Contents lists available at ScienceDirect

# Catalysis Today

# Production of high purity hydrogen by ethanol steam reforming in membrane reactor

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## ARTICLE INFO

## ABSTRACT

Production of hydrogen in the course of ethanol steam reforming (ESR) on bimetallic Pt-Ni and Pt-Ru nanocatalysts supported on detonation nanodiamonds (DND) was studied in conventional and membrane reactors. The highest hydrogen yield and purity were achieved in the case of Pt-Ru/DND catalysts at total metal content of 0.3% and atomic Pt/Ru ratio of 9/1. It is shown that realization of ESR process in the membrane reactor with simultaneous hydrogen removal through the Pd-Ru membrane produces hydrogen of high purity, free of any other gaseous products.

## 1. Introduction

During the last decade hydrogen has become to be one of the most demanded products for the energy industry as very light, powerful and environmentally clean fuel. At the same time, the contradiction between wide prevalence of hydrogen-containing compounds in the nature and its absence in free zero-valence state complicates the development of hydrogen energy substantially. Fuel cells (the low-temperature fuel cells, in particular) will become in the nearest future the main devices for application in hydrogen energy [1–3]. For the low-temperature fuel cells a special attention should be given to manufacturing of CO-free hydrogen because of irreversible poisoning of the catalytic materials even by trace amounts of carbon monoxide [4–7].

Reforming of carbon-containing materials (e.g., ethanol) can be also considered as an efficient method for hydrogen production [8,9]. Intensive development of renewable energy sources in recent years has led to the design of technologies for production of various biofuels (such as methane, methanol, and ethanol) from

biomass [10,11]. Subsequent biomethanol [12] or bioethanol [13] steam reforming enables to produce hydrogen from the renewable sources. These processes can be realized under far milder conditions than, for example, those of methane steam reforming. The bioethanol steam reforming seems to be more attractive due to the lower toxicity of its aqueous solution (8–12% $C_2H_5OH$) which can be used directly for steam reforming [13].

Ethanol steam reforming (ESR) requires substantial energy consumption, as follows obviously from the enthalpy value of the reaction:

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2, \quad \Delta H_{298}^\circ = +173\,\text{kJ/mol} \qquad (1)$$
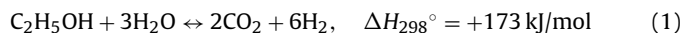
To increase the product yield the temperature needs to be increased – however, this leads to formation of numerous undesirable by-products [13]. This problem can be successfully solved with the membrane catalysis which allows to remove hydrogen selectively from the reaction zone [14]. Within the last decade a number of communications dedicated to realization of steam reforming process of alcohols in membrane reactors has been published [15–20]. The main advantages of such approach involve both the increase in hydrogen yield and the production of high-purity hydrogen.

Quite a number of heterogeneous catalysts were offered by different authors for ESR, in particular, Rh, Ru, Pd, Pt, Ni, Co, Cu on alumina, silica, magnesia, zirconia or ceria [12,13]. One of the problems is deactivation of the catalysts due to carbon deposition at high temperature. The application of supports made from the carbon-based materials (graphite, fullerenes, carbon nanofibers or

nanotubes) may solve this problem due to their resistance to car-bonization, high specific area, thermal stability and good adhesion to metals [21]. Nanodiamonds can also be considered under this approach.

The number of publications dedicated to application of nanopar-ticles in catalysis is permanently growing [22–24]. Detonation nanodiamonds (DND), or nanodiamonds produced by detonation synthesis technique, represent diamond nanoparticles consisting of carbon atoms in the sp$^3$-hybridization state [25,26]. The outer DND surface is partially oxidized and contains a large number of carboxyl, carbonyl, and hydroxyl groups. This allows the forming of the surface complexes with transition metal ions, which can serve as the precursors of active nanocatalysts for various reactions, electrochemical sensors, etc. Due to the presence of various func-tional groups and high specific surface area (150–450 m$^2$/g), DND are characterized by clearly pronounced sorption properties and can be used as not only support for metal nanocatalysts but also for their own catalytic activity [27–29]. An additional important advantage of DND is their relatively low cost (5 Euros per gram); high thermal stability makes them applicable for such high tem-perature catalytic processes as ESR. The activity of Pt, Ru, Ni, Pt-Ni, and Pt-Ru nanoparticles supported on DND was studied for the first time in a conventional tubular reactor [30].

The main goal of this study was the research of the membrane catalytic process of high-purity hydrogen production using Pt–M alloy (M = Ni, Ru) nanocatalysts deposited on DND in the presence of the commercial dense Pd-Ru membrane with 100% selectivity for hydrogen.

## 2. Methods and materials

### 2.1. Preparation of catalysts and the procedure for catalytic experiments

The catalysts were prepared by deposition of metal chlorides onto DND followed by IR radiation. A suspension of metal chlo-rides (Pt with Ru or Ni where the Pt:Ru (Ni) ratio was 9:1) and DND particles in dimethylformamide (DMF) was subjected to ultrasonic dispersion for 10 min and dried to a constant weight. Resulting powder was exposed to IR radiation for 2 min in an inert atmo-sphere; the intensity corresponded to the temperature of 700 °C. The samples of catalysts with 0.3 and 10 wt% of Pt–Ru or Pt–Ni alloys were prepared.

