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Abstract

Methanol Steam Reforming in the Traditional and Membrane Reactors over Pt-Rh/TiO_2-In_2O_3 Catalyst Using Surface-Treated Pd-Cu Foil Membranes †

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Abstract: The study of methanol steam reforming (MSR) over Pt-Rh/TiO_2-In_2O_3 catalyst was carried out in traditional and membrane reactors using Pd-Cu foil treated by various methods. This catalyst showed the highest catalytic activity in a conventional reactor. The best results (hydrogen yield) are achieved in a membrane reactor with the use Pt-Rh/TiO_2-In_2O_3 catalyst and Pd-Cu membrane after hard rolling. At the same time, the hydrogen recovery degree on the permeate zone on this membrane reached 60%.

Keywords: methanol steam reforming; pure hydrogen; Pd–Cu alloy membrane; membrane catalysis; surface treatment

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1. Introduction

The problem of searching for alternative energy sources attracts the attention of scientists and technologists all over the world within the last decades. One of the environmentally friendly and highly efficient energy carriers is hydrogen. The purity of the final product is one of the main problems of hydrogen production, because this parameter in many instances determines the efficiency of its practical application. Generating energy from hydrogen using fuel cells will be the main applications of hydrogen in the near future. [1–3]. One of the main limitation, which still hinder the development of low-temperature fuel cells is the use of proton conducting membranes, which can effectively operate at the temperatures not exceeding 90-100°C. However, under these temperatures all catalytic materials existing to the moment are irreversibly poisoned even with the trace amounts of carbon monoxide. This problem can be successfully solved with the use of membrane catalysis due to selective hydrogen removal [4].

The coal conversion (gasification) along with conversion of some other carbon-containing materials are considered as efficient method for hydrogen production [5]. The main disadvantage of these high-temperature processes is the formation of carbon monoxide as the main co-product. Catalysts used in these processes include the noble and some transition metals [6, 7]. The biofuel fermentation products such as, methanol, ethanol and some others can be considered as the most perspective raw materials. The significantly lower temperatures of these processes lead to a significant decrease in the carbon monoxide yield. Although the partial separation of hydrogen is not so complicated, the high hydrogen purification is quite a complex problem. This problem can be solved with the use of membranes based on palladium alloys [8, 9].

The methanol stream reforming includes the following reactions:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2,\ \Delta H_{298K} = +49.7\ kJ/mol \quad (1)$$

$$CH_3OH \rightarrow 2H_2 + CO,\ \Delta H_{298K} = +92.0\ kJ/mol \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2,\ \Delta H_{298K} = -41.2\ kJ/mol \quad (3)$$

Endothermic reactions (1) and (2) are reversible and exothermic reaction (3) is known as water-gas shift reaction. Selective removal of hydrogen in the case of membrane catalysis allows the production of admixture-free hydrogen. However, the efficiency of this process is significantly reduced due to the low productivity of membranes based on palladium alloys. Their hydrogen permeability is largely determined by the surface of the membrane and can be improved through treatment.

Therefore, the aim of the study was the development of membrane catalytic process for high-purity hydrogen production using palladium-copper membrane with a surface treated by various methods in the presence of Pt-Rh/TiO_2-In_2O_3 catalyst.

2. Methods

The catalyst (Pt-Rh/TiO_2-In_2O_3) was prepared by sequential reduction of metal precursors (hexachloroplatinic acid and rhodium III chloride) at room temperature in the liquid phase using 0.5 M $NaBH_4$ as a reducing agent [10].

MSR was carried out in a membrane reactor with Pd-Cu foil of 18 μm thickness at the temperatures from 280 to 400 °C. A sample (m=0.3 g) mixed with granulated quartz (fraction 1 - 3 mm) was placed in the reaction zone membrane reactor. C. Methanol – water mixture with the molar ratio 1:1 was fed by the infusion pump into the evaporator. At the evaporator outlet methanol and water vapors were mixed with the carrier gas and then fed into the reactor. Hydrogen diffused through the membrane was removed by argon flow.

3. Results and Discussion

The hydrogen permeability of the Pd-Cu membranes was studied. Samples were examined without preliminary purification and after treatments. Pd-Cu membrane foils with high hydrogen permeability were selected for catalytic studies in a membrane reactor using Pt-Rh/TiO_2-In_2O_3 catalyst. It is believed that the main function of the support in the steam reforming reaction is a water sorption, while the metal should preferentially sorb methanol. In this case, the methanol steam reforming occurs at the interface between the Pt-Rh alloy and the oxide support. The oxygen vacancies formation in the oxide structure leads to the water sorption increase and the diffusion rate of oxygen-containing groups on the surface increase.

