

Conversion of biological substrates to fuel components in the presence of industrial catalysts*

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Conditions were found under which the industrial aluminum—platinum catalyst AP-64 and the pilot zeolite system Pd—Zn/Al₂O₃/MFI (MFI is a high-silica ZSM-5 type zeolite) catalyze single-stage highly selective conversion of rapeseed oil and ethanol to either alkane or alkane-aromatic fraction of hydrocarbons suitable as engine fuel components. The hydrocarbon chain grows with participation of ethylene, which is formed in the argon medium directly from the ethanol molecule. Under these conditions, hydrogenation of this alkene on intermetallic clusters arising during the long-term reductive preactivation is suppressed. The alcohol supplies not only ethylene but also hydrogen. In the presence of Pd—Zn/Al₂O₃/MFI, ethanol is converted to alkanes and aromatic hydrocarbons according to independent pathways. Joint processing of alcohols and rapeseed oil in the presence of the Pd—Zn/Al₂O₃/MFI catalyst system is an efficient and promising route to C₃—C₁₁ hydrocarbons in the absence of an external source of hydrogen.

Key words: heterogeneous catalysis, processing of biomass products, catalyst activation, biofuel.

The search for economic routes for the production of petrochemicals and engine fuel components from primary biomass processing products is a topical challenge. In recent years, researchers' attention has been drawn to the chemistry of alcohols obtained by fermentation by plant carbohydrates and lipids produced by diverse agricultural crops, fungi and micro algae.¹

Previously, it was found² that long-term reduction of the industrial aluminum—platinum catalyst changes considerably its properties. Indeed, ethanol is usually dehydrated on the catalyst AP-64 to give ethylene and diethyl ether (DEE). However, in the presence of the same catalyst preactivated by hydrogen for a long period, ethanol is converted, under argon atmosphere, to the C₄—C₁₂ alkane fraction, while higher alcohols C₄ and C₅ are mainly converted to C₈ and C₁₀ alkanes.^{3,4}

A number of publications^{5–8} describes the transformation of ethanol and vegetable oils to aromatic hydrocarbons in the presence of zeolite catalysts based on ZSM-5. The principal drawback of these catalysts is fast deactivation caused by the formation of products of condensation.

This work reports the results of catalytic conversion of ethanol, a model mixture of carbohydrate fermentation

products, rapeseed oil, and their mixture to hydrocarbon fuel components. The industrial aluminum—platinum catalyst AP-64 and two pilot catalyst samples Pd—Zn/Al₂O₃/MFI (MFI is high-silica zeolite) based on a ZSM-5 type zeolite were used.

Experimental

Two study employed two types of industrial catalysts: the aluminum—platinum catalyst AP-64 (~0.6 wt % Pt on γ -Al₂O₃, specific surface area ~200 m² g⁻¹, pore volume 0.65 cm³; TU 2177-021-04610600-2000) and the catalyst based on MFI, a structural analog of ZSM-5, with the ratio SiO₂/Al₂O₃ = 37, and γ -Al₂O₃ modified with either 0.6 wt % Pd and 1 wt % Zn, or with 0.6 wt. % Pd and 1.2 wt.% Zn (manufactured by the OJSC Angarsk Plant of Catalysts and Organic Synthesis).⁹

The rapeseed oil of the brand name P (GOST 8988-2002) manufactured by "Russian Seeds" company served as a raw material. The fatty-acid composition of the oil transesterified with methanol is presented below.

| Component | Content in the oil (wt.%) |
|-------------------|---------------------------|
| Methyl stearate | 4.9 |
| Methyl oleate | 93.313 |
| Methyl gondoinate | 1.795 |
| Methyl erucate | 0.102 |
| Σ | 100.00 |

* Dedicated to Academician of the Russian Academy of Sciences I. P. Beletskaya on the occasion of her anniversary.

The procedure for determination of the fatty-acid composition of rapeseed oil was reported previously.¹⁰

Ethanol (analytically pure grade, GOST 5964-93), propan-1-ol (chemically pure grade, TU 6-09-4344-87), butan-1-ol (pure grade, GOST 6006-78), and isoamyl alcohol (pure grade, GOST 5830-79) were used as received.

The conversion of bio-substrates in the presence of Pd—Zn/Al₂O₃/MFI was studied on a PID Eng and Tech flow type fixed bed microcatalytic setup.¹¹

The activity of the AP-64 catalyst in the transformation of bio-substrates was studied on an original flow-circulation type laboratory setup with a fixed catalyst bed, which ensured continuous recycling of the reaction gases back to the reaction area.¹²

Immediately prior to experiments, both catalytic systems were reduced in a hydrogen flow (30 L h⁻¹) at 450 °C and a pressure of 50 atm.

The reaction of rapeseed oil was studied in a hydrogen flow in a molar excess with respect to the substrate (10 : 1), a temperature of 360–420 °C, a pressure of 50 atm, and a substrate space velocity of 0.6–2.4 h⁻¹.

The ethanol transformation was carried out in argon at a pressure of 5 atm, a temperature of 330 °C, and a substrate space velocity of 0.6–2.4 h⁻¹.

The gaseous reaction products were analyzed by gas chromatography in the on-line mode: the C₁–C₅ hydrocarbon gases were analyzed on a Kristall-4000M chromatograph (flame ionization detector, a HP-PLOT/Al₂O₃ column) and CO, CO₂, and H₂ were determined on a Kristall-4000 chromatograph (heat conductivity detector, an SKT column). Low CO concentrations (<0.4 vol.%) were determined by a Riken Keiki gas analyzer with an IR cell (RI-550A).

