DEVELOPMENT OF CATALYSTS FOR PORTABLE HYDROGEN GENERATION USING SODIUM BOROHYDRIDE

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During the last two decades it became obviously, that intensive evolution of industry and transport would lead to energy crisis. Fast decrease of fossil fuel promotes a search of alternative energy sources. It is a received idea, that hydrogen is a perspective energy carrier. Today, the main problem of using hydrogen consists in its storage, safety, transportation and distribution. The requirement to H_2 storage systems are determined by character of commercial applications. So, the large volumetric and gravimetric hydrogen density of fuel is very important for portable, mobile devises. The highest volumetric H_2 density is found in chemical hydrides. Among the hydrides, sodium borohydride ($NaBH_4$) is desirable due to high hydrogen content and the excellent stability. According to many researchers, catalytic hydrolysis of $NaBH_4$ is a promising method for hydrogen generation for use in portable fuel cells of mobile devises. The use of catalysts allows for pure hydrogen generation even at ambient temperatures. Obtained hydrogen is contained water vapor only. Therefore, it can be supplied to the anode of fuel cells without additional purification and humidification.

The research on the development of compact energy supply with portable hydrogen generators based on $NaBH_4$ is actively carried out today. The biggest success has been achieved by *Millennium Cell Inc.* with *Protonex Technology Corporation* that started to creation compact energy source (30-50 Watts) including a cartridge with a sodium borohydride solution. However, the used ruthenium catalyst has low specific activity. *Toyota Central Research & Development Laboratories* suggested a more active composition for hydrolysis – $Pt/LiCoO_2$ containing 1.5 wt.% Pt. To decrease the gas- and hydrodynamic resistance this composition was supported on the surface of a honeycomb monolith support. Unfortunately, this led to a significant decrease of the specific catalytic activity of the catalytic system as a whole.

Despite the increasing interest to hydrolysis of hydrides, the effect of the nature of an active component and a support on the hydrogen generation rate in the presence of supported metal catalysts formed immediately in hydride solutions are not widely discussed in the literature.

The aim of this study was to develop active and stable catalysts for portable hydrogen generators based on hydrolysis of $NaBH_4$. To solve this problem, we studied in detail the regularities of the catalytic hydrolysis of hydrides and the properties of the catalytic systems.

Our investigation shown, that the nature of a support and an active component of the catalyst affects the rate of hydrogen generation. We found that the activity of catalysts on all of the tested supports decreases in the order Rh > Pt > Ru > Pd. The rhodium catalysts based on Sibunit, γ-Al_2O_3, TiO_2 and $LiCoO_2$ exhibits the highest activity. It is likely that difference in the reactivity of rhodium catalytic systems is related to the interaction of the precursor of an active component with the support. According to data obtained by physicochemical methods (UV-vision, XPS, TEM, EXAFS and IR-spectroscopy), complexes of the precursor of an active component with the support are formed in the course of rhodium chloride supporting. Differences in the composition and structure of surface complexes depend on the nature of the support. The further reduction of these complexes in a reaction medium of sodium borohydride results in the formation of metal clusters, which exhibit various reaction properties.

These studies formed the scientific basis for development of active and stable catalysts for portable hydrogen generators based on hydrolysis of sodium borohydride.