Catalytic Oxidation of Methanol and Ethanol on Cu and Ce catalysts

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Highlights

- The hydrogen yield was 73.4% at 600ºC during oxidative steam conversion of biomethanol using 20%$Cu(NO_3)_2$ + 50%$Ce(NO_3)_3$ + 30%$Al(NO_3)_3$ + 50% glycine catalyst.
- 49% ethylene is formed in the bioethanol dehydration reaction on a 3%Cu/5%Ce/ZSM-5 catalyst.
- A catalyst prepared by the SCS method is preferable for the production of hydrogen, and a catalyst prepared by the impregnation method is optimal for the production of ethylene.

1. Introduction

The age of industrialization and the steady growth of the world population increase the demand for energy, which is expected to increase by a third from the current one by 2040, according to the forecast of the International Energy Agency. Currently, 84% of the total energy consumed worldwide is produced by fossil fuels, mainly liquid fuels and oil. The average consumption of fossil fuels is increasing at a rate of 1.1% per year [1], which leads to an accelerated increase in environmental pollution.

Bioalcohols are the most promising renewable raw materials with almost unlimited reserves that meet modern environmental requirements for fuel and chemical raw materials. A wide range of intermediate and target products of large-scale gas-petrochemical and fine organic synthesis are obtained from them.

2. Methods

A catalytic installation for the processing of bioalcohols was assembled and adjusted in the laboratory. A series of catalysts with different content of the active components was synthesized by the SCS method. Certain amounts of nitrate salts (Sigma, Aldrich) and glycine (LLP Labhimprom, Kazakhstan) were used as oxidizing agents, and glycine as the fuel with the 1:1 ratio (wt.%) for the preparation of a series of Cu – Ce – Al catalysts. The Cu and Ce content in the composition of catalysts varied from 5 to 35 wt.%. These salts were pre-ground in an agate mortar and then mixed in a porcelain cup. A mixture of the salts was placed in a quartz glass, to which 10 ml of distilled water was added. The content of the glass was heated to 80°C. The resulting mixture is stirred in air for several minutes until complete dissolution. Then the solution was placed in a muffle furnace heated to 500°C for ignition and high-temperature synthesis. After a few minutes, when the muffle furnace door is not fully opened, it is visually possible to observe combustion in the solution, in which this mixture rises over the walls of the glass when boiling.

3. Results and discussion

The activity of natural and synthetic carriers (ZSM-5, γ-Al_2O_3, CeO_2, Changkanai zeolite and clay of East Kazakhstan region) was studied in the reaction of bioethanol dehydration into target products at a volumetric rate of 1500 h^{-1}, atmospheric pressure and temperature variation from 200 to 500ºC. From the obtained data, it was determined that the carrier CeO_2 is optimal in terms of hydrogen yield, and γ-Al_2O_3 in terms of ethylene yield.

3%Cu/5%Ce/ZSM-5 catalyst was synthesized by traditional air impregnation, the activity of which was studied in the conversion of bioethanol at a temperature of 723 K, where the ethylene yield reaches 49%.
Catalysts based on Cu and Ce have also been synthesized by the SCS method: 20%$Cu(NO_3)_2$ + 50%$Ce(NO_3)_3$ + 30%$Al(NO_3)_3$ + 50% glycine, 50% $Cu(NO_3)_2$ + 20% $Ce(NO_3)_3$ + 30% $Al(NO_3)_3$ + 50% glycine. The activity of these compounds was studied in the oxidative steam conversion of biomethanol (CH_3OH : H_2O = 2.5 : 1) when the reaction temperature varies from 200 to 650ºC. The formation of hydrogen in the amount of 2.5% on a 20%$Cu(NO_3)_2$ + 50%$Ce(NO_3)_3$ + 30%$Al(NO_3)_3$ + 50% glycine catalyst was observed at a temperature of 300°C. It steadily increased to 73.4% at 600°C, then decreased again to 63.4% at 650°C. The formation of hydrogen also started from 1.6% at a temperature of 300°C and gradually increased to 39.6% at 550°C on 50%$Cu(NO_3)_2$ + 20%$Ce(NO_3)_3$ + 30%$Al(NO_3)_3$ + 50% glycine catalyst when studying activity. Then it decreased again to 29.5% at a temperature of 650°C. The reaction proceeds mainly towards the formation of hydrogen and a slight formation of CO on two catalyst compositions at high temperature and in trace amounts of methane, ethylene, ethane, propane and butanol.
A series of synthesized catalysts based on Cu and Ce prepared by the SCS method have been studied by XRD and BET methods. The surface of catalysts was determined by low-temperature nitrogen adsorption using the BET method at the Accu Sorb installation, Micromeritics, USA. Nitrogen (99%) with helium (99%) was used as a carrier gas. The pore volume and average pore diameter were calculated by the BJH method using desorption isotherm curves. It was found that the surface area of BET catalysts synthesized by the SHS method ranges from 5.23 to 22.21 m^2/g. The specific surface area of the catalysts of this system is low. This is probably due to the high combustion temperatures during the preparation of catalysts.
The phase composition and structure of the synthesized catalysts were characterized by X-ray diffraction. Some of the synthesized catalysts were studied in the laboratory of Modern Ceramics of the Institute of Nanoscience and Nanotechnology of the National Center for Scientific Research "Democritus" (Greece) under the guidance of Doctor of Chemical Sciences, Professor Xandopoulou G.G. Catalysts were studied by XRD on a Siemens Spellman DF3 spectrometer with Cu-Ka (λ = 1.5406Å) radiation in increments of 0.03°/1" in the range of 2θ from 5° to 100°. As a result of X-ray phase studies, it was found that the samples contain: CuO (JCPDS, 01-089-5899), $CuAl_2O_4$ (JCPDS, 00-033-0448), Al_2O_4 (JCPDS, 03-065-9743), Al_2O_3.

4. Conclusions

It was found that a 2.5% hydrogen yield is observed on a 20%$Cu(NO_3)_2$ + 50%$Ce(NO_3)_3$ + 30%$Al(NO_3)_3$ + 50% glycine catalyst at a reaction temperature of 300°C with a subsequent increase to 73.4% at 600°C and further reduction to 63.4% at 650°C. It was determined that the ethylene yield was 49% for 3%Cu/5%Ce/ZSM-5 catalysts in the bioethanol dehydration reaction. Thus, a catalyst prepared by the SCS method is preferable for the production of hydrogen, and a catalyst prepared by the impregnation method is optimal for the production of ethylene.

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Keywords

“Methanol, ethanol, catalyst, hydrogen”.