Conversion of Bio-ethanol into Olefins and Synthesis-gas

S.A. Tungatarova, A.Zh. Nauryzbaeva, T.S. Baizhumanova, Z.T. Zhekzenbaeva, E. Shaizadauly
JSC Institute of Organic Catalysis and Electrochemistry, 142, Kanaev str., Almaty, 050010 Kazakhstan
*corresponding author:tungatarova58@mail.ru

Introduction
The most important petrochemical raw materials and motor fuels are synthesized from petroleum. However, reducing the world's natural resources and the volatility of oil prices forced experts in chemistry to look for alternative sources of raw materials [1]. The use of coal and natural gas, as possible sources, results in emissions of carbon dioxide and toxic gases into the atmosphere. Bio-ethanol from biomass is more promising renewable source, which includes both "primary" biomass - plants containing starch (wheat, corn, potatoes, etc.), and the "secondary" - industrial and municipal waste [2]. The use of bio-ethanol as a motor fuel is complicated by the need to change the design of engines and the limited use in cold regions. In this connection, the attention of researchers in the field of chemistry is focused on creating of technological bases of the catalytic conversion of bio-ethanol to produce gasoline range hydrocarbons or synthesis-gas - raw material for the petrochemical industry [3-4].

Materials and Methods
The conversion of bio-ethanol to ethylene and synthesis-gas was investigated. The reaction was carried out on flow type installation at the temperature range 250-650°C and space velocity 3000-14000 h⁻¹. Reaction products (gaseous and liquid) were analyzed by "Chromatec-Crystal 5006M" chromatograph with CP-Sil 5 CB capillary column.

Dehydration reaction of bio-ethanol was studied on the modified Cu-containing catalysts supported on 20% Al₂O₃+80% H-ZSM-5 and conversion into synthesis-gas – on Ni-, Cu-, Cr-, Ce-, La/Al₂O₃-ZSM-5. The catalysts were prepared by moisture capacity impregnation of carrier, followed by drying at room temperature as well as at 300°C and calcination at 500°C for 3 h. The catalysts were reduced by hydrogen at 500°C for 60 min.

Results and Discussion
Effect of space velocity on the activity of 3% Cu/20% Al₂O₃+80% H-ZSM-5 catalyst at 400°C has been examined (feed rate of bio-ethanol - 0.6 ml/h, sample of catalysts - 4 ml). Varying the space velocity was performed in the range of 300 to 13500 h⁻¹. Data are presented in Table 1.

Table 1. Effect of space velocity on the activity of 3% Cu/20% Al₂O₃+80% H-ZSM-5 catalyst.

<table>
<thead>
<tr>
<th>Space velocity (h⁻¹)</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>CO₂</th>
<th>Liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>6.9</td>
<td>53.6</td>
<td>4.5</td>
<td>5.4</td>
<td>8.9</td>
<td>17.8</td>
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<tr>
<td>1500</td>
<td>2.7</td>
<td>86.7</td>
<td>1.3</td>
<td>2.7</td>
<td>3.4</td>
<td>3.1</td>
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<tr>
<td>3000</td>
<td>1.2</td>
<td>82.1</td>
<td>1.2</td>
<td>2.9</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>2.1</td>
<td>88.9</td>
<td>0.7</td>
<td>1.6</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>13500</td>
<td>2.0</td>
<td>94.3</td>
<td>0.6</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Selectivity by the liquid phase was 17.8 and 3.1%, respectively, for W = 300 and 1500 h⁻¹. Starting from W = 3000 h⁻¹ the liquid phase is not formed. The catalysts were reduced by hydrogen at 500°C for 60 min.

Influence of modifying agents of nickel and cerium oxides on the activity of 3% Cu/20% Al₂O₃+80% H-ZSM-5 catalyst was investigated at 1500, 3000 and 6000 h⁻¹. Introduction of 1% nickel into the 3% Cu/20% Al₂O₃+80% H-ZSM-5 catalyst has no modifying action at 1500 h⁻¹. Ethylene yield decrease in this case from 85% to 60%. Addition of nickel has a positive effect at 6000 h⁻¹ where yield of the main product is increased from 56 to 88.6%.

Addition of 1% of cerium into the 3% Cu/20% Al₂O₃+80% H-ZSM-5 catalyst has a promoting effect at all space velocities. Ethylene yield increases from 85 to 88% on the catalyst 3% Cu/1% Ce/20% Al₂O₃+80% H-ZSM-5 at 1500 h⁻¹, compared with a copper catalyst. The highest 93% yield is observed at the space velocity 3000 h⁻¹. The highest yields of synthesis-gas under the above conditions are observed on La- and Cr-containing catalysts, wherein the yield of hydrogen no more than 50-60%.

References
2. Jiandong Bia; Xinwen Guo; Min Liua; Xiangsheng Wanga Catysis Today 2010, 149, 143.