# Raney-type Ni-Co-Fe nanostructured catalysts for efficient hydrogen production by hydrolysis of sodium borohydride

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## Motivation

Production, transportation, and storage of energy present a significant challenge for modern society, especially in the context of worsening climate conditions resulting from the exploitation of fossil fuels such as coal, oil, and natural gas. Consequently, there is increasing interest in using renewable energy sources, such as hydrogen, and in developing affordable and environmentally friendly batteries for energy storage. The primary factors in the development of such batteries are high discharge capacity, cyclic stability, and cost. Our recent research has been focused on inexpensive and abundant skeletal nanomaterials such as Ni-Co and Ni-Cu alloys [1]. The electrochemical studies demonstrated substantial charge-discharge parameters of Ni-based nanomaterials in the first cycles as well as their effective catalytic properties in hydrolysis of $NaBH_4$ [2]. The aim of this work was to investigate the influence of the composition of Ni-Co-Fe-Al alloys and the conditions of aluminum leaching on the structure and catalytic properties of the obtained materials for hydrolysis of $NaBH_4$ .

## Synthesis

Raney powders, made from *Me*-Al alloys (*Me*=Ni, Co, Fe ) were obtained through the leaching process of aluminum in a 6M KOH solution at a temperature of 80°C (Fig.1). Powders of nominal composition Ni, Co, Fe, NiFe, NiCo and NiCoFe were obtained.

$$2(Ni\text{-}Al) + 2OH^- + 6H_2O \rightarrow 2Ni\downarrow + 2Al(OH)_{4-} + 3H_2\uparrow$$

$$2(Me\text{-}Al) + 2OH^- + 6H_2O \rightarrow 2Me\downarrow + 2Al(OH)_{4-} + 3H_2\uparrow$$

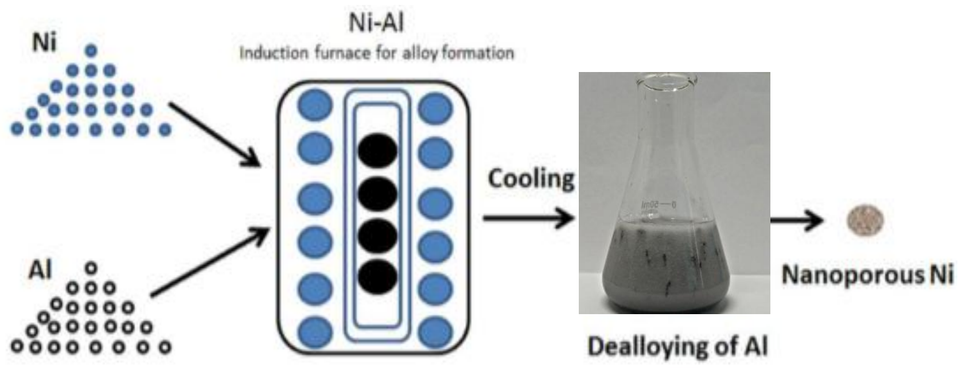


**Fig. 1.** Schematic illustration of Raney-type powder production.

The kinetics of $NaBH_4$ hydrolysis was studied at pseudoisothermal conditions in a setup similar to that described in [2].

