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Ethanol and methanol steam reforming on transition metal catalysts supported on detonation synthesis nanodiamonds for hydrogen production

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ABSTRACT

In this paper we report the results obtained by the comparative study of catalytic activity of monometallic (Ni, Cu, Ru, Pt) and bimetallic (Pt–Ni, Pt–Cu, Pt–Ru) catalysts synthesized on a surface of detonation nanodiamond (DND) supports in steam reforming of methanol and ethanol for hydrogen production. All obtained catalysts (M/DND) were characterized by TEM, FTIR spectroscopy, X-ray diffraction. The specific surface area of DND-nanocomposites was also evaluated by using BET technique. The obtained M/DND catalysts demonstrated high activity in methanol and ethanol steam reforming reactions. It has been shown that the most active monometallic catalyst is ruthenium one, while Pt–Ru catalyst demonstrates the highest activity in comparison with other bimetallic samples.

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Introduction

The problem of searching for alternative energy sources attracts the attention of scientists and technologists all over the world within the last decades. Hydrogen is considered as one of the most promising energy sources [1–5] due to its very low density, high power capacity and because it is one of the most environmentally friendly fuels [6]. A particular attention has

been also paid to the production of high-purity hydrogen with minimum level of carbon monoxide impurities, which can serve as a source of energy in low-temperature fuel cells (PEMFC) [7]. The reforming of hydrocarbons and alcohols presents the most common way of hydrogen production. The growing demand at renewable energy sources led in recent years to the design of technologies for production from biomass of various biofuels (such as biomethanol, bioethanol and biomethane) [8,9]. The followed steam reforming of

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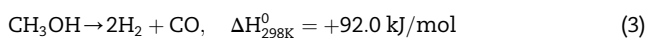
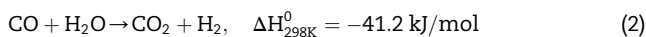
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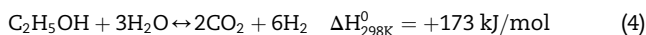
biomethanol (MSR) or bioethanol (ESR) [10] produces hydrogen in far milder conditions than in steam reforming of methane.

MSR includes the following main reactions:



Endothermic reactions (1) and (3) are reversible and are accompanied by volume increase, while exothermic reaction (2) is known as water-gas shift reaction. As a result of these reactions, a mixture of hydrogen and carbon oxides is formed; the ratio of the products depends on conditions and a catalyst nature. The Cu/Zn/Al₂O₃ catalyst with various additives, which increase the catalyst stability and the yield of hydrogen, works at the temperature range about 240–260 °C but deactivates due to sintering of copper, and change in its oxidation state. New supports for Cu/Zn catalysts were proposed [11] and some of VIII group metals were used instead of copper [12] to enhance stability of MSR catalysts and to decrease a yield of CO, which poisons an anode catalyst in PEMFC. The comprehensive reviews of these studies may be founded in Refs. [13–15].

ESR process seems to be more attractive than MSR due to its lower toxicity and possibility of ethanol aqueous solution use (producing from biomass), containing 8–12% C₂H₅OH [16]. The main reaction of ethanol steam reforming gives six hydrogen molecules from one alcohol molecule:



But reaction (4) is accompanied usually by a number of side reactions leading to the production of CO, acetaldehyde and methane. Since the general process is endothermic, the hydrogen yield increases with the temperature rise. The increase of the water/alcohol ratio in the initial reagent mixture and the reduction of pressure in the reactor also results in increase of a hydrogen yield [10]. Noble metals, nickel, cobalt, or copper, supported on various oxides (Al₂O₃, MgO, SiO₂, La₂O₃, CeO₂) are used as catalysts in ESR process in the temperature range between 300 and 800 °C [17,18].

The mechanism of ESR process on platinum metals and nickel, most widely accepted in the literature [13], includes the following stages: 1) the alcohol adsorption (by OH groups) on metals, 2) the subsequent break-up of adsorbed molecule and the formation of surface ethoxy-derivatives, 3) the formation of hydrogen, carbon monoxide and methane mixture, followed by the steam reforming of the produced methane. The role of a catalyst support is associated mainly with water molecules activation. The basic support, such as cerium oxide, provides preferentially ethanol dehydrogenation with acetaldehyde formation. The acidic carriers (e.g., Al₂O₃) give predominantly the products of ethanol dehydration.

More and more materials are proposed as supports for active metal to increase selectivity of hydrogen production and their resistivity to carbon deposition. It was demonstrated e.g. in Ref. [19] that catalysts, derived from Co/Mg/Al hydroxaltes, maintain cobalt owing to placing in appropriate environments in non metallic form Co²⁺, giving the active and

selective ESR catalyst stable in the temperature range up to 600 °C.

Recently the interest was attracted to the new carbon materials such as nanotubes, nanowires, graphenes and nanodiamonds, the unique properties of which make them applicable for using as adsorbents, catalyst supports and in some cases as catalysts [20]. The method of synthetic nanodiamonds (DND) preparation is based on a detonation of explosives or mixtures thereof with a negative oxygen balance (i.e. an oxygen content, less than stoichiometric one) in the closed volume and a non-oxidizing environment [21]. The core of formed particles has a structure of diamond with carbon atoms in the sp³-hybridization. A surface of DND particles presents a deformed carbon shell with a thickness of 1–4 carbon layers, depending on the kinetics of the cooling of the detonation products. The share of surface atoms is ~ 15% [21]. The structure and chemical composition of the shell is determined by syntheses conditions too. The presence of amorphous carbon with fragments of deformed diamond structures, onion-like carbon and graphite including carbon atoms in the sp³ or sp²-hybridization were shown.

The outer surface of DND's shell contains a large number of oxygenated groups (carboxyl, carbonyl, and hydroxyl). The presence of some protogenic groups provides the cation-exchange properties, opening up the possibilities of the surface modification [22,23], which allows the formation of surface complexes with ions of transition metal which can be precursors of active catalysts of various reactions, electrochemical sensors, etc. Due to the presence of various functional groups and high specific surface area (150–450 m²/g), DND are characterized by good sorption properties [24] and may be used in catalysis [25,26], being not only catalyst's supports but also exhibiting their own catalytic activity e.g. in ethylbenzene oxidative dehydrogenation [27–31]. It was shown that DND particles containing defective graphene on the surface demonstrate styrene productivity and selectivity superior that of nanographites, nanotubes and activated carbons.

Some investigations were devoted to the alcohols (methanol and ethanol) decomposition on nanodiamonds with hydrogen producing [32–34], that is of considerable interest for hydrogen energy as also the MSR and ESR processes. DND and DND modified by the treatment in the atmosphere of hydrogen, oxygen, mixture of nitric acid and hydrogen peroxide, as well as treated by infrared radiation were showed to be active ESR catalysts [35].

The problem of high purity hydrogen production (which is required for PEMFC application) can be successfully solved with the use of membrane catalysis due to selective hydrogen removal [see e.g. the recent reviews, [15,36]]. Within the last decade a number of papers dedicated to realization of alcohols steam reforming process in membrane reactors has been published [37–41]. The main advantages of such approach involve both the increase of hydrogen yield and also the production of the admixture-free hydrogen.

Therefore, the aim of the study is the hydrogen production by means of methanol and ethanol steam reforming using transition metals catalyst deposited on detonation nanodiamonds, particularly in membrane reactor.

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