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Production of olefins from bioethanol. catalysts, mechanism

Abstract. This review describes methods of catalytic obtaining from bioethanol of valuable industrial products – olefins, particularly ethylene. Among olefins, ethylene is the most popular key raw material of pethrochemical synthesis. The scope of appllication of ethylene is almost unlimited in petrochemical products: polyethylene, ethylbenzene, styrene, ethylene dichloride, vinyl chloride etc. It also examines catalysts for the production of olefins and their properties. The most promising and commercially advantageous process of ethylene production by catalytic dehydration of ethanol on catalysts based on modified alumina. And this review discusses the mechanisms of catalytic conversion of ethanol to ethylene.

***Keywords**:* natural gas, bioethanol, technology, fuel, alkenes.

Introduction

Bioethanol, unlike natural gas and refined oil products, is a more promising renewable source that meets current environmental requirements for chemical raw material. Bioethanol is a liquid alcohol fuel that is widely available renewable raw material; industrial manufacturing technology is well developed: the biochemical processing of sugar cane, grain-crops or wood. Obtained bioethanol is an aqueous solution containing about 12 wt. % ethanol. Of the total ethanol produced 80% has fuel application, 12% - technical and 8% - food [1-2]. Technically, light olefins (ethylene, propylene, butylene) - important intermediates in the petrochemical industry, of which the largest volume of production is ethylene, a key raw material in the production of polyethylene, ethylene oxide, ethylbenzene, with the further production of styrene. Ethylene is the most highly sought intermediate product of organic synthesis. Petrochemical capacity of individual countries is assessed in terms of production of lower olefins - ethylene and propylene, representing basic chemical raw materials for the production of polyethylene, polypropylene, plastics, styrene and other products. According to forecasts of a consulting company Nexant Inc. world consumption of ethylene in the next 10 years will grow from 100 million to 160 million tons per year. Demand for polyethylene will increase from 60 million to 100 million tons, and the polypropylene - from 40 million to 60 million tons a year. Kazakhstan does not have capacity for the production of olefins, plastics, motor fuel and other products, the need for which is met through imports, compiled annually, according to expert estimates, more than $ 2 billion.

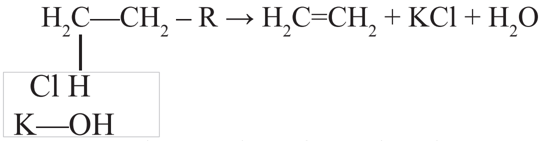
Production of olefins

In nature, alkenes are rare. Normally gaseous alkenes (ethylene, propylene, butylene) are isolated from gases of the oil processing (at cracking) or associated gases, and gases from the coking of coal. In industry alkenes are produced by dehydrogenization of alkanes in the presence of a catalyst (Cr_2O_3). For example, [3]:

$$\begin{array}{lcll} H_3C—CH_2—CH_2—CH_3\ -\ H_2 & \rightarrow & H_2C{=}CH—CH_2—CH_3 & \text{(butene-1)} \\ H_3C—CH_2—CH_2—CH_3\ -\ H_2 & \rightarrow & H_3C—CH{=}CH—CH_3 & \text{(butene-2)} \end{array}$$

From the laboratory methods of obtaining include the following [3]:

Splitting of halogen hydrogen from halogen alkyls under the action of an alcoholic solution of alkali:

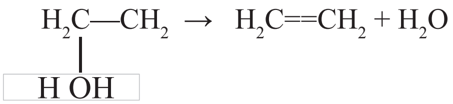


$$\begin{array}{l} H_2C—CH_2 - R \rightarrow H_2C{=}CH_2 + KCl + H_2O \\ \quad | \\ \text{Cl H} \\ \text{K—OH} \end{array}$$

