

ИССЛЕДОВАНИЕ ВЛИЯНИЯ КИСЛОТНОСТИ НА ПРОЦЕСС КАТАЛИТИЧЕСКОЙ ТРАНСФОРМАЦИИ Н-БУТАНОЛА В УГЛЕВОДОРОДЫ НА ЦЕОЛИТЕ H-ZSM-5

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Представленная статья посвящена изучению влияния кислотности цеолита H-ZSM-5 на процесс каталитической трансформации н-бутанола в углеводороды. В ходе исследований проведен синтез четырех образцов цеолита H-ZSM-5 гидротермальным методом с использованием гелей различного состава. Синтезированные образцы характеризовались сходными значениями удельной площади поверхности микропор 300-318 м²/г и мезопор 59-82 м²/г. При этом соотношение Si/Al в образцах варьировалось в диапазоне от 24 до 270, что способствовало изменению кислотности от 0,1 до 1,6 ммоль/г. Полученные цеолиты с различными кислотными свойствами были исследованы в процессе превращения н-бутанола в углеводороды при 400 °С и массовой объемной скорости подачи бутанола, равной 0,3 кг(ВнОН)/((кг(Кат)·ч). Научная новизна статьи заключается в определении корреляции кислотных свойств цеолита H-ZSM-5 и его активности в процессе каталитической трансформации бутанола. Впервые установлено, что повышение кислотности поверхности цеолита H-ZSM-5 способствует увеличению скорости трансформации бутанола с 0,16 кг(ВнОН)/((кг(Кат)·ч) до 0,27 кг(ВнОН)/((кг(Кат)·ч). Образцы цеолита с концентрацией кислотных центров 0,1 ммоль(NH₃)/г и 0,6 ммоль(NH₃)/г характеризовались отсутствием дезактивации в течение 24 ч, образцы цеолита с кислотностью 1,2 ммоль/г и 1,6 ммоль/г характеризовались падением активности на 15% и 52% вследствие увеличения скорости образования полиароматических углеводородов. Повышение кислотности цеолита с 0,1 до 1,6 ммоль(NH₃)/г приводит к увеличению концентрации ароматических углеводородов с 12 мас.% до 55 мас.%. При этом также наблюдается увеличение концентрации алканов с 14 мас.% до 32 мас.%, тогда как концентрация непредельных углеводородов снижается с 74 мас.% до 11 мас.%. На основании полученных данных определена корреляция начальной активности цеолита в реакции трансформации н-бутанола в углеводороды от количества активных центров.

Ключевые слова: н-бутанол, углеводороды, цеолит, H-ZSM-5, кислотный центр

STUDY OF THE EFFECT OF H-ZSM-5 ZEOLITE ACIDITY ON THE PROCESS OF CATALYTIC TRANSFORMATION OF N-BUTANOL INTO HYDROCARBONS

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The article is devoted to study of influence of the H-ZSM-5 zeolite acidity in the n-butanol to hydrocarbons catalytic transformation process. Four H-ZSM-5 samples were synthesized by hydrothermal method using different gel compositions. Synthesized samples were characterized by similar values of the micropores and mesopores specific surface areas 300-318 m²/g and 59-82 m²/g. However, the Si/Al ratio in the samples varied in the range from 24 to 270, which contributed to a

change in surface acidity from 0.1 to 1.6 mmol/g. Obtained samples with different acidic properties were tested in butanol to hydrocarbons transformation process provided at 400°C and 0.3 kg(BuOH)/((kg(Cat)·h) weight hourly space velocity. The novelty of the article is the determination of the correlation between the acidity of H-ZSM-5 and its activity in n-butanol catalytic transformation. It was found that an increase in the acidity of H-ZSM-5 zeolite surface promotes an increase in the rate of n-butanol transformation from 0.16 kg (BuOH)/((kg(Cat)·h) to 0.27 kg(BuOH)/((kg(Cat)·h). Zeolite samples with acid site concentrations of 0.1 mmol/g and 0.6 mmol/g were characterized by the absence of deactivation within 24 h, zeolite samples with the acidity of 1.2 mmol(NH₃)/g and 1.6 mmol(NH₃)/g were characterized by a decrease in activity by 15% and 52% due to an increase in polyaromatic hydrocarbons formation rate. An increase in the acidity of the zeolite from 0.1 to 1.6 mmol(NH₃)/g leads to an increase in the aromatic hydrocarbons concentration from 12 wt.% to 55 wt.%. An increase in alkanes concentration from 14 wt.% to 32 wt.% was also observed, while the concentration of unsaturated hydrocarbons decreased from 74 wt.% to 11 wt.%. Based on the obtained data, the correlation of the initial zeolite activity in n-butanol transformation into hydrocarbons on the concentration of the active sites was determined.

