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# Conversion of n-butanol to hydrocarbons over H-ZSM-5, H-ZSM-11, H-L and H-Y zeolites

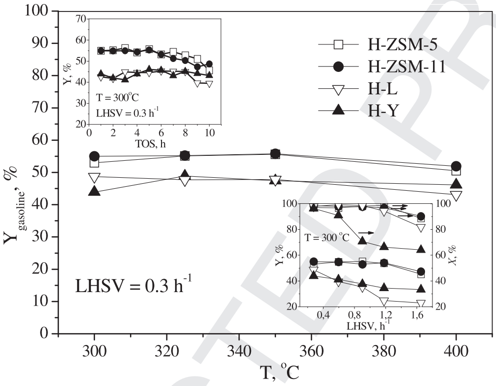
Anatoliy M. Varvarin *, Kostyantyn M. Khomenko, Volodymyr V. Brei

*Institute for Sorption and Endoecology Problems, The National Academy of Sciences of Ukraine, 13 General Naumov str., Kyiv 03164, Ukraine*

## HIGHLIGHTS

- ▶ H-ZSM-5, H-ZSM-11, H-L and H-Y provide 100% n-butanol conversion at $T \geqslant 300$ °C.
- ▶ The products are liquid hydrocarbons $C_{5-10}$, gaseous hydrocarbons $C_{<5}$ and water.
- ▶ The yield of liquid fraction is higher on the H-pentasils than on H-L and H-Y.
- ▶ H-ZSM-5 provides 50–55 wt.% yields of liquid hydrocarbons from spent alcohol.
- ▶ Liquid phase obtained on H-ZSM-5 includes aromatics mainly whereas on H-Y–olefins.

## GRAPHICAL ABSTRACT



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## ABSTRACT

n-Butanol conversion to hydrocarbons over H-ZSM-5, H-ZSM-11, H-L and H-Y zeolites at 300–400 °C using a fixed bed flow reactor has been studied. It was shown that all studied H-zeolites provide 100% alcohol conversion at $T \geqslant 300$ °C. The conversion products are liquid hydrocarbons $C_{5-10}$, gaseous hydrocarbons $C_{<5}$ and water. Their weight ratios are equal to 1:0.4:0.4 for H-ZSM-5 and 1:0.6:0.5 for H-Y (at 350 °C). The yield of liquid hydrocarbons over the H-pentasils is higher (52–55 wt.%) than/over large pore H-L and H-Y (43–48 wt.%). The liquid fraction obtained over H-ZSM-5 includes aromatics mainly whereas on H-Y–olefins. It was shown that H-ZSM-5 (Si/Al = 20) is capable to provide the yield of liquid hydrocarbons on the level of 50–55 wt.% from spent alcohol at load on a catalyst up to 20 mmol $C_4H_9OH\ g_{cat}^{-1}\ h^{-1}$.

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## 1. Introduction

Now conversion of bioalcohols, first of all of ethanol and butanol, over H-zeolite catalysts is considered as an alternative pathway for motor fuel production [1–9]. The catalytic transformation of ethanol into gasoline hydrocarbons has been extensively studied [1–6]. Less articles concern butanol conversion [7–9]. It was known that dehydration of butanol as well as ethanol is the first step of alcohol–gasoline conversion over solid acids [8]. Then formed butenes transform in gasoline hydrocarbons via dimerization, isomerization, aromatization, and alkylation reactions which occur in zeolite pores with participation of the B-sites [8].

In the present work the data of conversion of n-butanol into hydrocarbons over acid forms of some zeolites are presented.

## 2. Experimental

The ZSM-5 and ZSM-11 samples with an atomic ratio of Si/Al = 20 were synthesized hydrothermally according to the

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* Corresponding author. Tel./fax: +38 044 4525417.
*E-mail address:* an_atoliy@ukr.net (A.M. Varvarin).