A traditional tubular stainless steel reactor (TR) of 7 mm diam-eter was used for ESR in the plug flow apparatus. Samples of catalysts (loading 0.3 g; metal content 0.3 wt%) mixed with gran-ulated quartz (fraction 1–3 mm) were placed into the middle of reactor tube (volume of catalyst bed 4.5 cm$^3$). ESR was carried out at temperatures from 350 °C to 650 °C with a carrier gas (Ar) flow rate of 20 cm$^3$/min. The liquid mixture of ethanol and water with the molar ratio of 1:3 or 1:9 was fed by infusion pump P-600 into the evaporator. At the evaporator outlet ethanol and water vapors were mixed with the carrier gas and then fed into the reactor. Vaporous ESR products were condensed at the outlet of the reactor in a glass receiver cooled to 0 °C. Uncondensed vapors (water and ethanol) were fed to LHM 8MD chromatograph with thermal conductivity detector ($t$ = 160 °C, $I$ = 80 mA, a column with Porapak-T stationary phase, carrier gas He, flow rate 30 cm$^3$/min). Methane, CO, and CO$_2$ were analyzed in the same chromatograph with the use of the acti-vated charcoal column. Hydrogen and methane were analyzed with the use of Chrom-4 chromatograph with a thermal conductivity detector and CaA Zeosorb stationary phase column. The obtained data were treated by using Ecochrom program.

The other series of experiments was carried out in the mem-brane reactor (MR). The samples of catalysts (0.3 g, metal content 0.3 wt%) mixed with granulated quartz (fraction 1–3 mm) were placed into the reaction zone of the membrane reactor consisting of two parallelepiped-shaped stainless steel compartments with the following inner dimensions: 118 mm × 20.5 mm × 2 mm (reac-tion zone volume 4.5 cm$^3$). The two compartments were divided by a pinhole-free foil membrane of Pd–Ru alloy (6 mass% Ru; 118 mm × 20 mm × 50 μm). Two gaskets made of copper and of graphite ensured that the gaseous streams flowing in the permeate and the reaction zones did not mix with each other in the reactor.

Experiments in MR were carried out at the temperatures of 350 and 450 °C. The flow of sweep gas on the permeate side (from 40 cm$^3$/min to 100 cm$^3$/min) allowed to perform hydrogen removal from the reactor.

Each experiment was carried out within 3–5 h. Regeneration of the catalysts between experiments was carried out by heating in hydrogen for one hour at 450 °C. The ethanol conversion degree, $X$ (%), the catalyst selectivity, S (%), and the yield of products, $Y_i$ were calculated from the results of analysis by using the following equations:

$$X = \frac{\varphi_0 - \varphi_1}{\varphi_0} \times 100 \tag{2}$$

$$S_i = \frac{\varphi_i}{\varphi_0 - \varphi_1} \times 100 \tag{3}$$

$$S_{H_2} = \frac{\varphi_{H_2}}{\varphi_{H_2} + 2\varphi_{CH_4}} \times 100 \tag{4}$$

$$Y_i = \frac{\varphi_i}{\varphi_0}, \tag{5}$$

where $\varphi_0$ and $\varphi_1$ are the initial and the resulting ethanol concen-trations, respectively; $\varphi_i$ is the ESR product concentration ($i$ = H$_2$, CO, CO$_2$, or CH$_4$).

Hydrogen permeability of Pd-Ru membrane was measured directly in the membrane reactor before and after the comple-tion of ESR experiments with Pt-Ru/DND catalyst by feeding the flow of pure hydrogen to the reaction zone and the flow of argon (40 cm$^3$/min) to the hydrogen removal zone. Hydrogen permeabil-ity constant was calculated by using equation:

$$J \ [cm^2 \ s^{-1} \ bar^{-1/2}] = \frac{Q \times \delta}{S \times \left( \sqrt{P_1} - \sqrt{P_2} \right)} \tag{6}$$

where $Q$ is hydrogen flux through the membrane, cm$^3$/min; $\delta$ – the thickness of membrane, cm; $P_1$ – hydrogen partial pressure on the input side of membrane, bar; $P_2$ – hydrogen partial pressure on the output side of membrane, bar; $S$ – membrane area, cm$^2$.

### 2.2. Catalysts structure and morphology

The specific area and porosity of catalyst samples were mea-sured by low-temperature nitrogen adsorption in the porometer ASAP-2020N (Micromeritics Co., USA). The specific surface area was determined by using BET method in the range of relative pressure values from 0 to 1 using the equation for multimolecular steam adsorption. The micrographs of the samples were obtained by using a transmission electron microscope JEM-2100 (Jeol).

X-ray analysis of the samples containing 0.3 or 10% of metal catalyst was performed using the diffractometer "Rigaku D/MAX 2200", CuKα1 radiation. The software package Rigaku Application Data Processing was used for spectra analysis.

## 3. Results and discussion

X-ray patterns of Pt-Ru/DND and Pt-Ni/DND samples with 10 wt% metal content are similar, both having the peaks