. 2b) the value of cell parameter  $a = 3,5318 \text{ \AA}$  is between the values of pure Ni ( $a = 3,524 \text{ \AA}$ )

and pure Co ( $a = 3,544 \text{ \AA}$ ). This implies a presence of a solid-state solution of Co and Ni. Dominant peaks correspond to Ni crystalline cell, what means that Co atoms are incorporated into Ni crystals. In this case, Co impurity atoms substitute Ni host atoms in local crystalline environment of Ni through structural phase transition of Co from amorphous to crystalline solid-state solution. The crystal size of hyper-metallic  $d$  component is the same as that of Ni based catalyst (10-20 nm). The crystalline state of the hypo-oxide phase was not detected, what means that  $\text{TiO}_2$  is amorphous. This nano-structured state of the catalysts contribute to increase the surface area and hence, development of the electrocatalytic characteristics.



**Fig 2.** XRD spectra of catalysts thermally treated on  $250^\circ\text{C}$  a)  $10\% \text{ Ni} + 18\% \text{ TiO}_2 + \text{Vulcan XC-72}$ , b)  $10\% \text{ Co} + 18\% \text{ TiO}_2 + \text{Vulcan XC-72}$  and c)  $10\% \text{ CoNi} + 18\% \text{ TiO}_2 + \text{Vulcan XC-72}$  catalyst

XRD spectra for the catalysts thermally treated at 480°C are shown in the Fig. 3. All metallic phases show the same crystal characteristic as in previous series, i.e. crystalline Ni (Fig.3a), amorphous Co (Fig.3b) and solid-state solution of Co in Ni crystalline lattice (Fig.3c). At 480°C, TiO<sub>2</sub> transforms from amorphous to crystalline form as anatase.

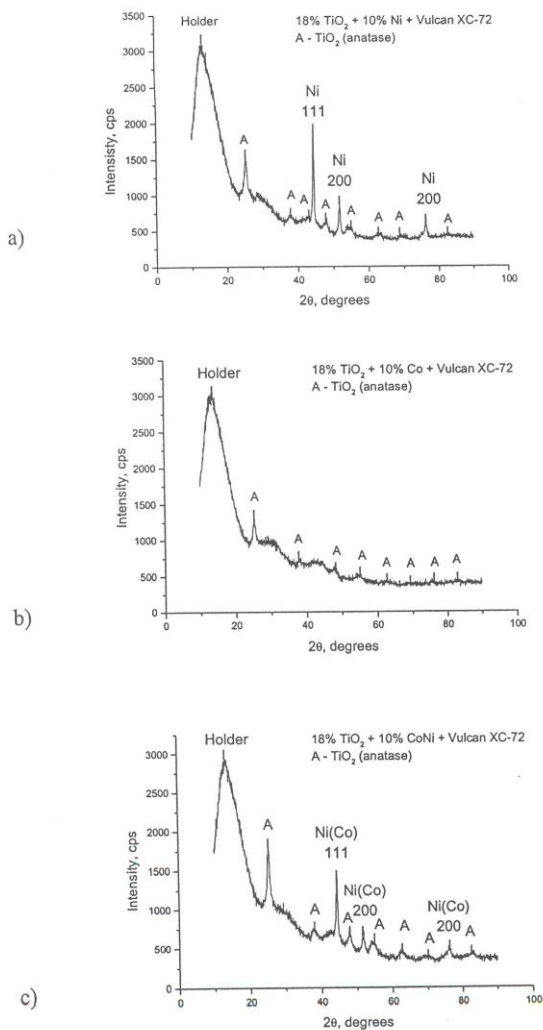


Fig 3. XRD spectra of catalysts thermally treated on 480°C a) 10%Ni + 18%TiO<sub>2</sub> + Vulcan XC-72, b) 10%Co + 18%TiO<sub>2</sub> + Vulcan XC-72 and c) 10%CoNi + 18%TiO<sub>2</sub> + Vulcan XC-72 catalyst

BET analysis has shown that the Ni based catalyst deposited on Vulcan with 18%TiO<sub>2</sub> has the highest specific surface area of 108 m<sup>2</sup>/g, while the CoNi based catalyst has 96 m<sup>2</sup>/g and the Co based has 70 m<sup>2</sup>/g. These high-developed surface areas of the nano-structured catalysts are in favor of achieving high electrocatalytic activities.

#### 4. CONCLUSION

As main conclusions of the investigations we can mention that:

- 1) The applied simplified sol-gel procedure provides synthesis of composite hypo oxide-hyper metal nano-structured *d*-electrocatalysts (below 2 nm for Co based catalyst and 10-20 nm for Ni and CoNi based catalysts),
- 2) Metallic phases have the same structure for both temperatures – crystalline Ni, amorphous Co and solid state solution of CoNi. TiO<sub>2</sub> prepared on 250°C is amorphous, while at 480°C it transforms to crystalline anatase,
- 3) Structural characteristic of these catalysts are basis for improved electrocatalytic activities for both hydrogen evolution in electrolytic processes and hydrogen oxidation in fuel cells.

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