Key words: n-butanol, hydrocarbons, zeolite, H-ZSM-5, acid site

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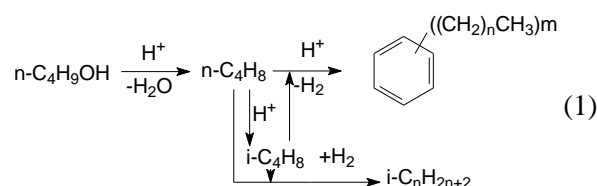
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INTRODUCTION

The global economy's shift toward the broad application of biofuel [1] because fossil fuel resources decrease needs rapid development of sustainable technologies for bio-renewable resources transformation into fuel compounds [2, 3]. Biobutanol is produced from lignocellulose biomass via the acetone-butanol-ethanol fermentation [4] process using genus *Clostridia* microorganisms [5]. Biobutanol can be directly blended into diesel fuel, but it is not applicable for direct blending to obtain gasoline [2]. Therefore, developing efficient routes for biobutanol transformation into gasoline range hydrocarbons is needed [6, 7]. Catalytic conversion of small chain alcohols – methanol and ethanol into aliphatic and aromatic hydrocarbons typically provided over different zeolites. The scientific community has extensively studied zeotypes since the seventies of the twentieth century [8-12]. However, the catalytic transformation of biobutanol to hydrocarbons is much less studied, with significant gaps in theoretical and experimental justification of catalyst structure influence on process peculiarities [13-15].

According to kinetic data and reaction products distribution [16], the n-butanol to hydrocarbons transformation process can be expressed by equation 1.



Butanol conversion passes through dehydration reaction with n-butene formation, n-butene isomerization to i-butene, n-butene, and i-butene aromatization with hydrogen release and n-butene, i-butene hydrogen transfer reaction with formation of alkanes. Zeolite acidity can be considered one of the critical factors for alcohols to the hydrocarbons transformation process [17, 18], but this issue was not studied well for the n-butanol transformation process [19, 20]. Typically, zeolite or zeotype acidity increase results in the appropriate increase of small chain alcohols chemical transformation depth and decrease of catalyst stability [21, 22]. Therefore, catalyst acidity strongly influences the process selectivity to hydrocarbons. The present article is devoted to the study of H-ZSM-5 zeolite acidity influence on the n-butanol catalytic transformation process.

MATERIALS AND METHODS

For H-ZSM-5 synthesis following reagents were purchased from a local supplier and used as it is: SiO₂ (chemical grade, 99.8 wt.%), NaOH (chemical

grade, 99.7 wt.%), Al₂O₃ (chemical grade, 99.8 wt.%), tetrapropylammonium bromide (TPABr, chemical grade, 98 wt.%) and NH₄NO₃ (chemical grade, 98.3 wt.%). For H-ZSM-5 samples initial gel solutions were characterized by following molar ratios of oxides 8Na₂O/100SiO₂/3TPABr/xAl₂O₃/3000H₂O (x = 0.05, 0.1, 0.25, 0.5 moles). Then 100 ml of gel was placed in a 300 ml autoclave with 175 ml of dead volume, and the autoclave was purged five times with nitrogen (chemical grade, 99.5 v.%) before reaction. Then it was heated up to 170 °C for 72 h under a 150 rpm stirring rate. Then synthesized samples were centrifuged and washed two times with distillate water excess. Then samples were shacked in 1M solution of NH₄NO₃ to obtain ammonium form of zeolite for three hours. Then the suspension was centrifuged, and zeolite was dried at 105 °C for 3 h, then calcination at 600 °C for one hour. Synthesized samples were designated as ZSM5-0.05, ZSM5-0.1, ZSM5-0.25, ZSM5-0.5 according to aluminum oxide concentration in reaction gel. Zeolite samples were characterized by nitrogen physisorption using the t-plot method applicable for micropores analysis using Beckman coulter SA 3100 nitrogen analyzer. Determination of zeolite samples surface acidity was made using AutoChem HP 2950 analyzer.

