# CHEMICAL KINETICS AND CATALYSIS

# Catalytic Conversion of Glycerol into Aromatic Hydrocarbons, Acrolein, and Glycerol Ethers on Zeolite Catalysts

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**Abstract**—The effect of the nature of zeolite catalysts H-ZSM-5, H-BETA, and SAPO-34 on the activity and selectivity in the conversion of glycerol into aromatic hydrocarbons, acrolein, and oxygenates (various glycerol ethers) was studied. H-ZSM-5 was found to be the most effective catalyst for the conversion of glycerol into aromatic hydrocarbons and mono-, di-, and trisubstituted glycerol ethers with methanol and isobuty-lene. These products are effective gasoline additives increasing its octane number. Zeolite SAPO-34 shows the lowest activity in aromatization and alkylation reactions; the main product formed on this catalyst was acrolein.

*Keywords:* glycerol, aromatic hydrocarbons, acrolein, ethers, zeolites **DOI:** 10.1134/S0036024418120397

In recent years, the search for renewable fuels has become a challenge because of the depletion of oil reserves and increased attention to environmental problems in the world. Vegetable oils and animal fats, i.e., triglycerides of fatty acids are potential sources of this fuel. Triglycerides are converted into fatty acids methyl esters, so-called "biodiesel", by transesterification with methanol catalyzed by alkalis. Glycerol forms as a by-product (1 kg per 9 kg of biodiesel) in the form of 80% aqueous solution, and bringing it to commercial quality requires high energy inputs [1]. Therefore, various methods for the processing of glycerol were proposed. The most promising among these is steam conversion of glycerol into syngas catalyzed by conventional nickel catalysts at temperatures above 600°C [2]. For bioglycerol, many ways of utilization were proposed, which are mainly aimed at the production of petrochemical products and intermediates, with propylene, propylene oxide, and 1,2- and 1,3propanediols used as the raw materials [3].

At the same time, the problems of bioglycerol utilization and quality upgrading of fuel mixtures can be solved at once. Among the methods for bioglycerol processing is the production of additives to motor fuels based on bioglycerol [4]. From this viewpoint, one of the promising ways of glycerol utilization is its aromatization on zeolites similar to that of aliphatic  $C_1-C_4$ monoalcohols to obtain the high-octane benzene– toluene–xylene (BTX) fraction of aromatic hydrocarbons (ArHs) for its use in gasoline compounding.

However, glycerol aromatization is the least studied, but rather complicated problem. Methanol and other alcohols can form during hydrogenolysis, leading to subsequent etherification of glycerol with alcohols [5]. As acrolein should always form during the high-temperature conversion of glycerol according to thermodynamics, the formation of acrolein methyl acetal and some other oxygenates is also possible in the presence of methanol [6, 7]. According to these studies, this process is basically the "new chemistry" of oxygenate additives increasing fuel octane number, which was not previously discussed in the literature. In addition, as glycerol aromatization on various industrial solid acid catalysts also forms unsaturated  $C_1 - C_4$ gases, the formation of glycerol tert-butyl ethers (GTBEs) is possible by glycerol alkylation with isobutylene [7-9] (also see review [10]).

The goal of this study was to investigate the catalytic properties of various zeolite catalysts for glycerol aromatization on zeolites. For this purpose, zeolites ZSM-5, SAPO-34, and H-Beta, differing in their acidity and porous structure, were selected.

## **EXPERIMENTAL**

## Catalysts and Their Preparation

Commercially available catalysts were used.

(i) Zeolite ZSM-5 (Zeolyst), CBV-3024E  $(SiO_2/Al_2O_3 = 30, surface area 405 m^2/g, pore volume 0.49 cm^3/g)$ . The starting sodium form of zeolite was converted into the ammonium form by two consecu-

**Table 1.** Composition of the gaseous reaction products (wt %) of glycerol conversion at  $340^{\circ}$ C and at a space velocity of 1 h<sup>-1</sup> of the 85% aqueous solution

Catalyst	H-ZSM-5	SAPO-34	H-Beta
C <sub>1</sub>	9.8	1.6	66.1
$C_2H_6$	6.8	6.8	11.0
$C_2H_4$	23.3	33.3	1.4
$C_3H_8$	13.2	10.0	7.2
$C_3H_6$	22.5	26.8	2.6
$i - C_4 H_{10}$	0.3	0.6	0.1
$n - C_4 H_{10}$	1.1	1.1	2.4
$C_4H_8$	17.1	7.1	4.1
$i-C_4H_8$	0.1	6.9	0.2
trans-C <sub>4</sub> H <sub>8</sub>	2.2	2.0	3.0
cis-C <sub>4</sub> H <sub>8</sub>	3.6	3.8	1.9
Total	100.0	100.0	100.0