Liquid organic reaction products in the aqueous and organic phase were identified by GC-MS using MSD 6973 (Agilent) and Automass-150 (Delsi Nermag) instruments and HP-5MS and CPSil-5 columns. Organic compounds were quantified by GLC on a Varian 3600 instrument, a Chromtech SE-30 column using trifluoromethylbenzene as the internal standard for the organic layer. The residual content of organic products in the aqueous phase was found by the GC/MS from the integral signal ratio by absolute calibration method.

Results and Discussion

In a flow type reactor in the presence of the aluminum–platinum catalyst in the temperature range of 250–400 °C, ethanol tends to be mainly dehydrated to give ethylene and diethyl ether (DEE). The yield of ethane is negligibly low under these conditions.^{13,14} However, hydrogen pretreatment of AP-64 even at moderate temperature markedly changes the catalyst selectivity. Indeed, in the presence of the H₂-pretreated catalyst at 100 °C, ethanol is mainly converted over a period of 2 h to gaseous products: C₁–C₄ alkanes, CO, and CO₂ in an overall yield of 75 wt.% (Fig. 1). In the presence of a catalyst pre-reduced for 12–14 h, the route of ethanol conversion under inert gas at 450–500 °C changes even more noticeably. After this long-term reducing treatment, the yield of methane decreases and the yield of C₃–C₁₂ alkanes increases (see Fig. 1).

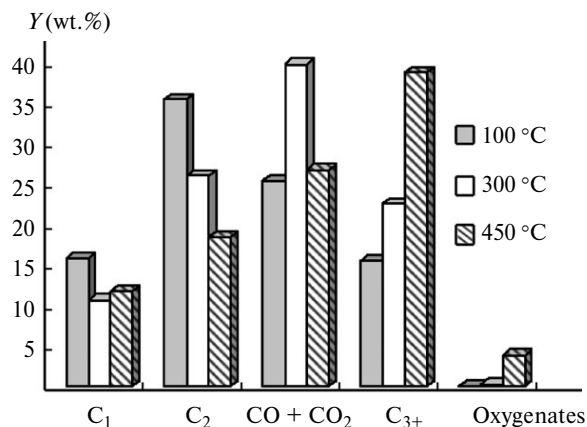
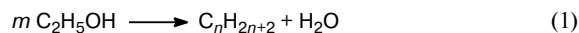


Fig. 1. Effect of the Pt/Al₂O₃ reduction temperature on the composition of ethanol conversion products; *Y* is yield; C₁, C₂, and C₃₊ are aliphatic hydrocarbons.

Dehydration of ethanol to give alkanes with longer carbon skeleton was found for the first time in the presence of a mixture of intermetallic compound with an aluminum–platinum or over fused iron catalyst,^{2,15} this reaction was called reductive dehydration of ethanol (RDE).



($n \geq 3$)

The RDE reaction occurs in rather narrow temperature and ethanol space velocity ranges, the optimal conditions being a temperature of 300–350 °C and an ethanol feed velocity of 0.5–0.9 h⁻¹ (Fig. 2). A temperature decrease below 300 °C and increase in the feed space velocity above 0.9 h⁻¹ result in almost complete loss of selectivity of formation of C₃–C₁₂ alkanes.¹⁶

The yields of the major products of ethanol conversion in the presence of AP-64 (330 °C, 5 atm, Ar, substrate space velocity 0.6 h⁻¹) are presented below.

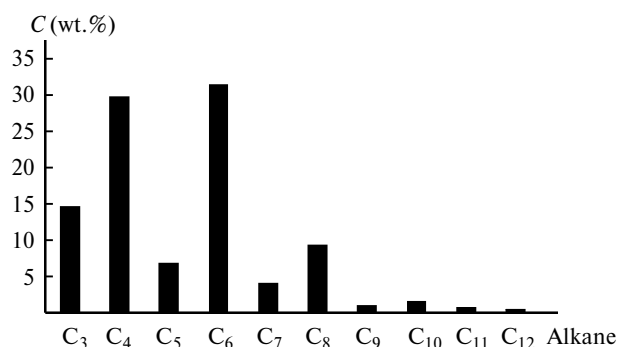
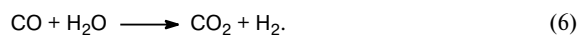
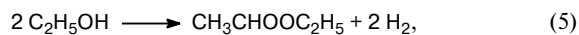
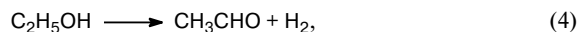
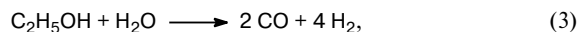
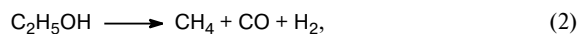


Fig. 2. Composition of the C₃–C₁₂ alkane fraction obtained during ethanol conversion in the presence of AP-64 at 330 °C, 5 atm of Ar, substrate space velocity of 0.6 h⁻¹.

| Product | Yield (wt.%) |
|---|--------------|
| Water | 22.10 |
| H ₂ | 0.08 |
| CO | 4.91 |
| CO ₂ | 12.39 |
| CH ₄ | 6.15 |
| C ₂ H ₆ | 21.03 |
| Oxygenates | 2.88 |
| C ₃ –C ₁₂ alkanes | 30.46 |

Gaseous products contain large amounts of carbon oxides and C₁ and C₂ alkanes. Liquid products contain, along with alkanes, minor amounts (totally ≤1%) of cycloalkanes, olefins, and aromatic hydrocarbons. Oxygenates mainly comprise diethyl ether and also acetaldehyde, ethyl acetate, and traces of butanol and hexanol. Hydrogen needed for the formation of alkanes according to Eq. (1) is generated, most likely, directly in the following catalytic reactions:

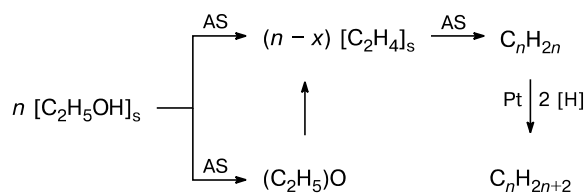


The intermolecular hydride transfer between the primary products of ethanol conversion may also occur.