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procedure described in [10,11]. Highly dispersed aluminum-containing silica (alumoaerosil) with $Al_2O_3$ content of 4.0 wt.% (Khlorvinil, Kalush, Ukraine) served as the source of silicon and aluminum. Tetrapropylammonium bromide (>98%, Fluka) and tetrabutylammonium bromide (99%, Aldrich) were used as templates for H-ZSM-5 and H-ZSM-11, respectively. The molar ratio of the components in the initial mixture corresponded to the formula: $100SiO_2$:$2.45Al_2O_3$:8.6RBr:11.4NaOH:$1580H_2O$ ($R = (C_3H_7)_4N^-$ or $(C_4H_9)_4N^-$). Calculated quantities of sodium hydroxide and template were dissolved in the distilled water. Then alumoaerosil was added to solution. The obtained suspension was stirred in order to obtain a homogeneous mixture which was further crystallized in a stainless-steel autoclave at 170 °C for 24 h. The obtained solid product was filtered, washed with distilled water, dried overnight at 100–110 °C, and calcinated at 560 °C for 4 h to remove organic template.

Zeolite L (Si/Al = 2.9) was obtained by dissolution of the hydrated alumina in a solution of potassium hydroxide, by addition of sodium hydroxide and amorphous silica to the mixture with subsequent treatment in an autoclave at 150 °C for 46 h. The formed solid material was filtered, washed to a pH about 9, and dried at 100 °C [12]. Also Na–Y faujasite (Si/Al = 2.6) (Reakhim, Russia) was tested.

H-zeolite samples were prepared by a twofold ion exchange with 2 M ammonium chloride at 90 °C under reflux, followed by washing with distilled water and calcination of samples at 550 °C for 4 h in air.

XRD patterns of the zeolites were recorded on a DRON-4-07 diffractometer with Cu K$\alpha$ radiation. Parameters of porous structure of catalysts were obtained from isotherms of nitrogen adsorption–desorption on a Quantochrome AS1Win analyzer. The total content of acid sites (BH) in the zeolites was determined by a standard method of back-titration of n-butylamine in cyclohexane with hydrochloric acid using bromothymol blue as indicator.

Catalytic experiments were performed in a flow steel reactor with a fixed catalyst bed at 250–400 °C under atmospheric pressure. The zeolite powder was pressed into pellets which were crushed. The sieved fraction (1–2 mm) of pressed zeolite (2.4 g, 4 $cm^3$) was placed in the reactor. The values of butanol LHSV were varied in the interval of 0.3–1.7 $h^{-1}$. It was corresponded to load on a catalyst of 5–28 mmol $C_4H_9OH$ $g_{cat}^{-1}$ $h^{-1}$. All zeolites were pretreated in an argon flow at 500 °C for 1 h. As a rule, the experiments were performed without any carrier gas. Its role was provided by the gaseous products of reaction. The liquid products were collected in an ice-cooled trap and separated into two phases (gasoline and water). The gaseous products were trapped using an ethanol bath refrigerated with liquid nitrogen. Propane–propene and butane–butene fractions were condensed in the interval temperature from −70 to −65 °C and from −35 to −30 °C, respectively. Ethane–ethene fraction which condenses at a temperature below −80 °C was not trapped. The liquid phases (organic and aqueous) and condensed gaseous products were weighted for mass balance calculation.

The liquid products, defined as gasoline, were analyzed using a gas chromatography (Chrom-5 with a 50 m capillary column), GC–MS spectroscopy (Thermo Trace GC Ultra/ISQ) and $^1H$ NMR spectroscopy (Bruker Avance-400). Usually gasoline is defined as a complex mixture of liquid aliphatic and aromatic hydrocarbons, ranging from $C_4$ to $C_{12}$ carbon atoms, whose boiling point range is 30–225 °C [13].

## 3. Results and discussion

The XRD patterns of synthesized ZSM-5, ZSM-11, L- and Y-zeolites are identical with those published in [14]. The values of surface area ($S_{BET}$), pore volume ($V_S$) and other textural parameters of zeolite samples are shown in Table 1. The content of acid sites in the structure of medium pore H-ZSM-5 and H-ZSM-11 zeolites is higher than that of large pore H-L and H-Y.

