



# Bimetallic carbon nanocatalysts for methanol steam reforming in conventional and membrane reactors



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## ABSTRACT

In this paper we report the results obtained by a comparative study of catalytic activity of bimetallic (Ru–Rh, Ni–Cu) catalysts synthesized on a surface of different carbon supports: detonation nanodiamonds (DND), infrared pyrolyzed polyacrylonitrile, carbon black Vulcan-XC-72, in steam reforming of methanol (MSR) for hydrogen production. All obtained catalysts were characterized by N<sub>2</sub> physisorption, SEM, TEM, FTIR spectroscopy, X-ray diffraction. It was shown, that activity of catalysts and products distribution depends on metal type, support material and the specific surface area. Support effect was investigated for Ru–Rh system. DND showed the best properties as a catalyst support. Ru–Rh system is more active than Cu–Ni as it is shown on the example of DND supported catalysts. Comparative study between conventional (CR) and membrane (MR) reactors was carried out. MR represented a flow system with a plane Pd-containing membrane. The effect of different catalysts on the MR performances as well as a general comparison of the experimental results was considered. Obtained results demonstrate the ability of the membrane to increase the reaction conversion. The hydrogen stream produced from the MR is ultra pure: especially, it is CO-free and thus suitable to be directly fed to a polymer electrolyte membrane fuel cell.

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## 1. Introduction

Atmosphere of big cities becomes more polluted by products of incomplete combustion, nitrogen and sulfur oxides as a result of technical progress. This significantly affects on ecology. From this viewpoint, an attractive technology is a conversion of chemical energy into electrical one by fuel cells (FC) which produces water only. However, absence of hydrogen in nature in a pure form defines urgency of the problem of its synthesis [1]. Methane can be considered as a promising feedstock for technical hydrogen obtaining. Nevertheless, its nonoxidative coupling is accompanied by significant energy consumption and occurs at high temperatures with low productivity or requires a forced activation [2]. Steam reforming of methane [3,4], or its high-temperature conversion, flowing due to partial oxidation by oxygen, are much more economically feasible [5]. However, process leads to a syngas evolution, wherein the ratio of hydrogen to CO is usually less than 2:1 [6]. Such hydro-

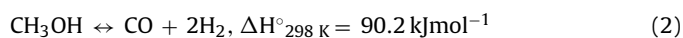
gen is unsuitable for low-temperature fuel cells due to poisoning of its catalyst even in the presence of trace impurities of CO [7,8].

Steam reforming of alcohols, which are much more chemically active than methane, proceeds at considerable lower temperatures [8–12]. It is important that alcohol, produced from biomass (bio-alcohol), can be considered as a renewable raw material. 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 dramatically 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) [13]. Methanol is a toxic substance, but at the same time it is biodegradable, it is a liquid at ambient conditions.

In the MSR in addition to the target Reaction (1):



also the reactions of methanol decomposition (2), and water-gas shift (WGS) Reaction (3) occur:



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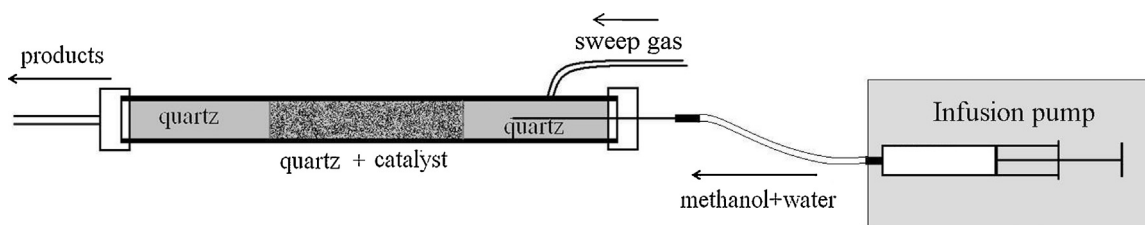


Fig. 1. Scheme of the conventional flow reactor.