2. Hydrogenating of acetylene in presence of catalyst (Pd):

$H—C \equiv C—H + H_2 \rightarrow H_2C{=}CH_2$

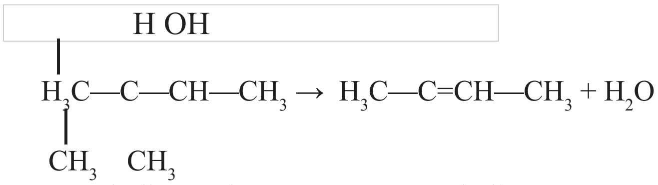
3. Dehydration of alcohols (splitting of water). Used as the catalyst acid (sulfuric or phosphoric) or - acids (sulphuric or phosphoric) or $A1_2O_3$:



$$\begin{array}{l} H_2C—CH_2 \rightarrow H_2C{=}{=}CH_2 + H_2O \\ \quad | \\ \text{H OH} \end{array}$$

ethyl alcohol

In these reactions, hydrogen is split off from the least hydrogenated (with the least number of hydrogen atoms) carbon atom (principle of A.M.Zaitsev):



$$\begin{array}{l} \qquad \text{H OH} \\ \quad | \\ H_3C—C—CH—CH_3 \rightarrow H_3C—C{=}CH—CH_3 + H_2O \\ \quad | \\ CH_3 \quad CH_3 \end{array}$$

3-methylbutanol-2 2-methylbuten-2

Withdrawal of water from the saturated alcohol is called dehydration. This is one of the most common ways to produce olefins.

Production of ethylene and its application

At present, almost all of the ethylene is produced by the pyrolysis of naphtha and liquefied petroleum gas (propane-butane fraction). This process is endothermic and requires a high temperature reaction - 780-1200° C. As the coolant steam at a ratio of 1:1 is used. Assessment of industrial emissions (2009) shows that the production of ethylene by the technology releases 180 million tons of carbon dioxide CO_2 into atmosphere. Therefore, due to environmental issues, the reduction of natural resources, the high price of crude oil is becoming urgent task of producing olefins C_2-C_4 from alcohols C_1 to C_4, which can be used as a cheap raw material for the production of olefins. Currently under development are two types of catalytic processes for production of ethylene from alcohol:

- MTO process (dehydration of methanol to olefins).
- Catalytic dehydration of ethanol.

The most part of research on transformation of methanol to light C_2-C_4 olefins was carried out on zeolite catalysts, mainly H-ZSM-5 and different types of SAPO [4]. The effect of process conditions, pore size and additions of various elements that regulate the acid-base properties of zeolites is studied. But for more than 30 years of research, the MTO process has not been brought to industrial applications. Currently running a pilot plant UOP/HYDRO MTO (company Norsk Hydro, Norway) for the production of ethylene and propylene using SAPO-34 [4]. The main challenges to the practical use of the MTO process, with rapid deactivation of zeolite catalysts due to coke formation, after which the activity and selectivity to light olefins decrease sharply. Therefore, the duration of run of the catalyst before regeneration is 3-5 minutes. Active zeolite catalysts in the MTO process related to their microporous structure (or rather narrow channel sizes) and a pair of acidic and basic center definite strength.

The second method of producing ethylene is dehydration of ethyl alcohol. The method of producing ethylene by catalytic dehydration of ethanol has been applied in countries such as Brazil and India. Ukraine plans to organize in the near future the same process. Russian companies also show interest in alternative sources of olefins by dehydration of alcohols. CJSC “North Donetsk association “Nitrogen”” has signed a contract with the Institute of Catalysis, Russian Academy of Sciences to develop baseline data for the design of process steps for producing ethylene by catalytic dehydration. The first phase of the work was to find the most efficient and inexpensive catalyst for this process.

Today, the scope of appllication of ethylene is almost unlimited in petrochemical products: polyethylene, ethylbenzene, styrene, ethylene dichloride, vinyl chloride. Ethylene oxide, ethylene glycol, ethanol, vinyl acetate - olefins and linear alcohols - all of the most common derivatives of ethylene, produced by industry. Household products that are derived from these chemicals can now be found everywhere, from soap and plastic building materials and finishing products, detergents and motor oils.

Ethylene and propylene are produced in the greatest volume, but they have a very simple structure. The best part of their property - the presence of a double bond between two carbon atoms, so that they are chemically active substances.

Analysis of the needs of the international market for the petrochemical production shows that Kazakhstan will be the most cost-effective development of basic petrochemical plants to produce polyethylene, polypropylene, styrene and polystyrene, ethylene glycol and benzene, especially that the consumers are expected to be from the Central Asian region and China. Today, China’s petrochemical complexes cover the demand of the domestic market for polystyrene and propylene by only 50%.

