

# LOW-TEMPERATURE REFORMING OF ETHANOL OVER NICKEL-COPPER CATALYST

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## Introduction

Hydrogen is promising fuel for various power plants, low-power devices (1-50W) included [1]. The latter can be portable fuel cells and charging units to energize notebooks, cell phones, etc. However, accumulation and storage of molecular hydrogen nowadays present a problem because of safety concerns during hydrogen capacitors exploitation and their small capacitance to hydrogen. One of possible pathways to overcome the difficulties can be hydrogen production from hydrocarbons, e.g. alcohols (methanol or ethanol), by water-vapor catalytic conversion. In this case ethanol has a number of advantages over methanol such as low cost, low toxicity, ease of transporting, exploitation, and production from renewable sources (bioethanol). When hydrogen is used to supply portable fuel cells, integration of a fuel cell and a fuel microchannel converter seems most perspective [2]. In this case, the catalyst should be placed on the channel walls, where highly developed catalyst surface can hardly be obtained. In this work we studied low-temperature steam reforming of ethanol over a bimetal nickel-copper catalyst deposited onto a quartz fiber of small specific surface.

## Experimental

The catalyst was prepared by impregnation quartz fibers in water solution of nickel and copper nitrates of corresponding quantities for 24 h. Then the fibers were dried at 120°C and annealed at 600°C. The catalyst was reduced in a hydrogen flow at 550°C in the reactor for 4 h just before the experiment. The catalyst charge (without the support) was 0,4g, with the copper content in the catalyst 15 wt %.

Ethanol reforming was performed in a cylindrical flow microreactor 70mm long and 6mm inner diameter. The process temperature was varied from 200 to 400°C. The rate of gas-carrier (argon) was varied in the range 20 to 100 cm<sup>3</sup>/min. Ethanol-water molar ratio was 1,2:1. The analysis was performed by the gas chromatographic method in two phases: A5 molecular sieves (to register gases a column 2m long) and polysorb (to register ethanol and water a column 2m long).

## Results and discussion

It was shown earlier [3] that the main products of ethanol-water mixtures reforming over a nickel catalyst are hydrogen, methane and carbon monoxide. All these products are present approximately in equal amounts (one third of the total gas phase) in the whole range of temperatures studied (200-400°C). Small amounts of acetaldehyde, as a product of ethanol dehydrogenation, were observed. It was noted that water is not involved in the process, which points to the absence of the shift-reaction, i.e. the process is a catalytic pyrolysis of ethanol. The results of this investigation of ethanol-water reforming over the nickel-copper bimetal catalyst are presented in Fig.1. It is seen that the major products of reforming are hydrogen, methane, carbon monoxide and carbon dioxide. The conversion of ethanol starts at 200°C and completes almost by 90% at 350°C. As the

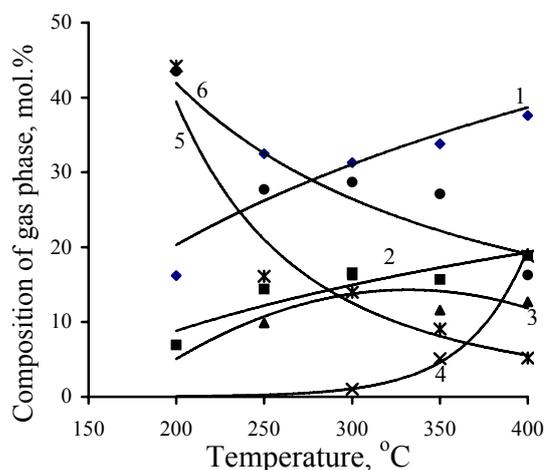


Fig.1. Temperature dependence of the gas phase composition during the conversion of ethanol and water: 1- hydrogen, 2 – methane, 3 – carbon monoxide, 4 – carbon dioxide, 5 – ethanol, 6 – water.

conversion proceeds, the concentration of all products increases. The concentration ratio of hydrogen, methane and carbon monoxide remains constant, with the hydrogen concentration being twice as high as those of methane and carbon monoxide. At 300°C carbon dioxide appears in the

gas phase, its content increases abruptly at 350<sup>0</sup>C and makes 20 mol% at 400<sup>0</sup>C. At this temperature, the carbon monoxide concentration reaches the maximum and then drops to 10 mol%, evidently due to the shift-reaction and carbon monoxide disproportionation. The selectivity of hydrogen and methane slightly decreases (by 10-15%) as the temperature rises because of an increase of CO<sub>2</sub> content in the gas phase; the selectivity of carbon monoxide reaches the maximum at 350<sup>0</sup>C. At temperature below 300<sup>0</sup>C, the selectivity of carbon dioxide is low but increases abruptly with temperature. The water content in the gas phase grows lower by three times (from 45 mol% to 16 mol%) as a result of the shift-reaction and, partially, gas phase dilution with a large number of gaseous products formed. The results obtained suggest that the resistance to diffusion exerts no appreciable effect on mass transfer in the gas phase. Also the conversion of the ethanol-water mixture should produce 2 moles of hydrogen per 1 mole of ethanol. In fact, only 1 mole of hydrogen is produced directly from ethanol, the other is obtained from water as a result of shift-reaction and, partially, from water-vapor conversion of methane. These suggestions are supported by the literature thermodynamic calculations which show that the equilibrium constants of these reactions in the studied temperature range are fairly large.

## Conclusions

The experiments showed that the bimetal nickel-copper catalyst on quartz fibers is highly efficient for ethanol reforming at relatively low temperatures, in spite of its rather small specific surface.

The low-temperature reforming is accompanied by evolution of large amount of carbon monoxide and methane. The hydrogen obtained would require a fairly elaborate purification procedure (especially from carbon monoxide) to be used in a fuel cell.

## References

1. Haryanto A., Fernando S., Murali N., Adhikari S. Current status of hydrogen production techniques by steam reforming of ethanol: a review // *Energy & Fuel*. 2005;19: 2098-2106.
2. Pattekar A.V., Kothare M.V. A microreactor for hydrogen production in micro fuel cell applications // *IEEE J. of Microelectromechanical systems*. 2004; 13(1): 7-18.
3. Lapin N.V., Red`kin A.N., Bezhok V.S., Vyatkin A.F. Hydrogen production by catalytic pyrolysis of ethanol over a nickel catalyst. *Zh. fiz. khim.* 2009;83(10). (in print).