The main stages for the hydrogen transfer through the membrane are: adsorption of hydrogen molecules on the surface, dissociation, transition into the bulk (dissolution), diffusion, and exit from the surface. If solubility and diffusion are completely determined by the nature of the membrane alloy, then the first and last stages are determined by the surface state. During rolling, carbon containing products sorption takes place on the membrane surface. Therefore, a significant part of the surface is excluded from the transfer process. The use of surface-treated membranes in catalysis should increase the efficiency of processes occurring at low temperatures. The main products of methanol steam reforming over Pt-Rh/TiO_2-In_2O_3 catalyst were hydrogen and carbon dioxide formed by the reaction (1).

The hydrogen permeability of the foil increased after treatment. However, the maximum amount of hydrogen passed through the membrane is reached after mechanical hardening (Figure 1).

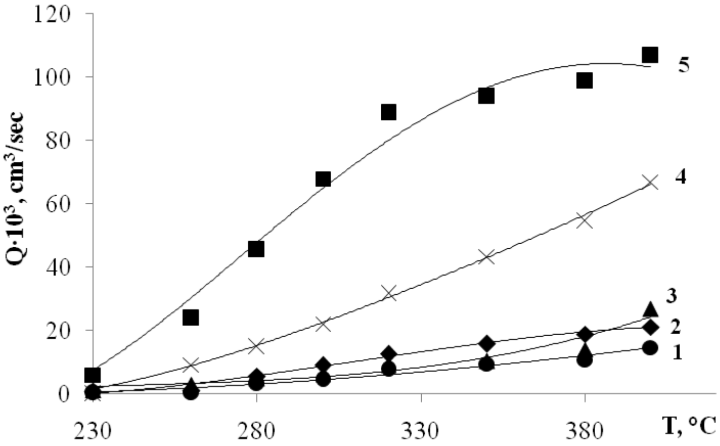

Figure 1. The amount of hydrogen that passed through the membrane: 1 - without pre-treatment; 2 – after ultrasonic cleaning; 3 – after ultrasonic cleaning and photonic treatment; 4 – ionic beam treatment; 5 - after deformation ordering.

When comparing the yields of hydrogen in traditional and membrane reactors (Figure 2), it can be seen that the yields are almost the same. The main advantage of using a membrane reactor is the possibility of producing high-purity hydrogen.

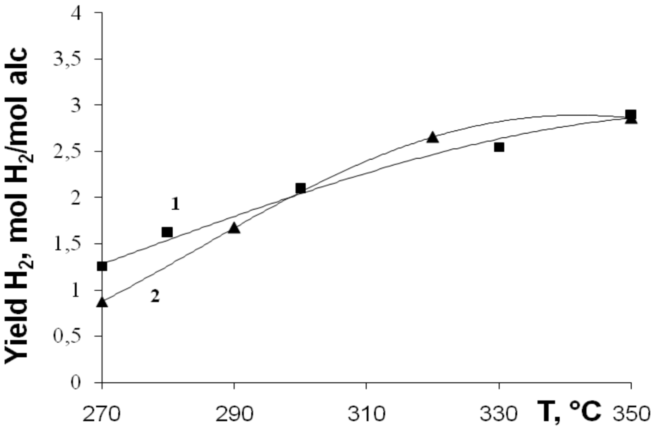

Figure 2. Comparison of hydrogen yields in traditional (1) and membrane (2) reactors.

The hydrogen recovery degree on the permeate zone reached 60% for the foil after mechanical hardening, while this parameter was not exceed 20% for the membrane after ultrasonic cleaning and ion photon treatment. The pure hydrogen yield in the permeate zone in the temperature range of 340 - 400°C was higher for the membrane after deformation ordering than for the membrane after double-sided photonic treatment (Figure 3).

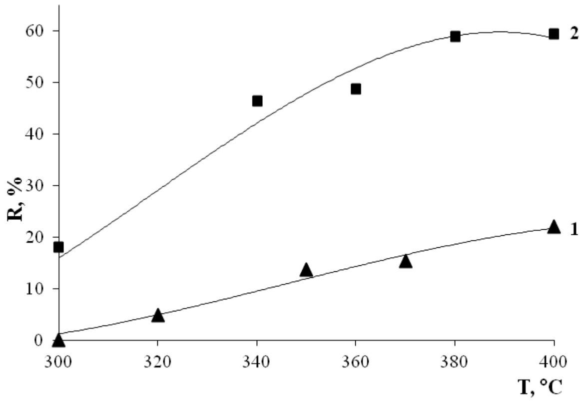

Figure 3. The hydrogen recovery degree in the permeate zone for membrane: 1–after ultrasonic cleaning and photonic treatment; 2 – after deformation ordering**.**

4. Conclusions

The methanol steam reforming process on the membrane-catalytic systems using PdCu foil membranes with a surface treated by various methods was studied. The highest hydrogen permeability and hydrogen yield was achieved with the use of a membrane-catalytic system Pt-Rh/TiO_2-In_2O_3 catalyst and Pd-Cu membrane after deformation ordering. In this case, the hydrogen recovery degree on the permeate zone reached 60%.

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Conflicts of Interest: The authors declare no conflict of interest.

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