New Aspects of Bioethanol One-Step Catalytic Conversion Into Fuel Components

Andrey Chistyakov[1]*, Mark Tsodikov[1], Maria Chudakova[1], Alexandr Gekhman[2], Iliya Moiseev[2], Francis Luck[3].

[1]A.V. Topchiev Institute of Petrochemical Synthesis RAS
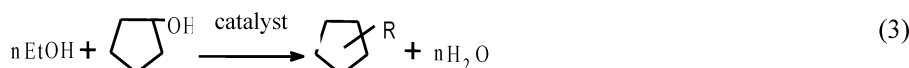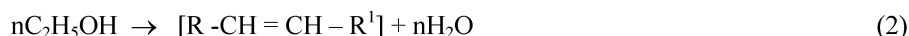119991, Russia, Moscow, Leninskii av., 29,   chistyakov@ips.ac.ru
[2]N. S. Kurnakov Institute of General and Inorganic Chemistry RAS
119991, Russia, Moscow, Leninskii av., 31
[3]TOTAL S.A. 2 place Jean Millier, 92078 Paris la Defense Cedex

Alcohols produced via the biomass fermentation can be catalytically converted into effective hydrocarbon additives to fuels. In this work the results relates to alcohols treatment into alkane/alkene fraction in one step over original nanostructured catalysts are presented. Shown that glycerol being added to ethanol took part in hydrocarbon chain growth and led to considerable increasing of aim olefins C_4-C_{12+} fraction yield. Using XAFS, XPS, TPD and kinetic methods probable reaction pathways and relationships between the catalysts structure and its activity and selectivity were determined.

1. Introduction

Nowadays a significant interest has been concentrated on effective approaches related to renewable biomass conversion into fuels. A number of alcohols e.g. ethanol, butanol, iso-pentanol and glycerol produced via treatment of biomass can be incorporated into gasoline and bio-diesel, either directly or after chemical/catalytic conversion into more effective additives. New reactions of the aliphatic alcohols $C_2 - C_5$ giving rise to large amount of branched hydrocarbons was described by Tsodikov et al., 2008:

$$nC_2H_5OH + H_2 \rightarrow C_{2n}H_{4n+2} + nH_2O, \tag{1}$$

$$nC_2H_5OH \rightarrow [R\text{-}CH = CH - R^1] + nH_2O \tag{2}$$

$$n\,EtOH + \text{(image: cyclopentane-OH)} \xrightarrow{\text{catalyst}} \text{(image: cyclopentane-R)} + nH_2O \tag{3}$$

In recent works it was shown that in depend on catalytic composition either alkanes or olefins could be obtain. Hydrogen required for alkanes formation (according to reaction 1) was formed in situ through the parallel reaction of partial ethanol dehydration. In this paper the results of reaction pathways investigation are presented.