Catalysts of receipt of olefins

According to the literature the most promising for use in a wide range of dehydration of alcohols are individual and modified aluminum oxides. For individual alumina found a significant effect on the activity of sodium and iron admixtures. Thus, small amounts of sodium admixtures lead to a sharp decrease in activity and selectivity to olefins alumina dehydration of ethanol, propanol and butanol; iron admixtures lead to cracking and coking processes. Therefore, greater activity and selectivity to olefins can be expected with the use of aluminum oxide, which is substantially does not contain the above mentioned admixtures.

Traditional methods of preparation of aluminum oxide (reprecipitation or hydration products hydrargillite thermal decomposition) do not allow obtaining high-purity alumina. Known species precipitation method (ammonium nitrate technology) gives a fairly pure aluminum oxide containing sodium impurities <0.01%, but it is associated with significant runoff. One of the low-waste methods for high-purity aluminum oxide is based on the hydrolysis of aluminum alkoxides. This method also allows you to receive the modified alumina at joint hydrolysis of aluminum alkoxides and modifying connections [5, 6], of which the most interesting is the introduction of tetravalent cations. The best-known foreign producer of alcoholate alumina is a firm BazoYuegtapu.

Development of catalysts based on aluminum oxide to processes of C2-C4 olefins from alcohols C1-C4, as well as studying the effect of acid-base properties on the specific catalytic activity in the dehydration of alcohols to olefins is devoted to work [7], at the Institute of Catalysis SB RAS. The problem of synthesis of active catalysts for the dehydration of alcohols was solved in two ways: by obtaining high-purity alumina and modified by alcoholate technology (does not contain an admixture of sodium) and by modifying the finished aluminum oxides obtained by means of reprecipitation and hydration products of thermal activation gidrargilita (contain an admixture of sodium). With the use of NMR spectroscopy and SAXS revealed that alcohol solution of aluminum alkoxide has the set of complexes with tetrahedral, octahedral environment of aluminum and pentacoordinated aluminum complexes. In solutions of trimetilata and triizopropilata-aluminum tetrahedral and pentacoordinate forms of aluminum dominate. Octahedral shape dominates in trietilata aluminum solutions. According to SAXS, there are four main areas of the particle distribution in aluminum hydroxides, and four types of complexes in the initial solution triizopropilata aluminum. It is assumed that there is a limited number of options for the interaction of these aluminum complexes with each other during the hydrolysis, which causes loss and further growth of particles of a certain size.

Shown that the modification of aluminum oxide on the hydrolysis step by adding tetravalent elements is an effective method that allows a wide range regulation of the acid-base and catalytic properties. Developed a new technique that can determine not only strong, but also weak electron-centers using EPR spectroscopy. The advantage of using this method, compared with the known, is manifested in increasing the number of electron centers detected by 5-10 times and the possibility of reducing the temperature of pre-treatment of samples to 200° C to study the thermally unstable samples or samples obtained at low calcination temperatures. Using the new technique revealed that the introduction of chloride and sulfate ions increases the concentration of electron centers and the specific rate of production of ethylene, and the presence of sodium cations (even small amounts of sodium - 0.3 wt.%) reduces the concentration of electron centers and speed. Aluminum oxides, modified by chloride ions are recommended for practical use.

The linear dependence [7] between the specific rate of production of olefins (ethylene-butylene) in the dehydration of ethanol and n-butanol and the amount detected on aluminum oxide catalysts of electron centers (including weak) were first obtained. Comparison of data on the concentrations of electron centers of different strength with the data on the catalytic activity led to the conclusion that it is the weak acceptor centers play an important, and perhaps decisive role in the dehydration of alcohols and are catalytically active centers in the process. Found that the rate of formation of olefins in the dehydration of alcohols decreases linearly with increasing concentration of electron donor (basic) centers and increases linearly with increasing concentration of electron acceptor (acid) centers [7].