According to provided experiments n-butanol completely transforms into gaseous and liquid hydrocarbons and water at $T \geqslant 300$ °C over all studied zeolites. Full conversion of n-butanol on H-ZSM-5 at these temperatures was observed in [7] also. The yield of liquid hydrocarbons (Y, wt.%) from spent alcohol at different temperatures over various zeolites is shown in Fig. 1. The *Y* values are practically unchanged in the interval of 300–400 °C and reach 52–55 wt.% for H-ZSM-5 and H-ZSM-11 and 43–48 wt.% for H-L and H-Y zeolites. The yield of formed water is equal to 21–23 wt.% of total products that almost corresponds (24%) to the stoichiometrical dehydration of butanol to butenes. In contrast, 39 wt.% of ethanol is lost stoichiometrically as water at its conversion to hydrocarbons.

The obtained breakups of gaseous hydrocarbons formed at 350 °C over H-ZSM-5 and H-Y (LHSV = 0.3 $h^{-1}$) are as follows: $C_1$–$C_2$–5, $C_3$–8, $C_4$–10 wt.% and 6, 10, 12 wt.%, respectively.

Thus, the weight ratios of formed liquid hydrocarbons:gaseous hydrocarbons:water are equal to 1:0.4:0.4 for H-ZSM-5 and 1:0.6:0.5 for H-Y (at 350 °C).

The liquid phase yields are not changed significantly with time-on-stream (TOS) (Fig. 2). The zeolite activity is kept at least for 8–9 h at rather high temperature (300–350 °C). It is not typical of acid catalysts. Evidently that formed water prevents coke deposition on the catalyst surface. The effect of water on deactivation of H-ZSM-5 at ethanol conversion to hydrocarbons was studied in [16–18].

The yield of liquid product obtained over H-ZSM-5 and H-ZSM-11 does not significantly decrease at increasing LHSV values from 0.3 to 1.65 $h^{-1}$ (Fig. 3). In contrast, for H-L and H-Y the yield diminishes by 15–25 wt.%. Conversion of n-butanol begins to decrease on H-ZSM-5 and H-ZSM-11 at LHSV >1.2 $h^{-1}$ whereas it falls on H-L and H-Y at 0.9 and 0.3 $h^{-1}$, respectively (Fig. 3).

The H-ZSM-5 and H-ZSM-11 samples keep their activity at high loads on a catalyst up to 20 mmol $C_4H_9OH$ $g_{cat}^{-1}$ $h^{-1}$ (LHSV = 1.2 $h^{-1}$, Fig. 3). The productivity of H-L and H-Y samples decreases at loads above 10 mmol $C_4H_9OH$ $g_{cat}^{-1}$ $h^{-1}$.

The yield of liquid fraction over H-ZSM-5 decreases from 52–54 to 40–43 wt.% (300 °C, LHSV = 0.9 $h^{-1}$) in the case of using Ar as carrier gas due to the diminishing contact time of acid sites in zeolite pores with formed butenes for their subsequent transformation into heavier hydrocarbons.

The obtained liquid products include aliphatic, olefinic, and aromatic hydrocarbons (Tables 2 and 3). According to the

**Table 1**
Structural parameters and content of acid sites in studied H-zeolites.

| Catalyst | $S_{BET}$ ($m^2$ $g^{-1}$) | $V_S$ ($cm^3$ $g^{-1}$) | $V_{micro}$ ($cm^3$ $g^{-1}$) | $V_{meso}$ ($cm^3$ $g^{-1}$) | Pore size (nm) [15] | BH (mmol $g^{-1}$) |
|---|---|---|---|---|---|---|
| H-ZSM-5 | 390 | 0.219 | 0.162 | 0.057 | 0.51 × 0.55<br>0.53 × 0.56 | 1.7 |
| H-ZSM-11 | 380 | 0.224 | 0.165 | 0.059 | 0.53 × 0.54 | 1.5 |
| H-L | 300 | 0.197 | 0.089 | 0.108 | 0.71 × 0.71 | 0.9 |
| H-Y | 600 | 0.312 | 0.243 | 0.069 | 0.74 × 0.74 | 0.8 |

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