2. Experimental and Techniques

Ethanol was used without preliminary purification. In all cases, the catalytic tests were performed with 20 cm^3 of catalyst fractionized into 2-3 mm spheres in an isothermal fixed bed steel reactor, operated under plug-flow-circulation and plug-flow conditions. Alcohol feed was V = 0.5 h^{-1}, and gas circulation rate of 50 cm^3/min. Activity was measured at fixed temperature in the interval 300-400°C under a total pressure of 0,5 MPa in Ar atmosphere. Ethanol was fed to an evaporator with a high-precision syringe pump (HPP 5001); alcohol vapor from the evaporator directed at a reactor. The reaction products directed at a cooled gas–liquid separator; then, the condensed liquid fraction was collected in a receiver. A mixture of argon with uncondensed products was returned to the reaction volume of the system with the use of a circulation pump. In case of plug-flow conditions tests argon with uncondensed products were directed into chromatographs. Gaseous reaction products were analyzed by on-line gas chromatography. The C_1–C_5 hydrocarbon gases were determined on a Kristall-4000 chromatograph: flame-ionization detector (FID); carrier gas, helium (70 cm3/min); Tcol = 120°C; P = 0.65 MPa; HP-PLOT/Al2O3 column, 50 m × 0.32 mm. Analysis for CO, CO2, and H2 was performed on a Kristall-4000 chromatograph: thermal-conductivity detector; carrier gas, high-purity argon (30 ml/min); SKT column, 150 m . 0.4 cm; Tcol = 130°C. Low concentrations of CO (<0.4 vol %) were determined using a Riken Keiki gas analyzer with an IR cell (Model RI-550A). Liquid organic reaction products in aqueous and organic phases were identified using MSD 6973 (Agilent) and Automass_150 (Delsi Nermag) GC–MS instruments: EI = 70 eV; sample volume, 1 μl. First column: HP_5MS (0.32 mm × 50 m); Df = 0.52 μm; heating from 50°C (5 min) at a rate of 10 K/min to 270°C; Tinj = 250°C; constant flow rate of 1 ml/min; split ratio, 1/(100–200). Second column: CPSil-5 (0.15 mm × 25 m); Df = 1.2 μm; heating from 50°C (8 min) at a rate of 10 K/min to 270°C; Tinj = 250°C; Pinj = 2.2 bar; split ratio, 1/300. The concentrations of organic substances were quantitatively determined by GLC on a Varian 3600 instrument with a Chromtech SE-30 column of size 0.25 mm × 25 m; Df = 0.3 μm; heating from 50°C (5 min) at a rate of 10 K/min to 280°C; Tinj = 250°C; Pinj = 1 bar; split ratio, 1/200; FID. Trifluoromethylbenzene was used as an internal standard for the organic layer, and internal normalization was used for the aqueous layer. The ethanol content of the aqueous phase was determined by GC–MS from the ratio between the integral signals of the alcohol and water using the absolute calibration method.The catalysts described in this study were prepared by impregnation of γ-Al$_2$O$_3$ by an organic solution of mono- and bi-metallic alkoxides (Drobot D.V., et al. 2002) and carboxylates (Kozitsyna N. Yu. Et al., 2006) of II-VIII Periodic Table groups and standard treatment after the impregnation. Commercial Pt/Al$_2$O$_3$ was tested as well. Before each experiment all catalysts were treated during 12-14 h with hydrogen at 450^{0}C. The catalysts were studied with XPS (XSAM-800, Kratos) and XAFS (on the spectrometers of Siberian Synchrotron Research Center and Russian Research Center "Kurchatov Institute") techniques.

3. Results and Discussion

It was found that depending on the composition and nature of the catalyst the ratio of alkanes and alkenes in the reaction products changed, as well as the content of normal and branched structures ratio did (table 1). These data suggest that the mechanism of hydrocarbons formation can be different. To check this assumption, we tried to identify the possible intermediates of the process.

Table 1: Comparative data on the composition of hydrocarbons fractions obtained in the presence of investigated catalytic systems

Catalyst	Alkanes/olefins ratio	n-/ iso- hydrocarbons ratio	Total yield of C_3-C_{12} hydrocarbons, wt.%
Re-Ta/Al_2O_3	1 / 8	1 / 1	36
Re-W/Al_2O_3	1 / 8	1 / 1	30
Zn/Al_2O_3	1 / 2.5	1 / 1	42
Pd-Zn/Al_2O_3	1 / 1.5	4 / 1	50
Pt/Al_2O_3; Pd/Al_2O_3	11 / 1	9 / 1	49

For this purpose, we used the well-known industrial platinumalumina catalyst (AP-64). Another vigorous peculiarity of these reactions was that ethanol conversion significant effected on flow-circulation or flow mode conditions because of during experiment (3.5 h) under multiplicity of circulation 50 cm^3/min the residence time of gaseous products differed from 9.6 to 1152 seconds respectively. Fig. 1 presents ethanol conversion products yield over over Pt/γ-Al_2O_3 catalyst in a flow mode (Fig. 1a) and flow-circulation (Fig. 1b) mode. As one can see under flow-circulation conditions ethanol mainly converted into C_3–C_{12} alkanes, whose total yield was 36.9 wt.%. Gaseous products contained a considerable amount of carbon oxides (CO and CO_2), methane and ethane. The liquid products contained small amounts of cycloalkanes, olefins, and aromatic hydrocarbons, the total concentration of which was no higher than 1.5 wt.%. In case of ethanol conversion in flow mode the yield of C_{3+} aliphatic hydrocarbons decreased to 20 wt.%, and the concentration of C_2 and C_{3+} olefins considerably increased; ethylene prevailed among these olefins and oxygen-containing compounds yield also increased among which considerable amount of acetaldehyde was found. The formation of considerable amounts of ethylene and acetaldehyde upon of ethanol conversion under flow conditions suggested that mode change to flow-circulation conditions facilitated return of ethylene and partially acetaldehyde to the reaction zone as potential intermediates that could take part in aliphatic hydrocarbons formation.

