

Conversion of Bio-Ethanol into Olefins and Synthesis-Gas

Svetlana A. Tungatarova*, Erdaulet Shaizada, Aidana Zh. Nauryzbaeva,
Tolkyn S. Baizhumanova, Zauresh T. Zheksenbaeva, Irina S. Chanysheva

D.V. Sokolsky Institute of Organic Catalysis and Electrochemistry, 142, Kunaev str., Almaty, 050010, Republic of Kazakhstan
tungatarova58@mail.ru

Catalytic conversion of ethanol and ethanol-water mixture to ethylene on Cu-containing catalysts supported on 20 % Al₂O₃-80 % H-ZSM-5 was investigated. Acidic characteristics were determined by infrared spectroscopy of ammonia and a specific surface – by BET method. Optimal conditions for the catalytic conversion of ethanol and ethanol-water mixture to ethylene with 93 % and 96 % yields were found.

1. Introduction

The volatility of price for oil stock in the world, which is observed in the last few years, leads to a corresponding volatility in 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, for example ethanol-water azeotrope obtained from biomass on ZSM-5 modified by Ga₂O₃, Fe₂O₃, Fe(NO₃)₂, Zr(NO₃)₂ (Makarfi et al., 2009), producing of hydrogen, which can be used as raw material in fuel cell, vehicle fuel (Göllei et al., 2014), biomass-derived carbohydrates to fuels and chemicals (Westa et al., 2009), hydrogen production on monolithic catalysts (Zamaniyan et al., 2012), bioethanol to ethylene over nanoscale zeolite catalysts (Bi et al., 2010), synthetic gasoline and diesel fuel from dry reforming of methane (Er-rbib et al., 2012), bioethanol from brewer's spent grains (Caetano et al., 2013). 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 on copper-containing catalysts (Tungatarova et al., 2012), bimetallic catalysts (Palma et al., 2013), Pd-Zn containing catalysts (Chistyakov et al., 2013), Pt-containing catalysts (Tsodikov et al., 2014) can be one of the possible alternatives of oil. This path is often seen as the most viable way to reduce CO₂ emissions into the atmosphere.

Processes for processing of bioethanol into valuable petrochemical products are promising for Kazakhstan, as our country is rich in agriculture from which it is possible to obtain bioethanol (Alimgazin et al., 2005).

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 for oligomerisation (Cant et al., 2013), epoxidation (Diao et al., 2015), carbonylation (Yang et al., 2014), oxidation (Reza et al., 2013) and hydration process (Pejpichestakula et al., 2013). 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. Production of polyethylene has an important place in the consumption of ethylene. 57 % of world consumption accounts for its share. Petrochemical potential of individual countries is assessed in terms of production of lower olefins - ethylene and propylene, which are the basic chemical raw materials for the production of polyethylene, polypropylene, plastics, styrene and other products. The process of preparation of hydrocarbons from ethanol is economically viable even in the

purchase of ethanol from external sources at the present price ratio, according to research conducted in (Petkovic et al., 2009). Profitability of the process can be drastically improved by organization of the joint plant on two-stage scheme: biomass → bioethanol → commercially important products (ethylene, aromatics, butadiene, etc.). The absence of sulfur - and nitrogen-containing compounds in the conversion products of alcohol is one of the advantages the using of bioethanol. The lower catalyst cost in comparison with known samples containing noble metals and alloys is also important.

At present, almost all ethylene produced by the pyrolysis of naphtha and liquefied petroleum gas (propane-butane fraction). This process is endothermic and requires a high temperature reaction - 780-1,200 °C. Water vapor in the ratio of 1:1 is used as a coolant. The 180 Mt of carbon dioxide, CO₂ is released into the atmosphere during the production of ethylene by such technology. Therefore, the problem of obtaining of the C₂-C₄ olefins from C₁-C₄ alcohols becomes relevant due to the unstable price of crude oil, because of environmental concerns and the decline of natural resources and their uneven distribution in the different regions.

2. Experimental

Catalytic conversion of ethanol and ethanol-water mixture into ethylene was studied in this paper. The studies were conducted on the flow installation (Figure 1), the main element of which is a cylindrical reactor with an internal diameter of 18 mm and a length of 420 mm. The reactor was placed in the oven. Oven temperature is regulated by a high-precision temperature controller. To study the activity of the synthesized catalysts a portion of catalyst (4 mL) was loaded into the reactor. The upper and lower part of the reactor was filled with quartz particles.

