Copper -containing catalysts for catalytic conversion of bio-ethanol

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Introduction

The steady growth of the price for oil stock in the world, which is observed in the last few years, leads to a corresponding increase in the prices of major petroleum products. Active search of new base material, which can replace oil as in the production of fuel and in the chemical industry is carried out at the present [1]. Natural gas and coal usually considered as an alternative. However, they are non-renewable sources of energy like oil. Furthermore, there is a problem of atmospheric pollution with carbon dioxide, since any organic material is converted into it by burning, and this leads to an increase of its content in the atmosphere.

Ethanol, which was obtained from biomass [2] can be one of the possible alternatives of oil. The four directions the transformations of bioethanol are leading in strategy development on a global scale. It is a synthesis of ethylene, aromatic hydrocarbons with possible subsequent their hydrogenation into jet fuel, the production of biofuels, the synthesis of butadiene by Lebedev-Ipatiev.

Olefins are widely used in industry [3]. Due to the presence of double bond the olefins are reactive which makes them important product in the various processes of organic chemistry. For example, ethylene is the most important raw materials of petrochemical industry. At present, almost all ethylene produced by the pyrolysis of naphtha and liquefied petroleum gas. This process is endothermic and requires a high temperature reaction. Therefore, the problem of obtaining of the olefins from C1-C4 alcohols becomes relevant due to the high price of crude oil, because of environmental concerns and the decline of natural resources and their uneven distribution in the different regions.

Materials and Methods

Catalytic conversion of ethanol into ethylene was studied in this paper. The studies were conducted on the flow installation. The gaseous reaction products (ethylene, propylene, butylene, etc.) were analyzed on chromatograph "Chromatek-Crystal 5000M" with a capillary column CP-Sil 5 CB. Analysis of the liquid products of the reaction and the initial mixture was carried out on a column filled with sorbent DB-1 № 128-1052. Dehydration of ethanol was studied on supported Cu -containing catalysts. The catalysts were prepared by incipient wetness impregnation of the support, followed by drying at room temperature and at 300°C and calcination at 500°C.The catalysts were reduced in a flow of H2 at 500°C for 60 minutes

Results and Discussion

Effect of varying the space velocity from 300 to 13500 h-1 on activity of Cu/20% Al2O3 H-ZSM-5 catalyst in the dehydration of ethanol at T = 400oC, CEtOH = 78.9 g/m3 was studied. The results demonstrate that the liquid hydrocarbons, such as benzene, toluene, o-xylene, trace amounts of acetaldehyde are formed at lower space velocities. Selectivity by the liquid phase was 17.8% and 3.1 at W = 300 and 1500 h-1, respectively. Since W = 3000 h-1 the liquid phase is not formed. The highest conversion of ethanol (98%) is observed at W = 1500 h-1. At a given space velocity the maximum yield (85%) of ethylene is formed. Selectivity by ethylene increases with increasing of space velocity of the reaction, and the conversion of ethanol decreases passing through a maximum at 1500 h-1.

By infrared spectroscopy of ammonia adsorption were studied acidic characteristics of 20% Al2O3HZSM-5. In the IR spectrum of ammonia adsorbed on the surface of 20% Al2O3HZSM-5 (Catalyst 1) reduced with hydrogen at 400oC after adsorption of ammonia at 400oC were identified absorption bands (a.b.) 3355, 3250, 3170, 1670, 1610, 1450 cm-1. A.b. 3355 and 1610 cm-1 are related to ammonia which forms a coordination bond with Lewis centers. A.b. 3250, 3170, 1455, 1670 cm-1 are assigned to the valence and deformation vibrations of the NH4+ ion [4]. The relative intensity of the absorption bands associated with the Lewis centers is more than the intensity of a.b. of the NH4+ ion. After vacuuming of the sample at 400oC remain the a.b. of ammonia 3320, 1650 cm-1 associated with the Lewis acid sites. After the reduction of the 20% Al2O3HZSM-5 (Catalyst 2) in a stream of hydrogen at 500oC appear a.b. 3350, 3220, 3090, 1745, 1625, 1540 and 1480 cm-1. A.b. 3350 and 1625 cm-1 are assigned to the ammonia coordinately associated with Lewis centers; a.b. 3220, 3090, 1745 cm-1 are assigned to the ammonium ion associated with Brönsted centers. A.b. 1540 and 1480 cm-1 indicate the presence of an amide group [5] that appears in the case of strong adsorption of ammonia on the catalytic acidic centers. The absorption bands of the ammonia from the Catalyst 2 in comparison with the Catalyst 1 are shifted into a low frequency region of the spectrum, i.e. there is a strengthening of the bond ammonia-active center. It should be noted that the relative intensity of the a.b. of ammonia on the Lewis centers is higher than that of the Catalyst 1. After evacuation the a.b. relating to the Lewis acid sites 3450, 1600 cm-1 remain in the IR spectra. The introduction of copper in the Catalyst 2 alters the structure of the active centers of catalyst. A.b. 3400, 3355, 3225, 1670, 1605, 1555 cm-1 were recorded in the infrared spectrum of the ammonia adsorption on the Cu/20% Al2O3H-ZSM-5 (Catalyst 3). A.b. 3400, 3355, 1605 cm-1 relate to the ammonia chemisorbed on the Lewis centers, the relative intensity of which is higher than that of the Catalyst 2. It is assumed that a.b. 3225, 1670, 1555 cm-1 can be attributed to the Brönsted centers. After evacuation the a.b. 1550 cm-1 which characterizes the deformation vibration of the ammonia on Lewis sites remains in the IR spectrum.

Thus, the investigated catalyst on the base of copper oxide showed high activity in the dehydration of ethanol to ethylene. The obtained results indicate that the predominance of strong acid sites is specific for the investigated catalysts. This phenomenon has a positive influence on the process of dehydration of bioethanol to ethylene.

References

1. Makarfi Y.I.; Yakimova M.S.; Koval L.M.; et.al. *2nd International IUPAC Conference on Green Chemistry*: Moscow, 2010.

2. Yeletsky P.; Larichev Yu. *XX International Conference on Chemical Reactors CHEMREACTOR‐20*: Luxemburg, 2012.

3. Westa R.M.; Kunkesa E.L.; Dante A. *Catalysis Today*  **2009**, *147*, 115-125.

4. Moiseev I.; Tarasov V.; Trusov L. *The Chemical Journal* **2009**, 12, 24–29.

5. Jiandong B.; Xinwen G.; et.al. *Catalysis Today*  **2010**, 149, 143-147.