Table 2. Performance of the catalysts in glycerol conversion

Characteristic	H-ZSM-5	SAPO-34	H-Beta
Yield of liquid catalysate, %	92.7	96.2	72.3
Acrolein selectivity, %	12.5	63.1	21.0
ArH selectivity, %	41.3	33.0	36.7
Oxygenate selectivity (meth- anol + glycerol ethers), %	46.2	3.9	42.3
Glycerol conversion, %	84.2	12.5	70.5

tive treatments with a 0.5 M ammonium nitrate solution at  $80^{\circ}$ C for 3 h with constant stirring. The sample was then dried in air at  $100^{\circ}$ C for 2 h and calcinated at  $550^{\circ}$ C for 5 h (heating rate 5 K/min) to obtain H-ZSM-5.

(ii) Zeolite H-BETA (Zeolyst) CP811Tl (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 40, 0.05% Na, surface area 725 m<sup>2</sup>/g, pore volume 0.58 cm<sup>3</sup>/g).

(iii) The zeolite-like silico aluminophosphate SAPO-34 (ASC Material) in the H<sup>+</sup> form (10 wt % SiO<sub>2</sub>, 40 wt % Al<sub>2</sub>O<sub>3</sub>, 0.01% Na, surface area  $550 \text{ m}^2/\text{g}$ , pore volume 0.27 cm<sup>3</sup>/g).

#### Catalytic Tests

The reaction was performed in a quartz tube flow reactor with a diameter of 7 mm equipped with a thermocouple pocket. The catalyst (in powder form) bed volume was 2 cm<sup>3</sup>. The 85% aqueous glycerol solution (modeling the industrial biodiesel preparation byproduct) was fed in the reactor with a plunger pump at a space velocity of 1 h<sup>-1</sup> (flow rate 2.4 g/h). A trap cooled to  $-10^{\circ}$ C connected to the reactor outlet was used to separate the gaseous and liquid products. The

amount of the gas formed in the reaction was measured with a gas meter; the liquid products were collected into a glass trap receiver. The activity of the catalysts was evaluated at 340°C. The yield of the liquid catalysate was determined from its amount relative to the supplied water—glycerol mixture.

## Product Analysis

The gaseous products were analyzed on a model 3700 chromatograph (NPO Granat) with two columns: SE-54 capillary column with a flame ionization detector and Hayesep-Q packed column (for separating CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>) with a thermal conductivity detector. The analysis was performed under the isothermal conditions at 55°. The liquid reaction products separate into two phases (upper organic layer and lower aqueous oxygenate one). Each layer was analyzed using two independent chromatographic columns with a flame ionization detector. The carrier gas was helium.

The upper layer was analyzed on the model 3700 chromatograph using an SE-54 capillary column in a programmed temperature mode ( $60^{\circ}$ C for 4 min, then heating to 200°C at a rate of 6 K/min). The lower layer was analyzed on a Thermo Focus GC chromatograph with a Thermo TR-5MS capillary column connected with a Thermo DSQ II mass spectrometer (scan range 35–350 amu, scan rate 5 scans per second).

# **RESULTS AND DISCUSSION**

Tables 1 and 2 show the performance of the catalysts in the conversion of glycerol on the catalysts under study. The compositions of the hydrocarbon and aqueous parts of the catalysate are presented in Table 3.

The liquid catalysate obtained on all the catalyst samples is a two-layer liquid with different product distributions over layers. The upper layer of the catalysate (dark yellow because of tarry byproducts in the form of condensed aromatics) consists mainly of ArHs and contains dissolved acrolein; the lower (light yellow) aqueous oxygenate layer contains acrolein and oxygenates, including methanol and the products of glycerol etherification with methanol and isobutylene formed during the glycerol conversion.

A comparative analysis shows (Tables 1 and 2) that H-ZSM-5 is the most active and selective catalyst for glycerol conversion into the liquid products. The conversion of glycerol at 340°C is 84.2% with a sufficiently high yield of the liquid catalysate (~92%). This sample shows the maximum selectivity for highoctane ArHs (41.3%) and maximum oxygenate selectivity (46.2%). These oxygenates including methanol and various glycerol ethers are presented in Table 3 as methyl glycerol ethers (mono-, di-, and tri-MGs), as well as *tert*-butyl glycerol ethers (mono-, di-, and tri-TBGs) without specifying their contents in detail.