In the presence of the aluminum–platinum catalyst, the gaseous reaction products were found to contain 0.08 wt.% of hydrogen despite the intense hydrogen transfer in the reaction system.

Hydrocarbons with even numbers of carbon atoms predominate (<70 wt.%) in the alkane fraction (see Fig. 2). The effect of potential intermediates on the alkane yield indicates that the hydrocarbon chain grows at the expense of diethyl ether and ethylene.¹⁶ All the available data can be interpreted within the framework of Scheme 1, which includes oligomerization of the intermediate ethylene followed by hydrogenation of the resulting olefins on platinum sites^{12,16} (see Fig. 2).

Scheme 1



AS are the acid sites of the support, s is the molecule sorbed on the catalyst surface.

The formation of a minor amount of alkanes with odd numbers of carbon atoms can be due to secondary cracking of hydrocarbon reaction products.

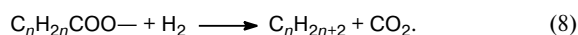
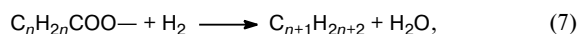
A XAFS study of the structure of the catalyst AP-64 after long-term reduction demonstrated that Pt₂Al clusters are formed on the catalyst surface. The X-ray absorption spectra coincide to a high accuracy with the spectra of Pt₂Al synthesized from the elements.^{16,17}

The temperature-programmed desorption of ammonia revealed the presence of strong Brønsted acid sites.¹⁶

The industrial aluminum–platinum catalyst subjected to long-term preactivation shows high activity in ethanol dehydration followed by carbon chain growth and mild hydrogenation of C=C bonds of oligomerization products. Among important advantages of this catalyst is substantial retardation of C–C bond cleavage processes on this catalyst as compared with processes that occur on the same catalyst pre-reduced for a short time. In the latter case, ethanol is mainly converted to ethane.

In the presence of the industrial aluminum–platinum catalyst subjected to long-term reductive pretreatment, the reaction pathway changes not only for ethanol but also for fatty acid triglycerides (FATG). FATG are converted to an alkane fraction (Fig. 3), the IR spectra of which do not show absorption bands for CO (1200 cm⁻¹) or CO₂ (1750 cm⁻¹) groups. Thus, in the presence of the aluminum–platinum catalyst, rapeseed oil is completely converted to alkanes and water.

The C₁₆ and C₁₇ alkanes (total yield ~80 wt.%) are formed upon the reduction and decarboxylation of the acyl groups of the oil. Apart from these major products, other alkanes are formed, their composition being represented by a continuous broad spectrum (see Fig. 3). These alkanes are likely to arise upon hydrocracking of the primary products. The carbon chains of the major components of the alkane fraction are either equal to or one carbon shorter than the alkyl chain length of the fatty acid of the initial oil. Apparently, the major pathways of oil conversion are hydrogenation and decarboxylation of the FATG acid groups:



Since the gaseous reaction products contain only traces of carbon oxides, they have evidently been hydrogenated during catalysis to methane, which is formed in a 1.5 wt.% yield.

The reaction products were also found to include C₂₃–C₂₈ alkanes containing more carbon atoms than the fatty acids in the initial oil. The total yield of C₂₃–C₂₈ alkanes was ~5 wt.%, which suggests that a glycerol fragment has been incorporated into the intermediates formed from acyl groups.

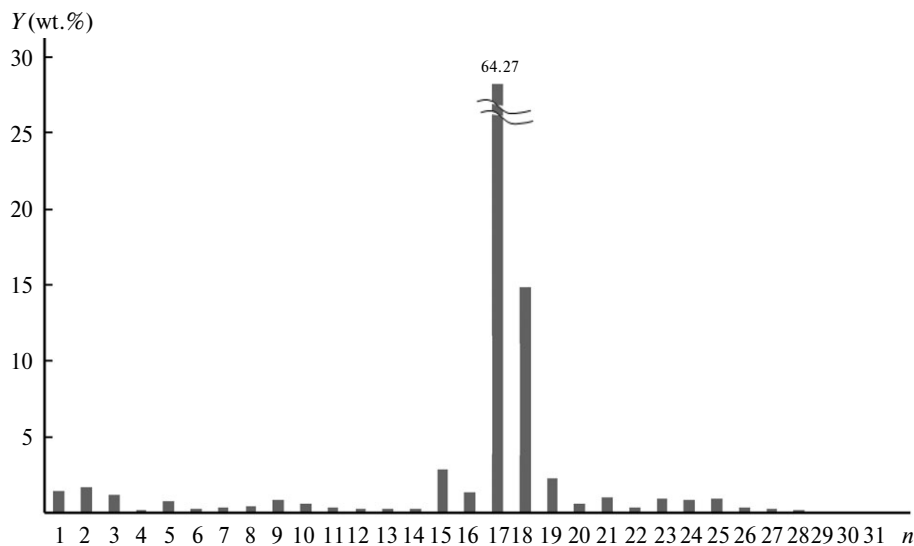


Fig. 3. Yield of the alkane products of rapeseed oil conversion; n is the number of carbon atoms in the alkane.