## Results

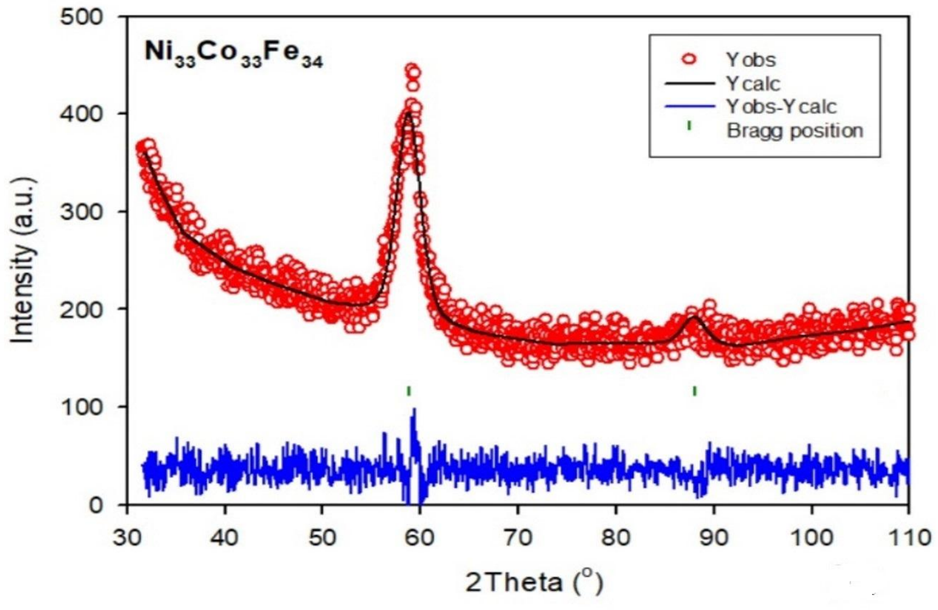


**Fig. 2.** X-ray diffraction patterns of the $Ni_{33}Co_{33}Fe_{34}$ sample after the leaching:

X-ray diffraction analysis revealed the formation of nanocrystalline metallic phases with crystallite sizes ranging from 4 to 8 nm (Fig.2). Nitrogen adsorption measurements showed specific surface areas of 50-75 $m^2$ $g^{-1}$. The obtained powders consisted of agglomerated particles with sizes of approximately 10-40 μm and contained less than 5 wt.% residual Al after leaching. The hydrolysis rate increased linearly with increasing $NaBH_4$ concentration in the range of 0.1-1.0 mol $L^{-1}$ (Fig.3), whereas increasing the solution pH from 11 to 14 resulted in only a 15% decrease in catalytic activity. Temperature-dependent measurements yielded an activation energy of 17.7 kJ $mol^{-1}$ indicating favorable reaction kinetics.

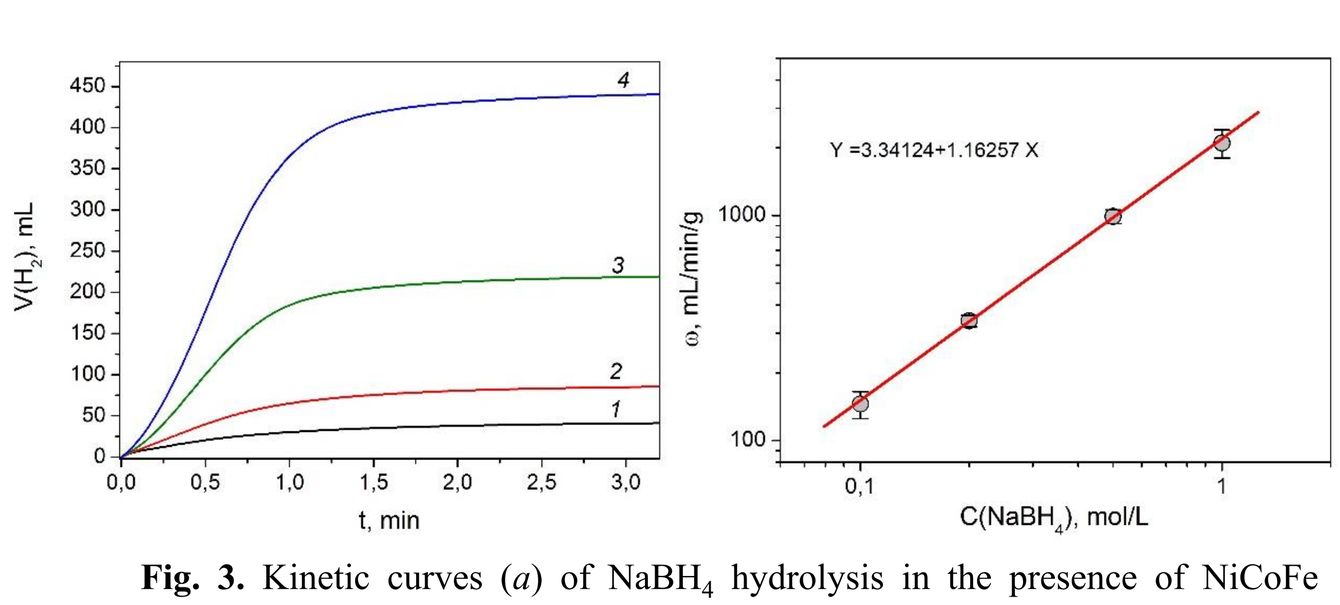


**Fig. 3.** Kinetic curves (*a*) of $NaBH_4$ hydrolysis in the presence of NiCoFe catalyst at different concentrations of $NaBH_4$ (*1*–0.1 M; *2*–0.2 M; *3*–0.5 M; *4*–1 M) and the dependence of the hydrogen generation rate on the initial $NaBH_4$ concentration plotted in logarithmic coordinates (b).

The catalytic performance strongly depended on the chemical composition of the catalyst. Among the investigated samples, the ternary $Ni_{33}Co_{33}Fe_{34}$ catalyst demonstrated the highest activity, providing a hydrogen generation rate of 2100 mL $min^{-1}$ $gcat^{-1}$. The obtained results demonstrate a pronounced synergistic effect between Ni, Co and Fe in Raney-type nanostructures and identify the $Ni_{33}Co_{33}Fe_{34}$ composition as a highly efficient catalyst for hydrogen generation from alkaline sodium borohydride solutions.

## Conclusions

Skeletal Ni–Co-Fe powders with different compositions were successfully synthesized by alkaline leaching of Al from Ni–Co–Fe–Al precursor alloys. The aluminum leaching process resulted in the formation of porous nanostructured materials, with their structural and morphological characteristics depending on the alloy composition. The synthesized materials demonstrated promising parameters as a catalysts for $NaBH_4$ hydrolysis.

## References

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2. Kytsya A., Berezovets V., Verbovytskyy Y., Bazylyak L., Kordan V., Zavaliy I., Yartys V. A. (2022). Bimetallic Ni-Co nanoparticles as an efficient catalyst of hydrogen generation via hydrolysis of $NaBH_4$. J. Alloys Compd., 908, 164484.

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