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Influence of the support structure and composition of Ni–Cu-based catalysts on hydrogen production by methanol steam reforming

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ABSTRACT

Cu and Ni were supported on ZrO₂ by sequential impregnation method, and tested in the steam reforming of methanol (SRM) reaction for H₂ production as a function of temperature. Four bimetallic catalysts were investigated, differing in ratio of nickel and copper (Cu: Ni = 1: 4 or 4: 1) and annealing temperature. The synthesized catalysts were characterized by N₂ physisorption, DSC/TGA, X-ray diffraction, SEM, TEM. It was shown, that support structure has the main influence on composites activity, while the nature of a dominant metal affected on the selectivity of the resulting catalysts. The activity of catalysts decreases with increasing of materials crystallinity degree. The most active were samples coated with amorphous shell. The selectivity of copper catalysts is higher than nickel-based. Among the tested catalysts, the most active and selective catalyst was the sample Ni_{0.2}-Cu_{0.8}/amorphous ZrO₂.

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Introduction

During the last decades, problems related to environmental pollution have become even more acute. Therefore there is a need for new sources of a clean energy. From this point of view, conversion of a chemical energy into electrical one in a fuel cell (FC) is an attractive resolution of this issue, as a zero-pollutants emission system. The most common are low-temperature fuel cells with proton-exchange membrane [1–3]. However, hydrogen does not exist in nature in a pure form; therefore there is a problem of its synthesis [4]. Methane can be considered as a promising feedstock for technical

hydrogen obtaining. Nevertheless, its nonoxidative coupling is accompanied by significant energy absorption and occurs under high temperatures with low productivity or requires a forced activation [5]. Steam reforming of methane [6,7], or its high-temperature conversion, flowing due to partial oxidation by oxygen, are much more economically feasible [8]. The use of membranes with mixed oxygen and electron conductivity allows to carry out this process effectively and relatively safe [9–13]. However, process leads to a syngas evolution, wherein the ratio of hydrogen and CO is usually less than 2: 1 [14]. Such hydrogen is unsuitable for low-temperature fuel cells due to poisoning of its catalyst even in the presence of trace impurities of CO [3,15].

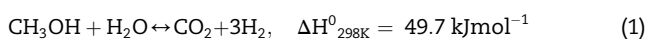
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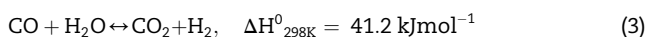
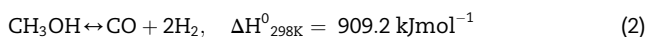
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Steam reforming of alcohols, which are much more chemically active, proceeds at considerable lower temperatures [16–19]. It is important also that alcohols produced from biomass (bio alcohols) can be considered as a renewable raw material [20]. Methanol has a number of advantages compared with other precursors for hydrogen production. Since it has only one carbon atom, methanol is one of the simplest compounds that significantly reduces the number of reaction byproducts. The absence of the C–C bonds in the molecule allows to conduct reforming at relatively low temperatures (200–350 °C), bearing in mind that reforming of ethanol usually takes place at 400–500 °C [21]. Methanol is a toxic substance, but at the same time it is biodegradable, it is a liquid at ambient conditions and it has a high hydrogen-to-carbon ratio.

In the steam reforming of methanol (SRM) in addition to the target reaction (1) occur also



a reaction of methanol decomposition (2), and water-gas shift reaction (3) [19]:



Reactions 1 and 2 require heat supplying, and the last one (WGS) occurs with heat evolution.

As a result a mixture of hydrogen and carbon oxides is obtained; the ratio of products depends on the process conditions and the catalyst used. The problem of reducing the amount of carbon monoxide is very crucial because of poisoning by it the anode catalyst of the fuel cell [22]. This emphasizes the importance of the choice of a catalyst for SRM reaction.

Traditionally, copper-based catalysts distinguished by high activity and selectivity are applied in the SRM reaction [23–26]. It has been shown that the addition of copper to nickel catalysts increases their activity in reactions of methane and methanol steam reforming [27,28]. At the same time during the reaction of ethanol steam reforming on Ni–Cu catalysts, for example, a large amount of by-products is obtained [29].