Consider the data on the variation of the aluminum—platinum catalyst activity during operation. The aluminum—platinum catalyst without reductive pretreatment reaches the stable performance equal to that of the pretreated catalyst after 28 h (Fig. 4).

During the first 28 h, the aluminum—platinum catalyst not only exhibits high hydrogenating activity but also cracks the C—C bonds and isomerizes the alkanes formed. However, methanation is not very intensive, the maximum yield of light C_1 — C_3 alkanes being 21 wt.%. At 420 °C, the yields of both light and branched alkanes decrease after 28 h; the system reaches stable operation in which the yield of the target C_4 — C_{25+} fraction is main-

tained at 85—90 wt.% in relation to the weight of carbon passed and the content of iso structures is 2—3 wt.%. The yield of gaseous hydrocarbons does not exceed 5—6 wt.%; the predominant components among these are methane and ethane the content of which per carbon atom roughly corresponds to the theoretical amount of carbon obtained by decarboxylation of the fatty acids fed in the reactor. This selectivity is retained for the subsequent 22 h. The formation of heavy C_{23+} alkanes occurs throughout the whole experiment and becomes noticeably more pronounced after the catalyst has operated for the first 28 h (see Fig. 4). The amount of C_3 hydrocarbons is 70% lower than the number of stoichiometric C atoms in the glycerol

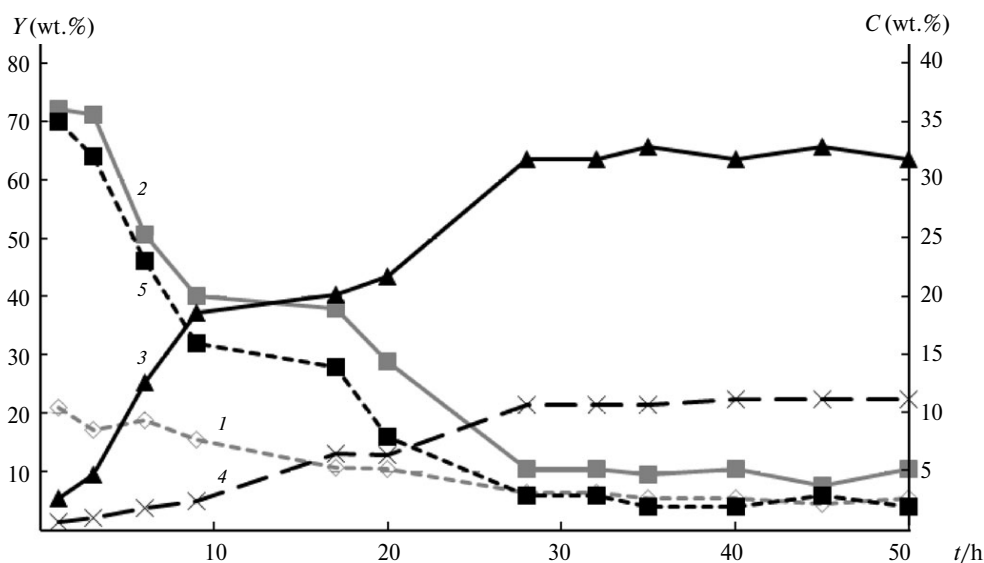


Fig. 4. Variation dynamics of the yields of rapeseed oil conversion products in long-time run on AP-64 without preactivation (420 °C, space velocity of 0.6 h⁻¹, 50 atm of H₂): alkanes C_1 — C_3 (1), C_4 — C_{16} (2), C_{17} (3), C_{18+} (4), iso structures (5).

moiety of FATG. This fact also indicates the possibility of intramolecular condensation of hydrocarbon parts of FATG with participation of the glycerol moiety.

These results indicate that the industrial aluminum—platinum catalyst efficiently produces a new-generation biodiesel in one step and markedly reduces the loss of valuable carbon stock of both glycerol and acid moieties, which is inherent in operation of other catalysts.^{1,18,19} The discovered new properties of the aluminum—platinum catalyst may considerably enhance the efficiency of bio-substrate conversion to valuable fuel components.

The pilot samples of the Pd—Zn/Al₂O₃/MFI catalyst proved themselves promising for obtaining hydrocarbons in high yields from ethanol and rapeseed oil. They are based on a structural analog of ZSM-5 developed for the conversion of dimethyl ether or dimethyl ether—methanol mixture to gasoline. The hydrocarbon yield on this catalyst is very high, although the selectivity of this system differs appreciably from that for the aluminum—platinum catalyst,²⁰ aromatic compounds being predominant reaction products.

In the presence of the two samples of the Pd—Zn/Al₂O₃/MFI catalyst, ethanol is converted almost completely. The major product is C₃—C₁₂ alkane-aromatic hydrocarbon fraction, which is formed in 70—83 wt.% yield in relation to the carbon passed (Table 1).