H-BETA zeolite exhibits slightly lower activity and selectivity for liquid products. The glycerol conversion at 340°C is 70.5%; the yield of the liquid catalysate is only ~72%, and increased formation of gaseous hydro-carbons  $C_1-C_4$  was observed. The selectivity for high-octane ArHs (36.7%) and oxygenates (42.3%) is slightly lower (by 4–6%), but comparable to the values obtained for zeolite H-ZSM-5. Among the products of the reaction on zeolite H-BETA, acrolein, which is the product of the thermal decomposition of glycerol, was present in much greater amounts than on H-ZSM-5.

An analysis of the product distribution in the organic and aqueous parts of the catalysate for these acid catalyst samples with high surface concentration of Brønsted acid centers shows (Table 3) that xylenes and ethylbenzene are dominant among ArHs formed on H-BETA and heavier alkyl aromatics  $C_{9+}$  prevail on H-ZSM-5.

Active formation of branched *tert*-butyl glycerol ethers was observed in the aqueous part of the catalysate among the products obtained on zeolite H-BETA; in contrast, methyl glycerol ethers formed on H-ZSM-5 (Table 3). This is consistent with the data of [11], which reported the use of wide-pore zeolites as effective catalysts of glycerol etherification with isobutylene and *tert*-butyl alcohol; zeolite ZSM, which also has satisfactory acidity, showed lower activity because of narrower pores, which is certainly a very important factor in view of the bulkiness of TBG molecules. This also agrees with the data of [12], which showed that H-BETA had low activity in glycerol etherification with monohydric alcohols such as methanol.

An indirect evidence for glycerol alkylation on H-ZSM-5 and H-BETA formed in the reaction with isobutylene is its low concentration in the hydrocarbon gas of the reaction, not exceeding 0.2 wt %; on zeolite SAPO-34, on which TBG does not form, the concentration of isobutylene in the hydrocarbon gaseous reaction products reaches 6.9 wt % (Table 2).

According to Table 2, acrolein is the main product of the reaction on SAPO-34. At low conversion of glycerol (12.5%), the selectivity of its formation is 63.1%, with only trace amounts of glycerol ethers formed (Table 2). The absence of MG among the products, in our opinion, is explained by the fact that, as is known [13], SAPO-34 is an effective catalyst of methanol conversion into  $C_2-C_3$  olefins. This is confirmed by the fact that ethylene and propylene form in maximum amounts (33.3 and 26.8%, respectively) in the hydrocarbon gaseous products of the reaction on SAPO-34, as compared to other catalysts (Table 2). Also, methanol was found in a low concentration in the aqueous phase of the catalysate (Table 3).

Our results obtained with the use of SAPO-34 do not contradict the data of [6, 14], which indicated

Catalyst	H-ZSM-5	SAPO-34	H-Beta			
Hydrocarbon part of catalysate						
Methanol	5.6	0.2	4.8			
Acrolein	16.0	48.0	26.8			
Aliphatic hydrocarbons C <sub>5+</sub>	4.8	7.4	0.8			
Aromatic hydrocarbons,	73.6	44.4	67.6			
including:						
Benzene	2.5	0.5	5.0			
Toluene	9.8	6.6	25.3			
Xylenes + ethylbenzene	20.6	20.4	20.7			
Alkylaromatics C <sub>9+</sub>	40.7	16.9	16.6			
Aqueous part of catalysate						
Methanol	10.2	0.5	4.0			
Acrolein	2.1	6.5	3.0			
Methyl glycerol ethers	12.0	_	2.5			
tert-Butyl glycerol ethers	3.4	0.2	11.8			
Unidentified	2.8	6.4	2.0			
Glycerol (unchanged)	19.9	70.0	44.7			
Water	49.5	16.4	31.9			
Total	100.0	100.0	100.0			

 Table 3. Composition of liquid products, wt %

active formation of acrolein on acid catalysts, i.e., high-silica zeolite with deposited silicotungstic acid; acrolein is an important petrochemical product used as a starting material for the synthesis of acrylonitrile, pyridine,  $\beta$ -picoline, and amino acids (methionine, proline) in chemical and pharmaceutical industry.

To summarize, in addition to acrolein, the products of the reaction on all catalysts included ArHs and oxygenates (methanol and various glycerol ethers), which are promising fuel additives that can be used in compounding of gasolines for increasing its octane number. In contrast to glycerol itself, the trisubstituted glycerol ethers obtained in small amounts in the reaction on the sample do not contain –OH polar groups; due to this, the stability of the resulting high-octane gasoline increases. Further prospects for the development of effective catalysts of the conversion of glycerol and other polyhydric alcohols are associated with the search for nanosized catalysts with molecular sieve properties [15–17] and hybrid nanomaterials [18–21].

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