To test this hypothesis the next experiments were carried out with additives of ethylene and acetaldehyde to ethanol. For these tests as the catalysts Pt/Al_2O_3 and W-Re/Al_2O_3 were used because of these catalysts possessed quite different coupling and hydrogenating activity (table 1).

Ethylene being added to the reaction mixture over AP-64 significantly increased yield of normal alkanes C_4 - C_{10}, mainly containing even number of carbon atoms in carbon skeleton. Fig. 2 shows the ratio of yield of alkanes formed from ethanol with ethylene
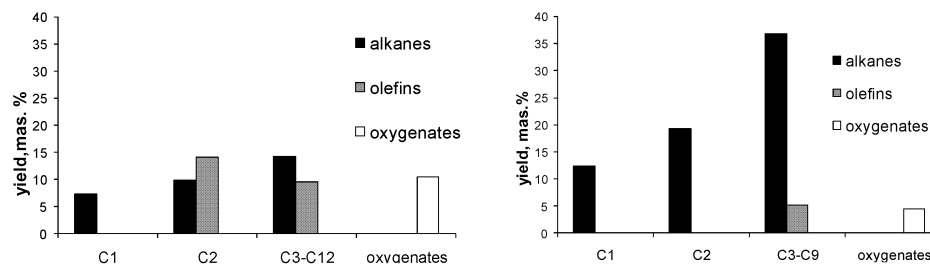
Figure 1: ethanol conversion products yield in the presence of platinumalumina catalyst in a flow (1a) and flow-circulation (1b) mode.

addition to alkanes yield without ethylene addition. At the same time acetaldehyde addition into initial ethanol led to unidentified high-tar oxygenates formation while the composition of the hydrocarbon fraction is practically unchanged.
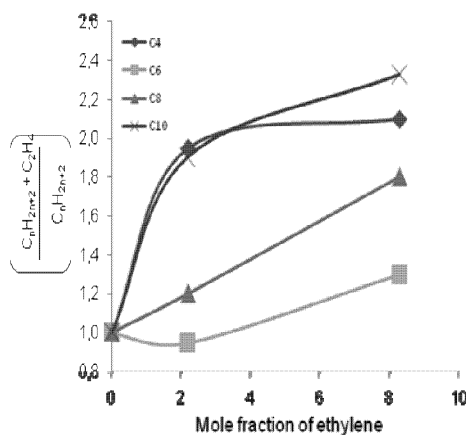

Figure 2: Dependence of ethylene addition on alkanes with even number carbon atoms increasing.

Another result was observed in the presence of W-Re/γ-Al$_2$O$_3$ catalytic system. Ethylene introduction into reaction zone did not lead to hydrocarbons C$_{3+}$ yield growth. In the gaseous products increase of ethylene content was equivalent of ethylene amount that has been introduced into the system. Addition to initial ethanol of 7 wt.% and 25 wt.% of acetaldehyde resulted in aim fraction yield increasing of 10 and 20 wt.% respectively (Fig. 3).

Attention should be paid to the fact that the obtained fraction of olefins consisted of 50 wt.% of hydrocarbons with n-structures and 50 wt.% branched structures, among which 3-methyl-substituted isomers dominated.

Based on obtained data mechanistic aspects of considered reactions could be suggested. Probable pathways of ethanol conversion into hydrocarbons shown on Fig. 5. Depending on catalyst nature growth of carbon chain realized via olefins condensation
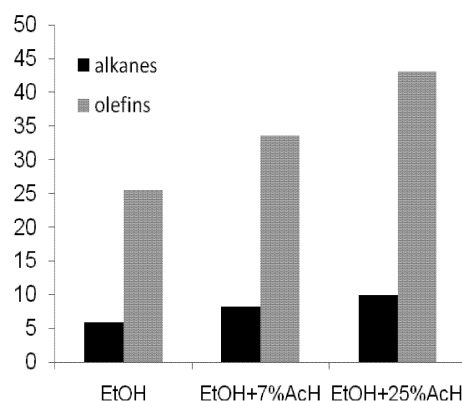
Figure 3: Olefins C₃-C₁₀ aim fraction yield (wt.%) of ethanol and its mixtures with acetaldehyde conversion over W-Re/Al₂O₃ catalyst.

and their subsequent hydrogenation (indirectly it confirms the fact that mainly normal hydrocarbons formed, its content was about 93 wt.%), or the route of aldehyde condensation and subsequent deoxygenation (in favor of this mechanism was the fact that formed olefins C_4-C_{10} consisted of 50 wt.% of iso-structure, moreover, 3 methyl-substituted alkenes dominated).