As catalysts for the production of ethylene from ethanol, composites based on TiO_2 and supported on zeolites [8] are used, which proved much more effective than an aluminosilicate zeolite or TiO_2. The rate of formation of ethylene on these catalysts is 8 times higher than in the aluminosilicate zeolite or TiO_2 at 420^0 C.

Catalytic dehydration of bioethanol to ethylene on CeO_2-ZrO_2, TiO_2/g- TiO_2 nanostructured HZSM - 5 zeolite catalysts are described in works [9, 10] (table 1).

Obtaining ethylene catalytic dehydration on $Ti0_2$/g-Al_20_3 catalysts was carried out in a multi-microchannel reactor [9]. Physics-chemical properties of the catalysts were studied by X-ray diffraction (XRD) and FT-IR spectroscopy. The effect of experimental parameters such as the concentration of ethanol, the reaction temperature and the flow rate of the liquid was studied. The conditions of high activity and relative stability TiO_2/ g-Al_2O_3 catalysts were determined. Reaction results show that the catalyst containing TiO_2 has a high conversion of ethanol of 99.96% and the selectivity of ethylene of 99.4%.

Table 1 – Product composition of the gas phase at different concentrations of ethanol (t-440 ^{0}C, LHSV-52 h^{-1}) [9]

EtOH wt %	Q_{gas} ml/min	Product composition of the gas phase, mol %					X_{EtOH} mol %	S_E mol %	$Y_{E,}$ g/$g_{cat.}$ h
		C_2H_6	C_2H_4	C_3	C_4	DEE			
12,0	47	0,40	99,55	0,05	0	0	99,7	99,2	4,4
30,0	103	0,25	99,6	0,13	0,01	0	99,9	99,3	9,8
50,0	170	0,19	99,5	0,24	0,04	0	99,8	99,2	16,0
70,0	227	0,24	99,15	0,40	0,12	0,01	99,7	98,8	21,2
93,8	281	0,23	99,0	0,45	0,23	0,02	99,7	98,6	26,1

Ethylene yield reached 26 g/g cat. per hour, which is a very important discovery for intensification and miniaturization process for producing ethylene from ethanol. The optimum concentration of ethanol 30-50 weight %, and the optimum temperature of 400-500^0 C. Miniaturization process for producing ethylene from bioethanol has been achieved in a microchannel reactor.

Active nano and micro HZSM-5 zeolite catalysts and the selectivity of ethylene compared to the dehydration of bioethanol to ethylene in a stationary reactor at 240^0 C and atmospheric pressure [10]. Nanostructured HZSM-5 zeolite catalysts showed better stability than the microstructure. At 95 vol. % of bioethanol in the reactant at the nanoscopic HZSM-5 zeolite catalyst conversion of ethanol and the selectivity of ethylene remained constant for 630 hours of reaction, while at the microstructural HZSM-5 zeolite catalyst conversion of ethanol after 60 hours of reactions decreased. At 45 vol. % of bioethanol in the reactants at the nanoscopic HZSM-5 catalyst bioethanol conversion and selectivity for ethylene were kept constant for 320 hours, and at the microstructural HZSM-5 zeolite catalyst conversion of ethanol and selectivity for ethanol in these conditions are reduced at the beginning of the reaction [10].

On a vanadium catalyst from fraction of hydrocarbons of C_2 - C_{22} of obtained biomass in the process of pyrolysis can be obtained ethylene, propylene and butylens [11, 12]. In catalytic pyrolysis up to 40-50% of ethylene and 60-65% of the gaseous olefin feedstock are produced. Verification of this process in terms of pilot [13] showed that depending on the feedstock used ethylene is formed with a yield of 40% and olefins of 60-65%. By thermal pyrolysis of ethylene yield usually does not exceed 25-26%. Thus, as a result of processing of vegetable raw materials liquid hydrocarbons as components of motor fuels and olefins, particularly ethylene, for the processes of petrochemical synthesis can be obtained.

Catalytic conversion of ethanol produced by fermentation of biomass is an alternative to traditional crude oil processing. So in [14] the results of the catalytic conversion of bioethanol into such valuable petrochemical products as olefins, gasoline range hydrocarbons and aromatic are shown. It is shown that, depending on the characteristics of the catalyst the composition of the resulting products can vary. Zeolites ZSM-5 are used as catalysts, which are active in the conversion reaction of ethanol to ethylene and other hydrocarbons. During the processing of bio-ethanol a number of valuable chemicals are produced, such as acetaldehyde, ethyl acetate, hydrogen, ethylene, and the liquid product composition that presents a wide range of hydrocarbons.