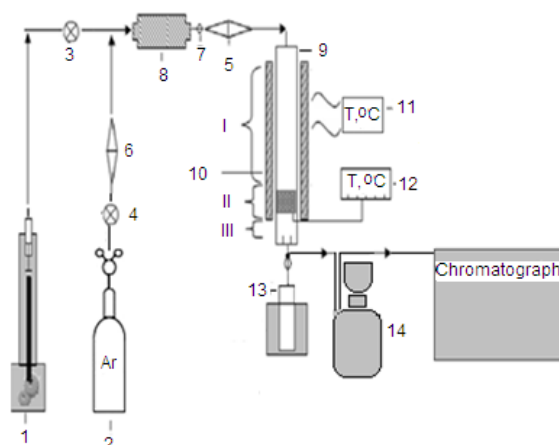


Figure 1: Diagram of flow installation. 1 - batcher for supply of ethanol, 2 - cylinder with an inert gas, 3, 4 - taps, 5, 6 - rheometers, 7 - samplers, 8 - mixer; 9 - quartz reactor; 10 - electric heating; 11 - temperature control; 12 - unit temperature measuring; 13 - bubblers; 14 - gasometer. I - area of preheating mixture; II - reaction zone; III - refrigerator

Thorough check of tightness of installation is performed after catalyst loading. Ethanol is supplied from the batcher for supply of ethanol (1) to the mixer (8) during the study. Inert gas (Ar) also enters into the mixer from the cylinder (2). A mixture of ethanol and inert gas is supplied into the reactor with electric heating (9). Raw material passing through the catalyst bed processed and as vapor mixture enters to the bubblers (13) and cooled. The liquid phase is condensed in the bubbler; the gas phase is collected in a gasometer (14).

The gaseous reaction products (ethylene, propylene, butylene, etc.) were analyzed on chromatograph "Chromatec-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.

20 % Al₂O₃-80 % H-ZSM-5 carrier has been used in the work. 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 catalyst was prepared by capillary impregnating the carrier by moisture capacity of an aqueous solution of copper nitrate.

3. Results and Discussion

Figure 2 shows the results on effect of the duration of experiment on the dehydration of ethanol on activity of 20 % Al₂O₃-80 % H-ZSM-5 catalyst. Ethylene, methane and water, propylene in trace quantities, and unreacted ethanol mostly found in the reaction product at T = 400 °C, space velocity WHSV = 13,500 h⁻¹, the concentration of ethanol C_{EIOH} = 8.8 g/m³. 20 % Al₂O₃-80 % H-ZSM-5 as carrier was reduced in a hydrogen stream at 400 °C and 500 °C. The results show that the reduction of carrier affects positively on yield of the main product - ethylene.

Analysis of the reaction products was carried out every 15 min for 2 h. As can be seen, the effect of the duration of experiment on the activity of 20 % Al₂O₃-80 % HZSM-5 (Si/Al = 40) for the production of ethylene is low. According to the results, we have decided to carry out experiments in 60 min. Reduction of 20 % Al₂O₃-80 % HZSM-5 (Si/Al = 40) in a stream of hydrogen significantly increases the yield of ethylene. Reduction with hydrogen at the reaction temperature 500 °C is the most positive effect on the performance of the process. The formation of alkanes besides the main product of ethylene is observed in the reaction products on unreduced and reduced 20 % Al₂O₃-80 % H-ZSM-5 carriers at 400 °C. Ethylene is produced mainly in the reaction products without the saturated hydrocarbons at reduction of 20 % Al₂O₃-80 % HZSM-5 (Si/Al = 40) at 500 °C.

3 wt. % of copper oxide was supported by incipient wetness impregnation on 20 % Al₂O₃-80 % H-ZSM-5. Effect of varying the space velocity from 300 to 13,500 h⁻¹ on activity of 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 catalyst in the dehydration of ethanol at T = 400 °C, C_{EIOH} = 78.9 g/m³, catalyst volume = 4 mL was studied.

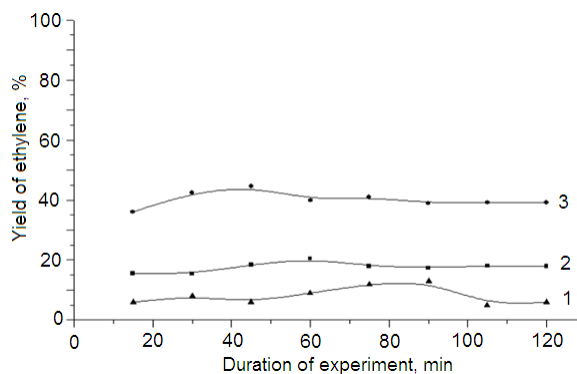


Figure 2: Effect of duration of the experiment on the yield of ethylene. 1 – 20 % Al₂O₃ – 80 % H-ZSM-5 unreduced; 2 – 20 % Al₂O₃ – 80 % H-ZSM-5 reduced at 400 °C; 3 – 20 % Al₂O₃ – 80 % H-ZSM-5 reduced at 500 °C