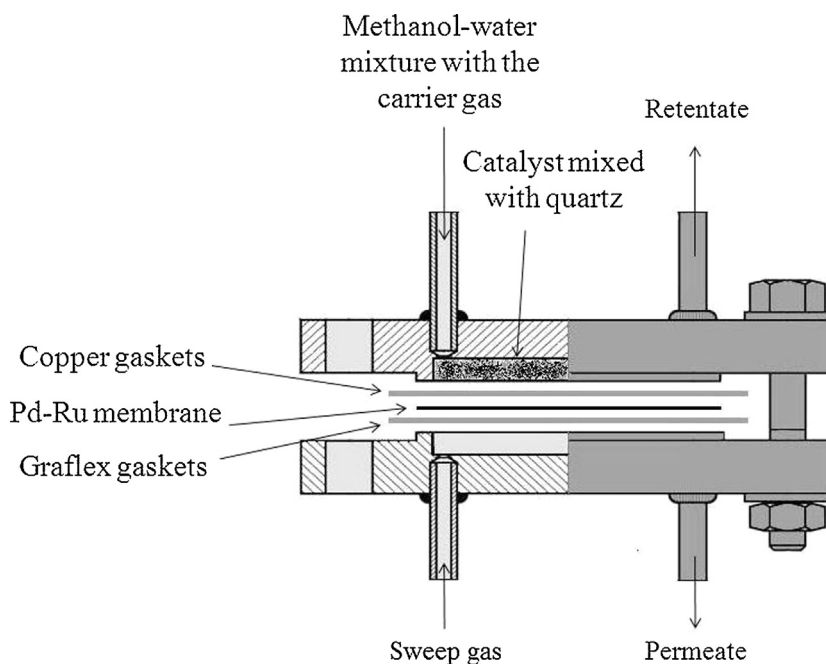


Fig. 2. Scheme of the membrane reactor.

Reactions (1) and (2) require heat supplying, and Reaction (3) 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.

Carbon monoxide is usually an undesirable product. Its formation according to Reaction (2) reduces hydrogen yield. The problem of reducing the amount of carbon monoxide is very crucial because it poisons the Pt-containing catalysts in a fuel cell. It imposes strict requirements to hydrogen purity and emphasizes the importance of the catalyst choice for MSR reaction [5,7].

Deactivation of catalysts for MSR can occur generally owing to a change in oxidation state, sintering of metal particles or coke deposition. It is known that resistance to deactivation of monometallic catalysts can be improved by adding promoters [14]. Cu-containing composites with various additives that increase the stability of the catalyst and the hydrogen yield are considered as the good catalysts for the MSR. For example, addition of Ni to the copper monometallic catalyst significantly increases its resistance to deactivation [15]. It was also shown that noble metals such as Rh, Ir, Pt, Ru, Pd, have high activity in steam reforming of alcohols [16]. Moreover, Rh is regarded as one of the most active in a number of noble metals [17]. In the works [18–22] Ru is considered as a promising catalyst for alcohol steam reforming processes also. The authors of [23] have reported a significant selectivity improvement of catalysts doped by Rh, owing to its activity in the WGS reaction. However, application of noble metals in catalysis is limited because of their high-value [24]. Therefore, of great interest are catalysts with a low

content of noble metals [25], as well as materials containing several metals [26–28].

An important issue is to increase selectivity of the composite and its resistance to carbonization. Therefore, new fine carbon materials are of great interest, such as nanotubes, nanowires, graphene and nanodiamonds (DND). The unique properties of these materials make them appropriate for use as catalyst supports [12,29,30]. It is important that application of carbon carriers mainly eliminates the problem of a catalyst carbonization. Moreover DND or fine-dispersed carbon black have high specific surface area and mainly mesoporous structure.

The problem of high purity hydrogen production (which is needed for PEMFC) can be successfully solved in the case of using of membrane catalysis by selective removal of hydrogen [13,31,32]. During the last few decades a large number of researches were devoted to carrying out of alcohols SR in membrane reactors (MR) [33–37]. The advantage of this approach lies not only in production of impurities free hydrogen, but in an increase of its yield also by selective extraction from reaction zone.

Compared with pure Pd membranes, membranes, made of some Pd alloys, have several advantages because of their higher hydrogen permeability, strength, thermal stability and catalytic activity [38–42]. The introduction of even small amounts (~1 wt%) Ru into palladium increases mechanical stability of the membrane during thermal cycling in hydrogen [43].

The aim of the work was to search new productive and selective to hydrogen catalysts for MSR on various carbon supports (DND, IR pyrolyzed polyacrylonitrile, carbon black Vulcan) and to

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