The experimental results showed that the conversion of ethanol in all cases is almost entirely, with the ethanol content in the aqueous fraction is less than 0.2%, even at high speeds. It was found that the volume rate of 2 h^{-1} is optimal for the production of liquid hydrocarbons. For small space velocity of ethanol and its increase, liquid yield decreases. This trend indicates that at very low space velocities with increasing contact time with the catalyst surface, the formation of hydrocarbons is decreased with other reactions. At very high volume flow rates, there is not enough contact time of the reaction mixture with catalyst for the complete oligomerization of ethylene.

Studies of bioethanol conversion on zeolite catalysts in a wide range of reaction conditions allowed the identification of the following major product groups:

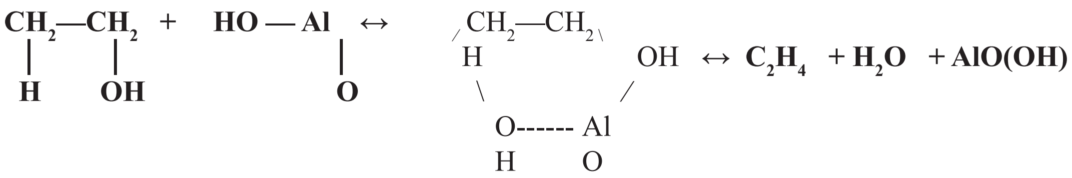
1. The products of disproportionation, which include benzene and xylenes presented ortho-, meta- and para-isomers.
2. Products of skeletal isomerization.
3. Fragmentation products, including ethylbenzene, toluene and metiletilbenzol (OIE).
4. Products of dealkylation, followed by ethylene oligomerization, isomerization and cracking of oligomers, with the main contribution given by saturated and unsaturated aliphatic hydrocarbons having a carbon number from two to six.
5. Products of alkylation of benzene by unsaturated aliphatic hydrocarbons, consisting of alkyl aromatic hydrocarbons with the number of carbon atoms in the side chain of more than three.

As a result of a comprehensive study of proposed methods for obtaining new zeolite containing catalysts, from which was developed a flexible conversion technology of ethanol into important products for the petrochemical [14], such as motor fuel, olefins and aromatic hydrocarbons.

Mechanisms of catalytic conversion of ethanol

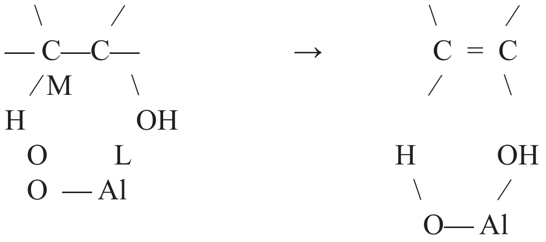
The mechanism of formation of olefins from alcohols to some extent depends on the structure of alcohol [7,14]. In multipoint adsorption of reactants they bind multiple bond with the catalyst at a certain distance from each other. This principle of geometric correspondence between the positions of the atoms in the reactants and the catalyst was clearly articulated in the multiplet theory of A.A.Balandin [15].

O.V.Krylov [16] showed that the geometric correspondence with the catalyst may be required not only for the source, but also for one of the intermediates involved in the rate-limiting step of the reaction. This is evidenced by the work, taking into account the possibility of adsorption centers of various kinds, which causes the polarization of relations. Activated complex of polar molecules with polar catalyst may take the form of a six-membered ring, because in this ring the voltage bond angles are minimal. For example, for the dehydration of alcohols on hydrated Al_2O_3, the following scheme is offered:



Coordinatively unsaturated Al ion polarizes the OH group of alcohol, and polarized hydrogen methyl group interacts with the OH group on the surface of the catalyst. As the result, catalyst exchanges protons with reagents.