These 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 WHSV = 300 and 1,500 h⁻¹ (Table 1). Since WHSV = 3,000 h⁻¹ the liquid phase is not formed; only gaseous reaction products were detected. Carbon dioxide is released at all space velocities other than WHSV = 13,500 h⁻¹. The highest conversion (X) of ethanol (98 %) is observed at WHSV = 1,500 h⁻¹. At a given space velocity the maximum yield 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 1,500 h⁻¹. Also the concentration of saturated hydrocarbons decreases with increasing of space velocity.

Table 1: Effect of space velocity on the activity of 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 catalyst at 400 °C

Space velocity, h ⁻¹	Selectivity, %					Liquid phase
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	CO ₂	
300	6.9	53.6	4.5	5.4	8.9	17.8
1,500	2.7	86.7	1.3	2.7	3.4	3.1
3,000	1.2	88.2	1.2	2.9	3.6	-
6,000	2.1	88.9	0.7	1.6	3.2	-
13,500	2.0	94.3	0.6	1.2	-	-

Effect of modifying additives such as Ni and Ce on the activity of 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 catalyst was investigated. Effect of modifying additives was investigated at the optimum reaction temperature of 400 °C and space velocity 1,500, 3,000 and 6,000 h⁻¹. Obtained results are shown in Figure 3. Introduction of nickel has no significant effect on the yield of ethylene at space velocity 1,500 h⁻¹ on 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 catalyst. It decreases from 85 % to 60 %. However, the addition of nickel at space velocity 6,000 h⁻¹ has a positive effect; the yield of the main product is increased from 56 to 88.6 %. Addition of cerium to the 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 catalyst has a promoting effect at all space velocities. Ethylene yield on 3 % CuCe/20 % Al₂O₃-80 % H-ZSM-5 catalyst is increased from 85 to 88 % compared with the copper catalyst at 1,500 h⁻¹. The highest 93% yield of ethylene was obtained at space velocity 3,000 h⁻¹.

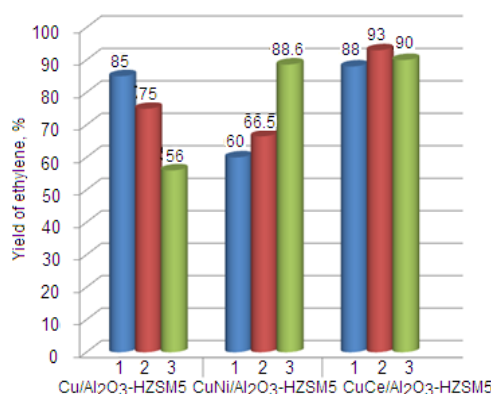


Figure 3: Effect of space velocity on the catalyst activity. 1 – 1,500 h⁻¹; 2 – 3,000 h⁻¹; 3 – 6,000 h⁻¹

Effect of water concentration on the activity of 3 % CuCe/20 % Al₂O₃-80 % H-ZSM-5 catalyst in the catalytic conversion of ethanol-water mixtures were also studied (Figure 4). As can be seen ethylene yield increases from 93 to 95.5 % passing through a maximum (96 %) at 1:0.5 with increasing water content in the ethanol-water mixture from 1:0 to 1:1. Further increasing the concentration of water decreases the activity of the catalyst. Ethylene yield decreased to 77 % at a ratio of 1:2. According to chromatographic analysis of the reaction products, with addition of water to ethanol, the formation of acetaldehyde, acetone and small amounts of formaldehyde in the reaction products is observed. 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 %.

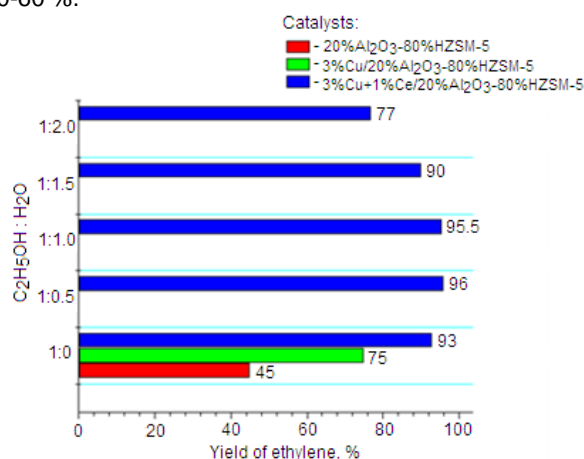


Figure 4: Effect of water concentration on the yield of ethylene at 450 °C

The surface of investigated 20 % Al₂O₃-80 % HZSM-5, 3 % Cu/20 % Al₂O₃-80 % HZSM-5 and 3 % CuCe/20 % Al₂O₃-80 % HZSM-5 catalysts was studied using the BET method. Comparison the catalyst activity in the reaction of conversion of ethanol to ethylene with their specific surface showed that the catalyst activity is almost independent of the surface (Table 2). Most likely, the activity is largely determined by the nature of modifying additives, structure and condition of the active centers.