Glycerol being added up to 40 wt.% to ethanol significantly increases aim fraction of hydrocarbons C_4 - $C_{10 +}$ yield. This way glycerol that converts into acrolein under temperature over 190 °C is a prospective co-reagent with ethanol in cross-coupling reaction because it has the both active centers: carbonyl group and π-bond, taking a part in cross-coupling reaction.

It was determined oxides WO_3 and Re_2O_7 active clusters of size 5-10 nm distributed on support alumina surface. Shown that activity and selectivity of this catalytic system was conditioned by Re (7+) specious which posses stability due to strong interaction with support surface.

With using XAFS spectroscopy and ammonia TPD it was estimated that catalytic activity of Pt/Al_2O_3 catalyst was conditioned by the reorganization structure connected with clusters of Pt_2Al intermetallic and strong brensted acidic sites formation was occur as shown on Fig. 4).
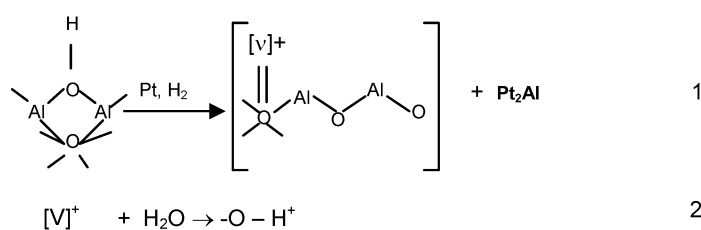

$[V]^+$ + H_2O → -O – H^+ 2

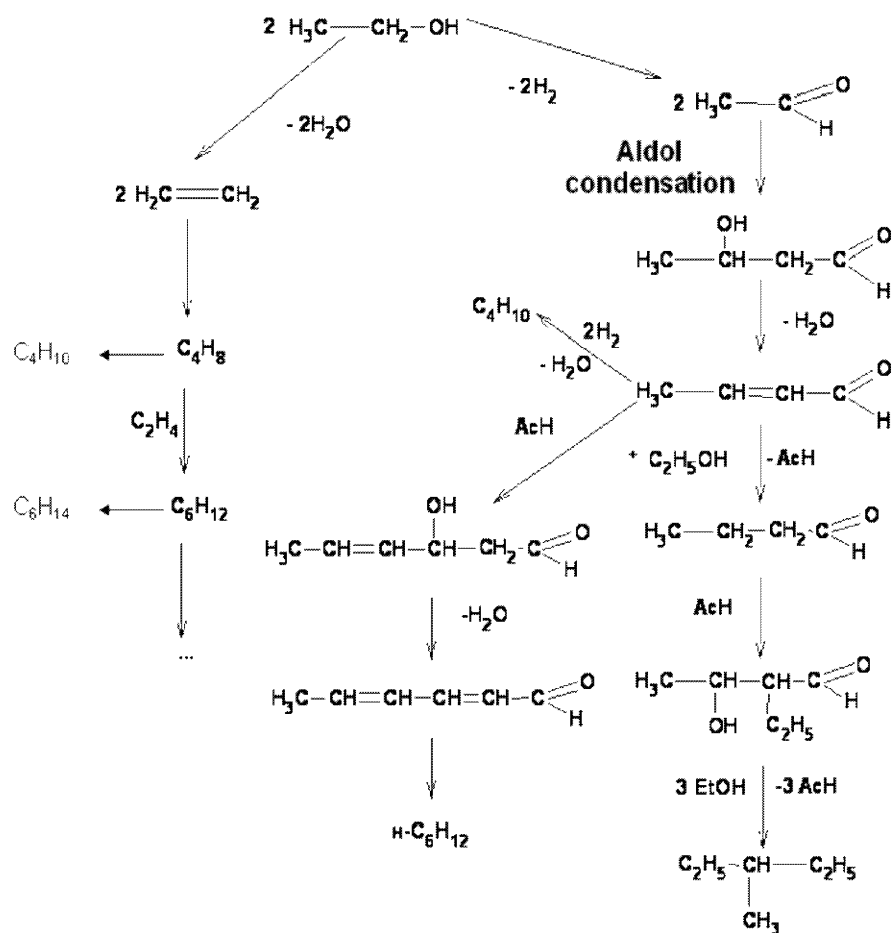*Figure 4: Platinum alumina catalyst genesis during reductive pretreatment*

Figure 5: Probable reaction pathways of ethanol conversion into hydrocarbons

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