Thus, palladium and zinc modification of a ZSM-5 type zeolite substantially decreases the yield of olefins compared with the yield of the products of ethanol conversion catalyzed by either non-modified H-ZSM-5 or that with supported metals.^{21—24}

A comparison of the results with the results for Pd—Zn/Al₂O₃ (see Ref. 25) shows a considerable increase in the total yield of the target hydrocarbon fraction, C₃—C₁₂, from 50 to 83%. Furthermore, the zeolite catalyst shows selectivity toward the formation of alkanes and aromatic hydrocarbons, whereas the alumina-supported Pd—Zn catalyst predominantly produces the alkane-olefin fraction.²⁵

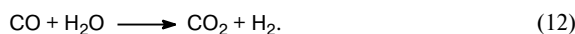
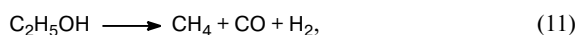
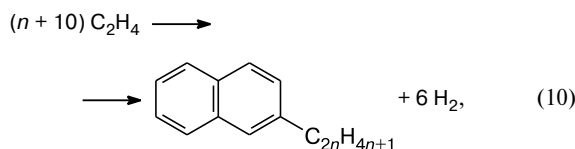
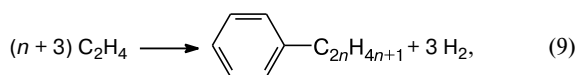
An increase in the zinc content in the catalyst by 0.2 wt.% results in much higher yield of ethane and aromatics (see Table 1). The increase in the ethane content is correlated with the decrease in the yield of the C₃—C₇ aliphatic hydrocarbons from 46 to 28% and increase in the yield of aromatics (see Table 1). The reaction proceeds in an inert medium; therefore, hydrogen needed for the formation of alkanes is for the most part supplied, in all probability, by aromatization of the intermediates formed from ethanol.^{22,26} The increase in the yield of the aromatic fraction is accompanied by enhanced formation of hydrogen and, as a consequence, by increased contribution of ethylene to ethane hydrogenation.

Apparently, ethylene is the key intermediate responsible for the carbon chain buildup.^{22,26} Hence, hydrogen formation and consumption in the system can be described by Eqs (9)—(12) and (13), respectively.

Table 1. Comparative data on ethanol conversion in the presence of Pd(0.6%)—Zn(1%)/MFI and Pd(0.6%)—Zn(1.2%)/MFI catalysts (initial Ar pressure 5 atm, 330 °C, ethanol space velocity 0.6 h⁻¹)

| Parameter | Pd(0.6%)—Zn(1%)/MFI | Pd(0.6%)—Zn(1.2%)/MFI |
|--|---------------------|-----------------------|
| Ethanol conversion (%) | >99 | >99 |
| Yield (wt.%) | | |
| Hydrocarbons | 61.2 | 60.9 |
| Water | 38.8 | 39.1 |
| Composition of hydrocarbon products (wt.%) | | |
| C ₁ | 0.64 | 0.27 |
| C ₂ | 11.98 | 26.72 |
| C ₂₌ | 3.94 | 2.03 |
| Aliphatic C ₃ —C ₇ hydrocarbons | 45.87 | 28.06 |
| Aromatic C ₆ —C ₁₂ hydrocarbons | 37.57 | 42.92 |
| Composition of the aliphatic C ₃ —C ₇ fraction | | |
| C ₃ | 34.07 | 45.47 |
| C ₄ | 33.07 | 29.91 |
| C ₅ | 21.72 | 9.60 |
| C ₆ | 7.82 | 10.12 |
| C ₇ | 3.32 | 4.90 |
| Composition of the aromatic C ₆ —C ₁₂ fraction | | |
| Benzene | 1.16 | 0.97 |
| Toluene | 16.73 | 28.61 |
| Ethylbenzene | 7.46 | 7.52 |
| Xylenes | 24.36 | 35.83 |
| Trimethylbenzene | 9.83 | 5.08 |
| Ethylmethylbenzene | 24.34 | 10.98 |
| Diethylbenzene | 10.15 | 4.83 |
| Methylethylbenzene | 2.31 | 2.89 |
| Methylnaphthalene | 3.66 | 3.30 |
| Dimethylnaphthalene | 0.00 | 0.97 |

Hydrogen formation:



Hydrogen consumption:

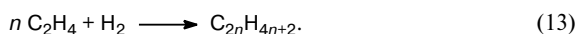


Table 2. Balance of hydrogen redistribution during the conversion of 0.7 moles of ethanol in the presence of a zeolite catalyst containing Pd(0.6%)—Zn(1%)

| Hydrogen donor (D) | Hydrogen formation* | | Hydrogen acceptor (A) | Hydrogen consumption** | |
|----------------------|----------------------------|----------------|-----------------------|------------------------|----------------|
| | Hydrogen evolution, m/mmol | | | m/mmol | |
| | D | H ₂ | | A | H ₂ |
| Benzene | 0.96 | 2.87 | Methane | 6.75 | 6.75 |
| Toluene | 13.73 | 41.18 | Ethane | 66.51 | 66.51 |
| Ethylbenzene | 4.54 | 13.61 | Propane | 66.59 | 66.59 |
| Xylenes | 17.82 | 53.46 | Butane | 34.53 | 34.53 |
| Trimethylbenzene | 5.28 | 15.85 | Pentane | 25.07 | 25.07 |
| Ethylmethylbenzene | 13.08 | 39.24 | Hexane | 8.13 | 8.13 |
| Diethylbenzene | 6.88 | 20.64 | Heptane | 3.87 | 3.87 |
| Dimethylethylbenzene | 1.97 | 5.90 | Hydrogen | 0.71 | 0.71 |
| Methylnaphthalene | 2.05 | 12.30 | — | — | — |
| Carbon monoxide | 3.12 | 3.12 | — | — | — |

* Totally 208.18 mmols of H₂ are evolved.** Totally 212.6 mmol H₂ are consumed.

The hydrogen amount liberated upon the formation of aromatic hydrocarbons present in the reaction products calculated in terms of the proposed model is consistent with the amount of hydrogen spent for the formation of the alkane fraction (Tables 2 and 3). In the presence of the Pd(0.6%)—Zn(1.2%) catalyst, the amount of hydrogen formed is 25 mol.% greater than for the Pd(0.6%)—Zn(1%) sample.