Samples were placed in cuvette and purged with helium under heating to 600 °C, cooled to 100 °C, purged with ammonia (10 wt.%) mixture in helium for one hour, and then heated in helium up to 600 °C with recording by heat transfer detector. Concentrations of alumina and silica were analyzed gravimetrically according to ISO 2598-1:1992 standard method. Butanol to hydrocarbons transformation reaction was provided in a tube reactor filled with H-ZSM-5 catalyst. Butanol was purged in the reactor by a pump through a heater [8, 9]. Butanol weight hourly space velocity (WHSV) was 0.3 kg(BuOH)/((kg(Cat)·h), reactor temperature was 400 °C, overall pressure in the reactor was 0.11 MPa. Catalyst regeneration was performed in a muffle furnace in the air by heating a zeolite sample up to 600 °C for three hours. Carbon depositions were determined gravimetrically after the reaction. Before analysis, 0.5g of used zeolite sample was washed with 75 ml of hexane. Hydrocarbon concentrations were analyzed using online gas chromatograph Kristall-2000M, and hydrocarbons composition was determined using gas chromatomass-spectrometer GS-MS Shimadzu 2010 QP according to ASTM D6730 - 21 standard method.

RESULTS AND DISCUSSIONS

Synthesized zeolite samples showed physicochemical characteristics typical for H-ZSM-5. The values of Si/Al, amount of chemisorbed ammonia, and

the t-plot surface area for synthesized zeolite samples are presented in Table 1. An increase in aluminum concentration during zeolite synthesis results in an appropriate decrease in Si/Al ratio, micropores surface area, and increase in surface acidity. At the same time, mesopores surface area has no correlation to aluminum concentration in the zeolite samples.

Table
Physicochemical properties of synthesized catalysts
Таблица. Физико-химические свойства синтезированных катализаторов

Sample	Si/Al	NH ₃ mmol/g	t-plot surface area, m ² /g	
			micro	meso
ZSM5-0.05	270	0.1	315	62
ZSM5-0.1	86	0.6	318	59
ZSM5-0.25	42	1.2	310	65
ZSM5-0.5	24	1.6	300	82

Ammonia chemisorption Fig.1 showed the presence of weak and strong Bronsted acid sites at 300-315 °C and 540-570 °C. The ratio of weak and strong Bronsted acid sites was 60/40 for all zeolite samples. An increase of aluminum initial concentration in zeolite samples results in an appropriate increase in the acidity of weak and strong Bronsted acid sites.

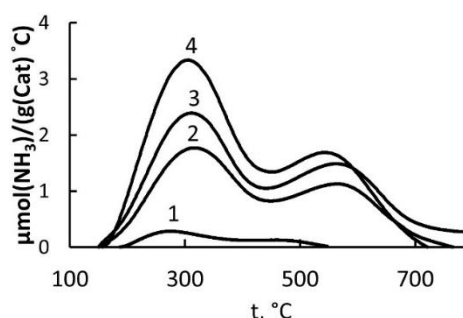


Fig. 1. Ammonia temperature-programmed desorption curves from synthesized zeolites (1 – ZSM5-0.05, 2 – ZSM5-0.1, 3 – ZSM5-0.25, 4 – ZSM5-0.5)

Рис. 1. Кривые десорбции аммиака с поверхности синтезированных цеолитов (1 – ZSM5-0,05, 2 – ZSM5-0,1, 3 – ZSM5-0,25, 4 – ZSM5-0,5)

