**Hydrogen production from ethanol and methane conversion**

1K. Dossumov, 2Y.G. Yergaziyeva, 2M.M.Telbayeva

1The Center of Physical and Chemical Methods of Research & Analysis of al-Farabi KazNU, 050012, 96 A, Toleby Str., Almaty, Kazakhstan

2The Institute of Combustion Problems, 050012, 172, Bogenbay batyr Str., Almaty, Kazakhstan

In connection with the transition to "green" technology worldwide, intensive work is under way to search for alternative sources of energy and energy carriers.The first place among the energy carriers in terms of heat of combustion is hydrogen. Hydrogen in terms of energy intensity exceeds all compounds that can serve as fuel: 2.5 times natural gas, 3.3 times liquid hydrocarbons of oil, 5 times coal, 6.6 times methanol, 8.5 times - cellulose, etc. Hydrogen is the only environmentally friendly fuel and reagent, the product of oxidation of which is water vapor or liquid water. Hydrogen is also used as a raw material in organic chemistry, petrochemistry, oil and gas processing. In the chemical industry, hydrogen is one of the main intermediates. It is used in the production of ammonia, methanol, synthetic fuels, at deep processing of oil and the production of high-octane motor fuel. Hydrogen is widely used in low-tonnage, science-intensive industries: electronic, pharmaceutical, food, metallurgy, the synthesis of chemically highly active substances and other industries. Consumption of hydrogen all over the world is steadily growing.

The traditional method of obtaining hydrogen is the electrolysis of water, but one of the obstacles to large-scale use of this method to this day is the large consumption of electric current. To obtain hydrogen, available chemical raw materials are needed. The production of hydrogen from natural gas and renewable raw materials can significantly increase the economic efficiency of the process

The aim of the work is catalytic production of hydrogen from natural gas methane and renewable raw materials - bioethanol.

The catalysts were prepared by the method of capillary impregnation of the carrier by its moisture capacity with a solution of nitric acid salts of the active phase. Testing of the activity of synthesized catalysts in the conversion of methane or bioethanol was carried out on an automatic installation of PKU-1. Analysis of the feedstock and the products obtained was identified on a gas chromatograph CHROMOS-1000. The morphology of the catalysts was studied by scanning (SEM) and transmission electron microscopy (TEM). The presence of acid sites in the catalyst composition was studied by infrared spectroscopy, pyridine was used as the probe molecule (IRS). The reduction characteristics of the catalysts were studied by the method of temperature-programmed reduction (TPR-H2).

The activity of Ni containing catalysts in the conversion of methane to hydrogen depends on several factors: the nature of the active phase, the carrier, the modifying additive, the technological parameters of the process, etc.

The introduction of modifying additions of lanthanum or cerium into the composition of the Ni / ɣ-Al2O3 catalyst leads to an increase in the content of the active sites of the catalyst (Ni and NiO), thereby increasing the catalyst's resistance to coke formation during the conversion of methane to hydrogen. The greatest yield of hydrogen (46 vol.%) is observed on the NiLa / Al2O3 catalyst under the reaction conditions Tr-750оС, the space velocity is 1000 h-1, the ratio in the initial mixture СН4:О2 = 2 : 1.

Subsequently, it was of interest to study the synthesis of hydrogen from renewable raw materials - bioethanol. To convert bioethanol to hydrogen as an active phase of the catalyst, oxides of transition elements Cu, Zr and Zn were studied. As an effective catalyst carrier, γ-alumina was selected. The greatest hydrogen yield is 20 vol. % is observed on a Cu / γ- Al2O3 catalyst. The activity of the catalysts for the formation of hydrogen in the bioethanol conversion reaction varies in the series: Cu / γ- Al2O3 (YН2-20%)> Zn / γ- Al2O3 (YН2-16%)> Zr / γ- Al2O3 (YН2-10%).

To increase the activity of the copper-containing catalyst, the effect of modifying additives, chromium and zinc oxides was studied. The results showed that modifying the Cu / γ-Al2O3 catalyst leads to an increase in its catalytic activity, the yield of H2 reaches up to 48 vol. % on CuCr / γ- Al2O3 and 50 vol. % on the CuZn / γ- Al2O3 catalyst. The increase in the activity of Cu / γ-Al2O3 with the introduction of modifiers is explained by the increase in the dispersion of the catalyst (Figure 1).



Fig. 1 - A micrograph of the CuCr/ γ-Al2O3 catalyst

Modification of Cu / γ-Al2O3 with chromium oxide leads to a decrease in the size of the catalyst nanoparticles from 20 to 2-5 nm, which has a positive effect on its activity in the conversion of bioethanol.

Figure 2 shows the comparative data of the influence of the nature of the feedstock and the reaction temperature on the yield of hydrogen.



Fig. 2 - Influence of the nature of the raw material and reaction temperature on the yield of hydrogen

From figure clear that, compared to methane, bioethanol is converted to hydrogen at lower temperatures (300° C), with a higher hydrogen yield of 50 vol. %.

Thys, the natural gas methane and renewable raw materials - bioethanol is expedient to be used as an effective, cheap source for obtaining the main energy carrier - hydrogen.

For the conversion of methane to hydrogen, a NiLa / Al2O3 - resistant to carbonization catalyst is developed. At effective process parameters (Tr - 750oC, W-1000 h-1, CH4:O2 = 2:1), the hydrogen yield is 46 vol. %.

For the conversion of bioethanol to hydrogen, a nanophase CuCr/ γ-Al2O3 catalyst was developed. Under optimal process conditions (Tr - 300°C, W - 1 h-1), the hydrogen yield is 50% by volume.