The Pd—Zn/Al₂O₃/MFI catalyst efficiently accelerates the transformation of ethanol to valuable fuel components. The yield of the alkane-aromatic fraction is much higher than in the presence of analogous non-zeolite cata-

lysts. When the catalyst contacts with the reaction mixture for 48 h, no detectable loss of activity or selectivity occurs, which was the case for analogous catalysts.^{21–24,26} The catalyst stability to surface carbon deposition attests to its high activity in hydrogen transfer reaction. Therefore, the Pd—Zn/Al₂O₃/MFI catalyst may be expected to be also efficient in the processing of heavier bio-substrates such as vegetable oils. During hydrogen preactivation, clusters of the intermetallic compound Pd_{0.5}Zn_{0.5} are formed on the zeolite surface.²⁷

In the presence of metal-containing zeolite catalysts (pentasil), FATG are destroyed to give a broad spectrum

Table 3. Balance of hydrogen redistribution during the conversion of 0.7 moles of ethanol in the presence of a zeolite catalyst containing Pd(0.6%)—Zn(1.2%)

| Hydrogen donor (D) | Hydrogen formation* | | Hydrogen acceptor (A) | Hydrogen consumption** | |
|----------------------|----------------------------|----------------|-----------------------|------------------------|----------------|
| | Hydrogen evolution, m/mmol | | | m/mmol | |
| | D | H ₂ | | A | H ₂ |
| Benzene | 1.08 | 3.24 | Methane | 2.88 | 2.88 |
| Toluene | 15.42 | 46.27 | Ethane | 152.69 | 152.69 |
| Ethylbenzene | 5.10 | 15.30 | Propane | 54.35 | 51.35 |
| Xylenes | 20.02 | 60.06 | Butane | 26.36 | 24.36 |
| Trimethylbenzene | 5.93 | 17.80 | Pentane | 9.29 | 9.29 |
| Ethylmethylbenzene | 14.69 | 44.08 | Hexane | 6.27 | 5.27 |
| Diethylbenzene | 7.73 | 23.19 | Heptane | 2.61 | 2.61 |
| Dimethylethylbenzene | 2.21 | 6.64 | Hydrogen | 1.07 | 1.07 |
| Methylnaphthalene | 3.51 | 21.03 | — | — | — |
| Dimethylnaphthalene | 2.30 | 13.82 | — | — | — |

* Totally 251.43 mmols of H₂ are evolved.** Totally 249.52 mmol H₂ are consumed.

Table 4. Composition of the products of rapeseed oil conversion under optimal conditions: 420 °C, 2.4 h⁻¹ (I) and 230 °C, 1.2 h⁻¹ (II)

| Products | Content (wt.%) | | Products | Content (wt.%) | |
|----------------------------|----------------|-------|--|----------------|--------|
| | I | II | | I | II |
| C ₁ | 1.04 | 0.54 | Toluene | 18.42 | 16.92 |
| C ₂ | 4.83 | 4.89 | Ethylbenzene | 4.81 | 3.79 |
| C ₂₌ | 0.32 | 0.18 | <i>o</i> -Xylene, <i>p</i> -xylene | 13.06 | 9.24 |
| C ₃ | 10.79 | 11.71 | <i>m</i> -Xylene | 3.15 | 2.23 |
| C ₃₌ | 0.75 | 0.37 | Propylbenzene | 0.94 | 0.00 |
| <i>iso</i> -C ₄ | 5.88 | 9.50 | Ethylmethylbenzene | 5.93 | 4.16 |
| <i>n</i> -C ₄ | 2.19 | 5.30 | 1,2,3-Trimethylbenzene | 1.40 | 0.80 |
| C ₄₌ | 1.81 | 1.49 | Methylphenylethylen | 1.01 | 0.61 |
| <i>iso</i> -C ₅ | 4.52 | 9.91 | 1,2-Diethylbenzene | 1.61 | 0.00 |
| <i>n</i> -C ₅ | 1.46 | 2.60 | α -Phenyl- β -ethylethylene | 0.96 | 0.00 |
| C ₅₌ | 1.12 | 0.66 | Naphthalene | 1.16 | 0.00 |
| 2,3-Dimethylbutane | 0.45 | 1.09 | α -Methylnaphthalene | 1.40 | 0.63 |
| <i>iso</i> -C ₆ | 0.94 | 2.04 | CO | 2.55 | 0.58 |
| <i>n</i> -C ₆ | 0.72 | 3.40 | CO ₂ | 0.21 | 0.33 |
| Benzene | 6.56 | 7.04 | Σ | 100.00 | 100.00 |

of products, aromatics being the predominant components,^{5–7} although this process tends to give methane in a high yield and the catalyst systems are rapidly deactivated.

Study of the conversion of rapeseed oil in the presence of Pd–Zn/Al₂O₃/MFI identified two optimal modes that provided the highest yields of the target alkane-aromatic fraction: space velocity of 2.4 h⁻¹ at 420 °C or space velocity of 1.2 h⁻¹ at 360 °C. In the former case, the highest yield of the target aromatic hydrocarbon fraction was obtained (79 wt.%), while in the latter case, the highest yield of C₃–C₆ aliphatic hydrocarbons was achieved (48 wt.%, Table 4).