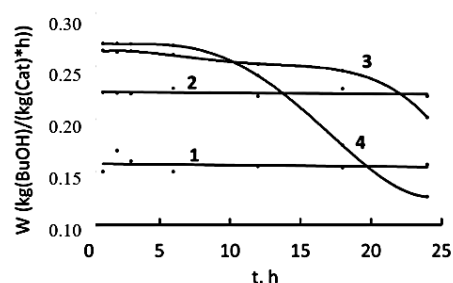


Fig. 2. Kinetic curves of butanol transformation rate on process time (1 – ZSM5-0.05, 2 – ZSM5-0.1, 3 – ZSM5-0.25, 4 – ZSM5-0.5)

Рис. 2. Кривые зависимости скорости трансформации бутанола от времени проведения процесса (1 – ZSM5-0,05, 2 – ZSM5-0,1, 3 – ZSM5-0,25, 4 – ZSM5-0,5)

Synthesized zeolites activity study in butanol to hydrocarbons transformation process showed that decrease of Si/Al ratio from 270 to 42 results in an appropriate increase of butanol transformation rate from 0.16 kg(BuOH)/(kg(Cat)h) to 0.26 kg(BuOH)/(kg(Cat)h), however further decrease of Si/Al ratio to 24 do not influence butanol transformation rate.

Zeolite samples ZSM5-0.05, ZSM5-0.1 characterized by Si/Al ratio 270 and 86 showed no deactivation, while ZSM5-0.25, ZSM5-0.5 samples with Si/Al ratio 42 and 24 showed strong deactivation after 20 h on stream and after 6 h on stream. Synthesized hydrocarbons consist of mainly three fractions – alkanes, alkenes, and aromatic hydrocarbon. Alkane fraction of butanol to hydrocarbons transformation process mainly contain following hydrocarbons: methane, ethane, propane, butane, 1, 2-methylbutan, 2-methylpentane, 3-methylpentane, *n*-hexane, 2-methylhexane, 3-methylhexane, *n*-heptane, 2-methylheptane, 3-methylheptane. Alkene's fraction is presented by the following hydrocarbons: 1-pentene, 2-methyl-1-butene, *trans*-2-hexene, *cis*-2-hexene, 1-methylcyclopentene. Aromatic fraction consists of following hydrocarbons: toluene, ethylbenzene, *p*-xylene, *m*-xylene, *o*-xylene, 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, 1,3,5-trimethylbenzene, *tert*-butylbenzene. Hydrocarbons fraction composition drastically depends on synthesized H-ZSM-5 samples structure and acidity (Fig. 3).

An increase of zeolite acidity from 0.1 to 1.6 mmol(NH₃)/g results in an increase of aromatic fraction concentration from 12 wt.% to 55 wt.% and alkanes fraction concentration from 14 wt.% to 32 wt.%, while alkenes fraction concentration decreases from 74 wt.% to 11 wt.%. Hydrocarbons fraction change can be attributed to an increase in aromatic hydrocarbons formation rate catalyzed by the increased quantity of acidic sites [14]. An increase in alkanes concentration is a result of a hydrogen transfer reaction that takes place during the aromatization process [20]. And alkenes concentration decreases as they are main reagents for aromatization and hydrogen transfer reactions. Taking into account the initial activity of synthesized zeolites (Fig. 2) and quantity of acid sites (Table 1), the correlation curve of initial H-ZSM-5 activity in butanol to hydrocarbons transformation rate on acid sites quantity was made (Fig. 4).

Fig. 4 shows that increase in H-ZSM-5 surface acidity up to 1.2 mmol(NH₃)/g results in an appropriate increase in butanol reaction rate, while the further increase in zeolite acidity leads to reaction rate stabilization. This behavior can be explained by diffusion limitations taking place in the case of high acid sites concentration [14, 19]. However, to overcome diffusion

limitations and to increase alcohols transformation rate, additional mesopores can be formed in the zeolite matrix.