Stereochemical features of the dehydration of alcohols are also found in [17], where explanation is given that on the surface of aluminum oxide basic and acid centers operate together, as shown below:



Here is an example bifunctionality of some metal oxides in the decomposition reaction of ethanol:

C_2H_5OH

At 350⁰ C and 1 atm

↙ ↘

Oxide	H_2+C_2H_4O First class, %	H_2O+ C_2H_4 Second class, %
AlO	1,5	98,5
Cr_2O_3	9,0	91,0
TiO_2	37,0	63,0
ZrO_2	55,0	45,0
Fe_2O_3	86,0	14,0
ZnO	95,0	5,0

This selectivity is a function of surface of different types of active centers that depend on the preliminary treatment (reduction, oxidization) of metal oxides.

When dehydration of primary alcohols (in the carbon atom bound to hydroxyl is connected with only one radical) assumed the following mechanism [18]:

1) proton (from any acid) is attached to the free electron pair of the oxygen atom to form substituted oxonium ion;

2) next, when heated, water splits from substituted oxonium ion, as the result carbocation CH_3-CH_2^+ must be obtained, but since such an ion is very unstable, it is stabilized by the loss of a proton and the formation of the double bond. Loss of water and protons (with dehydration of primary alcohols) occurs almost simultaneously with formation of olefin.

Works [18, 19] are devoted to technological development of a catalytic process for the conversion of ethanol important products for the petrochemical industry. The study aims to establish technological foundations of the catalytic conversion of ethanol to produce olefins, aromatics and hydrocarbons of gasoline range. A new flexible technology of catalytic bioethanol conversion process is developed, which includes obtaining nanostructured zeolite catalysts (catalyst HZSM-5), which ensures the production of olefins, components of motor fuels and aromatic hydrocarbons. We propose a method for a given class of hydrocarbons, depending on the module and the structuring of silica supplements. On the basis of the revealed laws, a scheme transformations provide an overview of the key problems of the kinetic conversion of bioethanol and mechanism defining and controlling process parameters.

Thus, among olefins, ethylene is the most popular key raw material of petrochemical synthesis. From this review follows that the most promising and commercially advantageous process of ethylene production by catalytic dehydration of ethanol on catalysts based on modified alumina. The mechanism of production of olefins from ethanol to some extent depends on the state of the catalyst surface, particularly on their acidic and basic centers. Selectivity of the process is also a function of the different active surfaces (oxidation, reduction) of the centers of the catalyst.

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Биоэтанолдан олефиндерді алу, катализаторлар, механизмі

Бұл шолуда биоэтанолдан өндірістік бағалы өнімдер – олефиндерді, оның ішінде этиленді каталитикалық әдіспен алу жолдары сипатталған. Мұнайхимия синтезі үшін олефиндердің ішінде ең негізгі керекті шикізат этилен болады. Мұнайхимия заттарын: полиэтилен, этилбензол, стирол, дихлорэтан, винилхлорид т.б. алу үшін этиленді қолдану аймағы іс жүзінде шексіз деп есептеледі. Олефиндерді алу үшін қолданылатын катализаторлар және олардың қасиеттері қарастырылған. Этиленді биоэтанолдан каталитикалық дегидратациялау жолымен модифицирленген алюминий оксиді катализаторында алу коммерциялық тиімді және болашағы зор. Этанолдың этиленге дейінгі каталитикалық конверсиясының механизмі талданған.

Түйін сөздер: табиғи газ, биоэтанол, технология,отын, алкендер.

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Получение олефинов из биоэтанола. катализаторы, механизм

В настоящем обзоре описаны способы каталитического получения из биоэтанола ценных промышленных продуктов – олефинов, в частности этилена. Среди олефинов этилен является наиболее востребованным ключевым сырьем нефтехимического синтеза. Область применения этилена считается практически неограниченной по нефтехимическим продуктам: полиэтилен, этилбензол, стирол, дихлорэтан, винилхлорид и др. Рассмотрены катализаторы получения олефинов и их свойства. Наиболее перспективен и коммерчески выгоден процесс производства этилена путем каталитической дегидратации биоэтанола на катализаторах на основе модифицированного оксида алюминия. Обсуждаются механизмы каталитической конверсии этанола до этилена.

Ключевые слова: природный газ, биоэтанол, технология, топливо, алкены.