Usually, Al_2O_3 and/or ZnO are used as support for copper and nickel catalysts [25,30,31]. However, it has been demonstrated [32–34] that addition of ZrO_2 to catalysts based on copper greatly enhances their activity and reduces the yield of CO. Some authors have noted even synergy between metallic copper and zirconium oxide [35,36].

The aim of this work were the development of Ni–Cu bimetallic catalysts on the oxide (ZrO_2) support and the study of obtained catalysts behavior in the reaction of methanol steam reforming in a temperature range 200–350 °C.

Experimental

Zirconium oxide was prepared by the precipitation method from zirconium oxynitrate $\text{ZrO}(\text{NO}_3)_2$ (99% ALDRICH) according to the technique described in detail in Ref. [37]. Zirconium

hydroxide was synthesized by deposition of zirconium oxynitrate solution (99% ALDRICH) with concentrated solution of hydroxyl ammonium at a constant pH 9. The resulting deposit after precipitation was decanted and centrifuged, and then incubated in Petri dishes in a freezer at –12 °C. After thawing, the precipitate was washed with deionized water, dried in an oven at 80 °C. Hydrated zirconium oxide obtained in the first step, has been divided into two parts, one of which was annealed for 1 h at 350 °C and the other – at 400 °C. The resulting samples were sequentially impregnated with aqueous solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (>98%) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98.5\%$ ALDRICH) at an appropriate concentration calculated so that the total metal content was equaled to 20% from the carrier weight. So-prepared suspension was dispersed in an ultrasonic bath for 1 h, and then excess of water was evaporated at 100 °C in a drying oven. The obtained catalysts were annealed in air at 350 °C or 400 °C (depending on the annealing temperature of support) for 1 h. Further, they were processed in atmosphere of H_2 (5%)/Ar (20 ml/min) for 3 h at 350 °C for metal reduction. Thus four bimetallic samples were prepared, differing in ratio of nickel and copper (Cu: Ni = 1: 4 or 4: 1) and annealing temperature.

Thermal analysis (DSC) of a xerogel was performed on the calorimeter (NETZSCH STA 449F1) under argon atmosphere in the temperature range of 300–500 °C at a heating rate of 10 °C/min. The surface area and pore size distribution were determined using the BET method from N_2 adsorption with an ASAP-2020N (Micromeritics Co, USA) instrument. X-ray diffraction analysis (XRD) of the samples was performed on X-ray diffractometer Rigaku D/Max-2200 (CuK α 1 - radiation). For spectra processing and qualitative analysis Rigaku Application Data Processing software package was used. Particles sizes (coherent scattering region) were estimated from the width of the XRD patterns peaks by Scherrer equation:

$$d = \frac{k \cdot \lambda}{(B - b) \cdot \cos \theta}, \quad (4)$$

where $k = 0.89$ – constant of Scherrer; $\lambda = 1.5406 \text{ \AA}$ – the wave length of used radiation; B – a half width at half maximum (2 θ); b – instrumental broadening (2 θ); θ – the unglue of a peak position.

TEM images were taken with a Transmission Electron Microscope JEM 2100 with an acceleration voltage of 200 kV, with a point resolution 0.23 nm. The chemical analysis data and SEM images were obtained using the Scanning Electron Microscopy technique on Carl Zeiss NVision 40 with adapter for element analysis; an acceleration voltage was 200 kV.

Steam reforming of methanol was carried out under atmospheric pressure in the conventional tubular reactor (tube length of 21.5 cm, i.d. 0.9 cm) in a temperature range of 200 to 400 °C. A catalyst sample (loading was 0.3 g) was mixed with granular silica (1–3 mm fraction) and placed to the middle of the reactor. Heating of the reactor up to a work temperature was carried out by electric furnace during constant argon flow (20 ml/min); the temperature of the reactor was measured by a chromel-alumel thermocouple. Catalysts were reduced in situ with a mixture of H_2 (5%)/Ar (20 ml/min) at a temperature of 350 °C for 3 h before each series of experiments. During the reaction, argon flow rate was constant and equaled to 20 ml/min. A liquid mixture of methanol and water, with a

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