The conversion of the oil does not give aliphatic hydrocarbons with more than six carbon atoms (*n*). The reactions give mainly C₄–C₈ hydrocarbons (62 wt.%), those with *n* > 6 being aromatic (see Table 4), which is attributable to the shape-selectivity effect of the catalyst.²⁸ The lack of temperature effect on the formation of aromatic hydrocarbons suggests that the cyclization occurs by so-called "hydrocarbon pool" mechanism described in relation to the preparation of identical alkane-aromatic fraction from methanol and ethanol.²⁹ According to this mechanism, dehydration and C–C bond cleavage of ethanol give separate fragments of [CH_x] radicals, which are condensed in the zeolite pores to give aromatic hydrocarbons with predominant yield of toluene and xylenes. The formation of aromatic hydrocarbons is accompanied by evolution of H₂, and ethanol oxygen mainly goes to a water molecule.²⁹

The contribution of decarbonylation and decarboxylation of the acid groups of fatty acid triglycerides of rapeseed oil to the conversion of the glycerol moiety was estimated from the balance of carbon and oxygen introduced in the reaction and recovered (Tables 5 and 6).

During conversion of fatty acid triglycerides, decarbonylation of the acid moiety at 360 °C is of low intensity, as the yield of carbon mono- and dioxide is less than one-tenth of the theoretically possible yield. An increase in the temperature to 420 °C considerably intensifies the formation of CO, its yield being ~1/3 of the theoretically possible value (see Table 5).

Oxygen present in the FATG molecule goes for most part into water, which is indicative of a great contribution of hydrogenation of C–O bonds (see Table 6).

In the early stages of FATG conversion, decarbonylation and decarboxylation of the acid moieties may take place followed by reduction of the resulting carbon oxides to methane. However, the total yield of methane and carbon oxide is 20 mol.% at 360 °C and 50 mol.% at 420 °C

Table 5. Carbon content in acid groups and glycerol moiety (mmol) that were passed through a catalyst bed during the experiment under different reaction conditions: 420 °C, 2.4 h⁻¹ (I) and 360 °C, 1.2 h⁻¹ (II)

| Parameter | I | II |
|------------------------------------|--------|--------|
| Carbon content, mmol-at. C | | |
| In glycerol | 67.61 | 35.03 |
| In carboxyl group | 67.61 | 35.03 |
| Σ | 135.22 | 70.06 |
| Recovered C, mmol | | |
| From CH ₄ | 12.40 | 3.09 |
| From C ₂ H ₆ | 61.39 | 29.92 |
| From C ₃ H ₈ | 140.40 | 73.22 |
| From CO | 17.40 | 1.91 |
| From CO ₂ | 0.91 | 0.69 |
| Σ | 232.5 | 108.83 |

Table 6. Oxygen content in ester groups (mmol) that were passed through a catalyst bed during the experiment under different reaction conditions: 420 °C, 2.4 h⁻¹ (I) and 360 °C, 1.2 h⁻¹ (II)

| Parameter | I | II |
|-----------------------|--------|--------|
| Fed | 135.23 | 70.06 |
| Recovered | | |
| O in H ₂ O | 115.38 | 66.68 |
| O in CO | 17.40 | 1.91 |
| O in CO ₂ | 1.81 | 1.38 |
| Σ | 69.97 | 134.59 |

of the theoretically possible value. The amount of the obtained propane is twice as high as the amount that could have formed from the glycerol introduced in the system.

Evidently, in the presence of Pd–Zn/Al₂O₃/MFI, reduction (hydrogenation) of C–O bonds and the subsequent cracking of the resulting carbon fragments occurs more intensively, while at higher temperature, the contribution of decarbonylation and decarboxylation increases.

Stability testing of the Pd–Zn/Al₂O₃/MFI catalyst demonstrated that almost complete conversion of rapeseed oil and the high selectivity with respect to the target alkane-aromatic fraction are retained for 50 h (Fig. 5).

It can be concluded that the conversion of rapeseed oil catalyzed by Pd–Zn/Al₂O₃/MFI is a complex process consisting of reactions that take place on metal and oxide sites.

The glycerol moiety of FATG is apparently converted completely to the propane fraction. The products obtained with this catalyst contain more C₃ hydrocarbons than could be expected if they were formed from glycerol. This

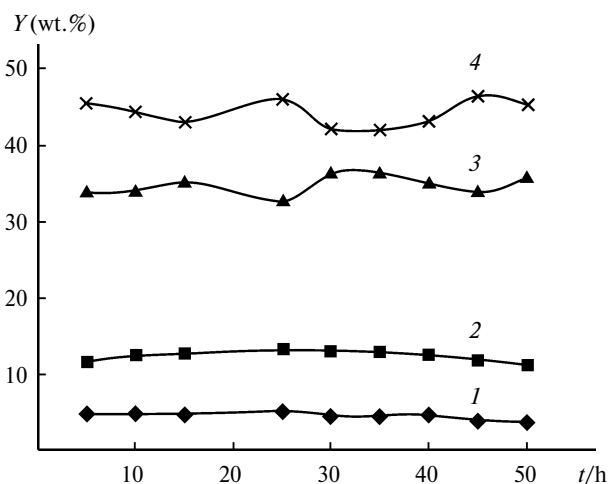


Fig. 5. Yields of the major products of rapeseed oil conversions during the endurance testing of the Pd–Zn/Al₂O₃/MFI catalyst at 360 °C and rapeseed oil feed space velocity of 1.2 h⁻¹: alkanes C₂ (1), C₃ (2), C₄–C₆ (3), aromatic hydrocarbons (4); *t* is the catalyst operation time.

attests to a secondary cracking of alkanes, because at elevated temperature (420 °C), an increase in the yield of propane is accompanied by a decrease in the content of aliphatic hydrocarbons.

The FATG conversion products predominantly contain alkylaromatic compounds that could have resulted from condensation, in zeolite pores, of CH_x hydrocarbon fragments arising upon cracking of the initial aliphatic chains of fatty acids.