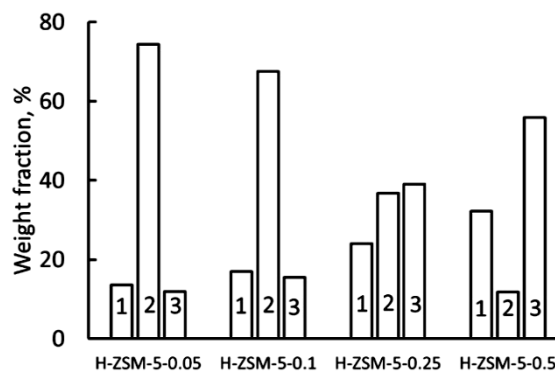


Fig. 3. Products distribution histogram for catalytic butanol transformation process (1 – alkanes, 2 – alkenes, 3 – aromatic hydrocarbons)
Рис. 3. Гистограмма распределения продуктов каталитической трансформации бутанола (1 – алканы, 2 – алкены, 3 – ароматические углеводороды)

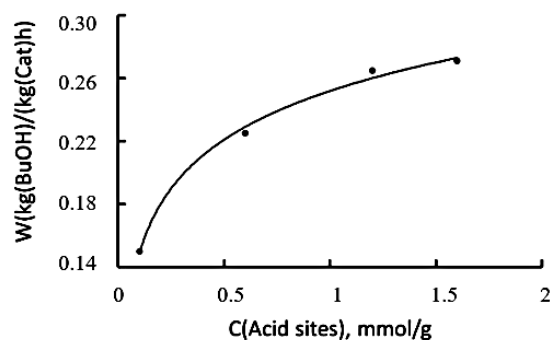


Fig. 4. Dependence of the initial rate of catalytic transformation of butanol on the number of acid sites for synthesized zeolites H-ZSM-5
Рис. 4. Зависимость начальной скорости каталитической трансформации бутанола от количества кислотных центров для синтезированных цеолитов H-ZSM-5

CONCLUSIONS

A series of H-ZSM-5 samples characterized by different initial amounts of alumina precursor were synthesized using the hydrothermal method. Zeolite samples had Si/Al ratios from 24 to 270, which resulted in zeolite surface acidity from 1.6 to 0.1 mmol(NH₃)/g. Micropores and mesopores surface areas were found to be 300-318 m²/g and 59-82 m²/g, which is typical for H-ZSM-5 zeolite. Ammonia chemisorption showed the presence of weak and strong Bronsted acid sites at 300-315 °C and 540-570 °C regions. Butanol transformation process was provided at 400 °C and 0.3 kg(BuOH)/((kg(Cat)·h) weight hourly space velocity. The reaction mixture contained water, gas, and liquid hydrocarbons fraction. Analyzed hydrocarbons consist of three fractions – alkanes, alkenes, and aromatics.

An increase of zeolite acidity from 0.1 to 1.6 mmol(NH₃)/g results in an increase of aromatic fraction concentration from 12 wt.% to 55 wt.% and alkanes fraction concentration from 14 wt.% to 32 wt.%, while alkenes fraction concentration decreases from 74 wt.% to 11 wt.%. An increase in aromatic hydrocarbons fraction concentration can be attributed to an increase in aromatization reactions rates due to an increase in acidic sites quantity. An increase in alkanes concentration in the reaction mixture is a result of a hydrogen transfer reaction taking place during the aromatization process. Alkenes concentration decreases as they are the main reagents for aromatization and hydrogen transfer reactions. An increase of H-ZSM-5 surface acidity up to 1.2 mmol(NH₃)/g results in an appropriate increase of butanol reaction rate, while the further increase of zeolite acidity leads to reaction rate stabilization. This behavior can be explained by diffusion limitations taking place in the case of high acid sites concentration. An increase in H-ZSM-5 surface acidity up to 0.6 mmol(NH₃)/g does not influence zeolite stability in butanol transformation reaction. The further increase of surface acidity favor increase of catalyst deactivation process, that can be subscribed to formation polyaromatics hydrocarbons and their strong adsorption over zeolite acid sites.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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