Steam reformin of methanol to hydrogen-catalysts preparing and testing

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Introduction

In recent years hydrogen is considered as a potential source of clean energy. From energy point of view, the use of hydrogen as a power for fuel cells is particularly cost effective. Compared to conventional heat engines they have a significantly higher efficiency. They are efficient energy sources, easy to use and having a minimum emission of harmful compounds energy sources. Products issued by cells consist only of an environmental inert steam and H_2/CO_2 mixture. The use of hydrogen in fuel cells will reduce atmospheric pollution and greenhouse gas emissions, but also reduce overall dependence of fossil fuels. Attention is focused on conversion of bioalcohols to H_2. Methanol may be preferable to other liquid hydrogen sources, such as gasoline, due to its high hydrogen content [1,2]. Moreover, it can be obtained from biomass.

Hydrogen can be produced in one step in the process of catalytic steam reforming of methanol (SRM) according to reaction (1):

$$CH_3OH_{(g)} + H_2O_{(g)} \xrightarrow{\text{catalyst}} CO_2 + 3H_2 \qquad \Delta H^{\Theta} = +49.5 \text{ kJ mol}^{-1} \quad (1)$$

The highest activity in this process have systems containing copper as the active phase dispersed on pure oxides or oxide systems such as ZnO, Al_2O_3, Zn/Al_2O_3, Cr_2O_3/Al_2O_3, ZrO_2/CeO_2 or ZrO_2/Al_2O_3. It is strong relation with catalysts manufacturing method. Similar catalysts prepared by different methods can present district catalytic properties [3]. The classical method of Cu-based catalysts' synthesis includes primarily processes such as (wet) impregnation and co-precipitation from aqueous solutions or other solvents. Preparation of catalysts by these methods is complex and needs using elevated temperatures and pressure, as well as a proper pH. In addition, these processes generate a significant amount of environmentally harmful waste.

The main task of our research is the creation of new catalysts precursors for SRM process by environmental friendly mechanical treatment (as a method of *green chemistry*). Earlier investigations showed that mechanochemical synthesis of solids by high-energy ball milling can be used to preparing new compounds [4, 5] and they are alternative methods to their conventional once by high-temperature and ecological hazardous syntheses.

Experimental

System such as Cu/Al_2O_3 and $Cu_3Fe_4(VO_4)_6$ [6] were prepared by high energy ball milling in a planetary ball mills.

<u>Cu/Al_2O_3 synthesis</u>

Homogeneous mixture of CuO (p.a. Fluka) with aluminium powder in stoichiometry of reagents (according to aluminothermic reaction (2)) was conducted to mechanical treatment using a planetary ball mill Fritsch GmbH *Pulverissette 6*. Vial and balls were made of WC. The milling conditions were as follows: argon atmosphere, rpm = 550, BPR = 40:1, milling time of samples I-III is 5 and 10 hours.

$$3CuO_{(s)} + 2Al_{(s)} = 3Cu^0_{(s)} + Al_2O_{3(s)} \quad (2)$$

<u>$Cu_3Fe_4(VO_4)_6$ synthesis</u>

Sample was synthesized by mechanochemical treatment of CuO (p.a., Fluka), Fe_2O_3 (pure, POCh) and V_2O_5 (p.a., POCh) mixture in molar ratio of 3:2:3, respectively (according to reaction (3)). Milling was carried out in a planetary ball mill (*Activator* 2S, Novosibirsk, Russia) using vial and balls made of Cr-Ni steel. The milling conditions were as follows: air atmosphere, rpm = 1200, BPR = 20:1, milling time up to 10 hours.

$$3CuO_{(s)} + 2Fe_2O_{3(s)} + 3V_2O_{5(s)} = Cu_3Fe_4(VO_4)_{6(s)} \quad (3)$$

Catalytic tests were performed in a pulse microreactor connected on-line with the chromatograph SRI 8610C equipped with TCD and FID detectors. Porapak Q and molecular sieves columns were used. Argon as a carrier gas, (30ml min^{-1}), catalyst in amount of 0.1g (fractions from 0.2 to 0.3 mm) were used. The reaction temperatures have been ranged from 250^oC to 500^oC. The temperature of the processes was chosen from preliminary studies.