Table 2: Specific surface area of catalysts

Catalysts	S _{BET} , m ² /g
20 % Al ₂ O ₃ – 80 % HZSM-5	308.6
3 % Cu/20 % Al ₂ O ₃ – 80 % HZSM-5	281.5
3 % CuCe/20 % Al ₂ O ₃ – 80 % HZSM-5	282.1

By infrared spectroscopy of ammonia adsorption were studied acidic characteristics of 20 % Al₂O₃-80 % HZSM-5 (Si/Al = 40). In the IR spectrum of ammonia adsorbed on the surface of 20 % Al₂O₃-80 % HZSM-5 (Si/Al = 40) (Catalyst 1) reduced with hydrogen at 400 °C after adsorption of ammonia at 400 °C were identified absorption bands (a.b.) 3,355, 3,250, 3,170, 1,670, 1,610, 1,450 cm⁻¹ (Figure 5). A.b. 3,355 and 1,610 cm⁻¹ are related to ammonia which forms a coordination bond with Lewis centers. A.b. 3,250, 3,170, 1,455, 1,670 cm⁻¹ are assigned to the valence and deformation vibrations of the NH₄⁺ ion (Paukshtis, 2010). 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 400 °C remain the a.b. of ammonia 3,320, 1,650 cm⁻¹ associated with the Lewis acid sites.

After the reduction of the 20 % Al₂O₃-80 % HZSM-5 (Si/Al = 40) (Catalyst 2) in a stream of hydrogen at 500 °C appear a.b. 3,350, 3,220, 3,090, 1,745, 1,625, 1,540 and 1,480 cm⁻¹. A.b. 3,350 and 1,625 cm⁻¹ are assigned to the ammonia coordinately associated with Lewis centers; a.b. 3,220, 3,090, 1,745 cm⁻¹ are assigned to the ammonium ion associated with Brönsted centers. A.b. 1,540 and 1,480 cm⁻¹ indicate the presence of an amide group (Kiselev, 1972) 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 3,450, 1,600 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. 3,400, 3,355, 3,225, 1,670, 1,605, 1,555 cm⁻¹ were recorded in the infrared spectrum of the ammonia adsorption on the 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 (Catalyst 3). A.b. 3,400, 3,355, 1,605 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. 3,225, 1,670, 1,555 cm⁻¹ can be attributed to the Brönsted centers. After evacuation the a.b. 1,550 cm⁻¹ which characterizes the deformation vibration of the ammonia on Lewis sites remains in the IR spectrum.

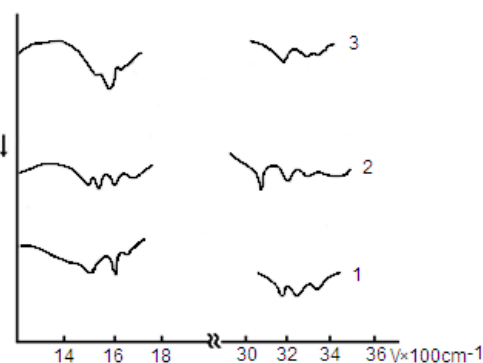


Figure 5: IR spectra of ammonia on the catalysts. 1 – 20 % Al₂O₃ - 80 % HZSM-5 (Si/Al = 40) (reduced by hydrogen at 400 °C); 2 – 20 % Al₂O₃ – 80 % HZSM-5 (Si/Al = 40) (reduced by hydrogen at 500 °C); 3 – 3 % Cu/20 % Al₂O₃ – 80 % H-ZSM-5

4. Conclusions

Thus, the investigated catalyst on the base of copper oxide showed high activity in the dehydration of ethanol to ethylene. It was shown that the optimal temperature is 400 °C. The maximum yield of desired product - ethylene – 85 % was obtained on 3 % Cu/20 % Al₂O₃-80 % H-ZSM-5 at 400 °C and space velocity 3,000 h⁻¹. The catalyst also works well in the catalytic conversion of ethanol-water mixture with a ratio of ethanol : water = 1 : 0.5, where the yield of ethylene reached 96 %. 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.

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