It is known that zinc-containing active components are highly active in the conversion of alkanes²⁹ and olefins³⁰ to alkylaromatic compounds. Presumably, the condensation of the carbon products of cracking according to the hydrocarbon pool mechanism occurs particularly on zinc active components.

The shape-selectivity effect of the zeolite support is manifested in the fact that the major product fraction C₄–C₈ does not contain liquid alkanes heavier than C₆. The content of branched alkanes reaches 80%.

During the ethanol conversion catalyzed by Pd–Zn/Al₂O₃/MFI, the system produces much more hydrogen than in the case of AP-64. In order to achieve higher energy efficiency, experiments on combined conversion of rapeseed oil together with alcohol were performed; this reaction was expected to occur in an inert medium without consumption of hydrogen.

The catalytic tests were conducted using a mixture of alcohols rather than pure ethanol, this mixture modeling the biomass fermentation products and consisting of ethanol (80%), propanol (5%), butanol (5%), and isoamyl alcohol (10%). The substrate composition included rapeseed oil (25%) + alcohol mixture (75%). The component ratio was chosen so as to ensure a threefold excess of H₂ produced from ethanol. The ~100% conversion of the substrates was confirmed by IR and ¹H and ¹³C NMR data.

The yields of the major products of joint conversion of rapeseed oil (25 vol.%) and alcohol mixture (75 vol.%) in the presence of Pd–Zn/Al₂O₃/MFI (420 °C, 5 atm, Ar, substrate space velocity of 1.2 h⁻¹) are presented below.

| Product | Yield (wt.%) |
|---|--------------|
| Water | 30.88 |
| CO + CO ₂ | 0.45 |
| CH ₄ | 0.73 |
| C ₂ H ₆ | 1.49 |
| C ₂ H ₄ | 0.87 |
| C ₃ –C ₆ alkanes | 10.49 |
| C ₃ –C ₆ olefins | 6.46 |
| C ₆ –C ₁₁ aromatics | 48.63 |

The combined conversion of ethanol and rapeseed oil affords much more olefins and aromatic hydrocarbons than separate conversion of either of the substrates (Table 9 and Fig. 6). The yield of light hydrocarbons remains at <5 wt.%, despite the elevated temperature (420 °C), whereas in the case of conversion of ethanol alone at 330 °C, the yield of C₁–C₂ hydrocarbons is 8–18 wt.%. The decrease

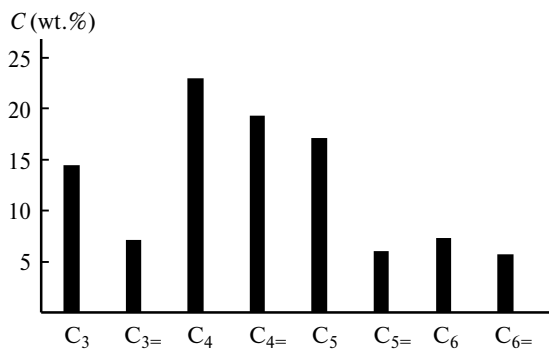


Fig. 6. Composition of aliphatic hydrocarbons resulting from joint conversion of rapeseed oil (25 vol.%) and alcohol mixture (75 vol.%) catalyzed by Pd—Zn/Al₂O₃/MFI (420 °C, 5 atm of Ar, substrate space velocity 1.2 h⁻¹).

in the yield of gases following the addition of the heavier substrate to ethanol was also observed previously for cross-condensation of glycerol and ethanol during their joint processing catalyzed by Re—W-, Re—Ta-, Cu-, and Ga-containing systems.^{20,27}

Among the aromatic products, toluene, xylenes, and trimethylbenzene are the major components; small amount of methylnaphthalene is also present (Fig. 7).

Thus, modified industrial aluminum—platinum catalyst and pilot samples of the Pd—Zn catalyst based on a ZSM-5 type zeolite are able to selectively convert the biomass processing intermediates to alkanes and alkane-aromatic mixtures suitable as engine fuel components. Alkanes and arenes are formed from ethylene and diethyl ether produced from ethanol. The hydrocarbon chain growth and aromatization take place on cluster intermetallic sites in argon under conditions where the ethylene hydrogenation is suppressed. The clusters are formed during the long-term reductive preactivation and participate in hydrogen transfer. Ethanol is not only a substrate giving rise to the alkane or aromatic molecule but also a source of

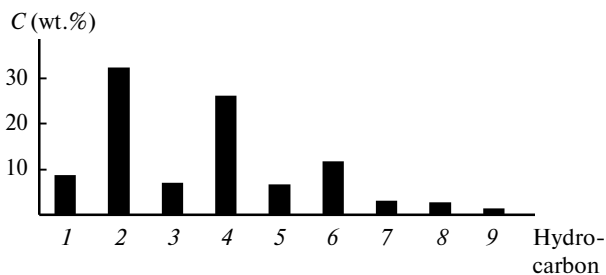


Fig. 7. Composition of aromatic hydrocarbons resulting from joint conversion of rapeseed oil (25 vol.%) and alcohol mixture (75 vol.%) catalyzed by Pd—Zn/Al₂O₃/MFI (420 °C, 5 atm of Ar, substrate space velocity 1.2 h⁻¹): benzene (1), toluene (2), *o*- and *p*-xylenes (3), *m*-xylenes (4), ethylbenzene (5), trimethylbenzene (6), phenylpropylene (7), tetramethylbenzene (8), methylnaphthalene (9).

hydrogen. The combined processing of alcohols and rapeseed oil on the Pd—Zn/Al₂O₃/MFI catalyst system is an effective and promising method for the preparation of C₃—C₁₁ hydrocarbons without an external source of hydrogen.

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