Results and Discussion

The results confirmed the possibility of hydrogen production by steam reforming of methanol using mechanochemically treated mixture, with creation copper-based catalysts. Characteristics of chosen samples is collected in *Table 1*.

High methanol conversions as well as molar ratios of hydrogen to carbon dioxide are shown in *Figures 1* and *2*, respectively. The results show that copper-based systems exhibit high catalytic activity and stability for SRM process.

The total methanol conversion degrees (see *Figure 1*) for samples I and III are similar (above 60%) and for sample II is close to 80%. Moreover, the selectivity to CO_2 (as a H_2/CO_2) is close to 3 (*Figure 2*) (according to stoichiometry) for I-III samples. The highest hydrogen yield was 70% for sample II.

Table 1: Characteristics of studied samples

No. system	Milling time [h]	S_{BET} [m^2 g^{-1}]	V_{BJH} [cm^3 g^{-1}]	S_{BJH} [Å]	SRM temp. [^oC]
I Cu/Al_2O_3	5	3.9	0.009	111.9	275
II Cu/Al_2O_3					300
III Cu/Al_2O_3	10	3.3	0.008	99.3	300
IV $Cu_3Fe_4(VO_4)_6$	8	8.4	0.026	138.4	450
V $Cu_3Fe_4(VO_4)_6$	10	9.8	0.027	125.8	450

Samples IV and V also exhibit catalytic activity in steam reforming of methanol, however, selectivity to CO_2 (as a H_2/CO_2) is lower than 3 (*Figure 2*). Despite satisfactory total conversion degrees of CH_3OH (close to 100%) (*Figure 1*) by-products (CH_4, CO) occur in product mixtures.

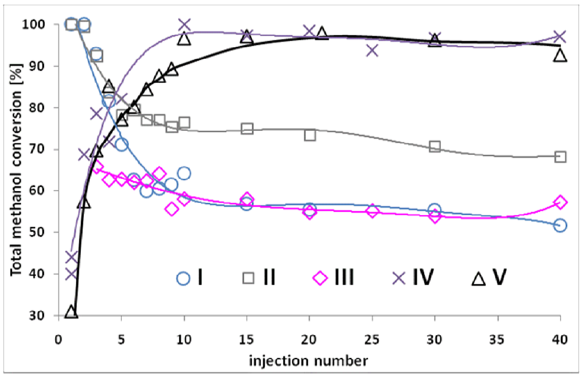

Figure 1: Total methanol conversion [%]

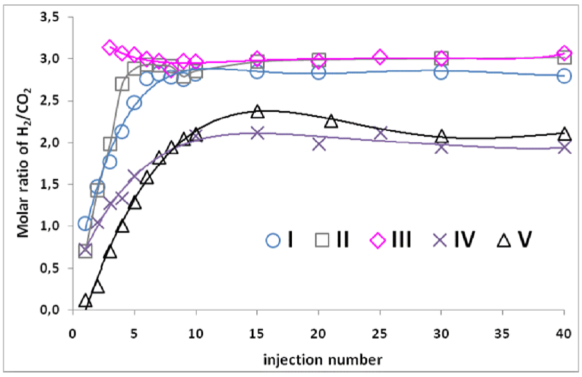

Figure 2: Molar ratio of H_2/CO_2

Conclusions

The results show the mechanochemical treatment as a promising method of preparing copper based catalyst. It was observed that the method used in preparation system gives a material with important properties for applications in catalytic processes, e.g. methanol steam reforming.

It is satisfactory that the best selectivity and activity toward hydrogen production was obtained by Cu/Al_2O_3 (II), i.e. system for the shortest milling time (5 hrs) and low temperature (300^oC).

Additionally, the results indicate that formation the active centers and not value of specific surface area influences the catalytic properties.

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