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КАТАЛИТИЧЕСКАЯ ТРАНСФОРМАЦИЯ МЕТАНОЛА НА ЦЕОЛИТЕ H-ZSM-5 В УСЛОВИЯХ МИКРОСТРУКТУРИРОВАННЫХ ПОТОКОВ

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Статья посвящена исследованию микроструктурированного монолитного катализатора, состоящего из основного слоя оксида алюминия, покрытого слоем H-ZSM-5, в реакции каталитического превращения метанола в углеводороды в условиях микроструктурированных потоков. Монолитный катализатор для микрореактора был сформирован из 90 мас.% оксида алюминия и 10% цеолита H-ZSM-5. Композицию прессовали в форме с последующей обработкой в водном растворе 0,1М гидроксида натрия в течение 3-х ч, сушкой при 105 °С в течение 2-х ч и прокаливанием при 600 °С. Синтезированный монолитный катализатор характеризовался диаметром 20 мм и длиной 50 мм, внутренние цилиндрические каналы имели диаметр 1 мм. На поверхность монолита был проведен вторичный рост цеолита H-ZSM-5. Монолит был помещен в 5 мас.% водный раствор бромида тетрапропиламмония, и после чего монолит помещался в автоклав, заполненный раствором прекурсоров молярного состава $7Na_2O:0,25Al_2O_3:100SiO_2:3500H_2O$ для гидротермального синтеза. Синтезированный катализатор был исследован методами хемосорбции аммиака, физической адсорбции азота, соотношение Si/Al было определено гравиметрическим методом. Каталитическое превращение метанола проводили в следующих условиях: массовая часовая объемная скорость метанола составляла 4 кг(MeOH)/(кг(Cat)×ч), температура реактора составляла 450 °С, общее давление в реакторе составляло 0,11 МПа. Применение монолитного микроструктурированного катализатора показало значительное повышение селективности процесса по отношению к образованию малых олефинов, включая этилен и пропилен. Скорость превращения метанола увеличилась с 2,8 кг(MeOH)/(кг (Cat) × ч) до 3,3 кг (MeOH)/(кг(Cat)×ч), а дезактивация катализатора не наблюдалась в течение 24 ч. Повышение селективности процесса превращения метанола в углеводороды, а также увеличение активности и стабильности монолитного микроструктурированного катализатора может быть объяснено увеличением массопереноса исходных реакционных веществ, промежуточных и конечных продуктов.

Ключевые слова: реактор с микроструктурированными потоками, метанол, углеводороды, цеолит, H-ZSM-5

CATALYTIC TRANSFORMATION OF METHANOL ON H-ZSM-5 ZEOLITE UNDER MICROFLUIDIC FLOW CONDITIONS

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The article is devoted to the study of microstructured alumina monolith covered with H-ZSM-5 layer in methanol to hydrocarbons transformation process in microfluidic conditions. The monolithic catalyst for the microreactor was formed using 90 wt.% alumina and 10% zeolite H-ZSM-5 mixture. The composition was pressed into a mold followed by treatment in an aqueous solution of 0.1M sodium hydroxide for 3 h, drying at 105 °C for 2 h and calcination at 600 °C. The synthesized monolithic catalyst was characterized by a diameter of 20 mm and a length of 50 mm. The inner cylindrical channels had a diameter of 1 mm. Secondary growth of H-ZSM-5 zeolite was carried out on the surface of the monolith. The monolith was placed in 5 wt.% aqueous solution of tetrapropylammonium bromide and then the monolith was placed in an autoclave filled with a solution of precursors of the molar composition $7Na_2O:0.25Al_2O_3:100SiO_2:3500H_2O$ for hydrothermal synthesis. The developed catalyst was analyzed by ammonia chemosorption, nitrogen physisorption, Si/Al ratio was determined gravimetrically. Methanol transformation reaction was performed in the following conditions: methanol weight hourly space velocity was 4 kg(MeOH)/((kg(Cat)×h), reactor temperature was 450 °C, overall pressure in the reactor was 0.11 MPa. Application of monolith microchannel catalyst showed a considerable increase in process selectivity to small olefins including ethylene and propylene. Methanol transformation rate rose from 2.8 kg(MeOH)/((kg(Cat)×h) to 3.3 kg(MeOH)/((kg(Cat)×h) and catalyst deactivation was not noticed for 24 h. The increase in methanol to hydrocarbons transformation process selectivity to olefins catalysts activity and stability can be subscribed to enhanced mass transfer of reaction substances, intermediates, and products.

Key words: microfluidic reactor, methanol, hydrocarbons, zeolite, H-ZSM-5

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INTRODUCTION

Microfluidic chemistry is of particular interest for high-performance synthesis of valuable substances due to enhanced mass [1] and heat transfer [2] in small diameter channels [2, 3]. Different types of microfluidic reactors [4], including plate [5] and capillary [6, 7] microchannel reactors, were fabricated and tested in various processes, mainly in fine organic synthesis [8-11] showed a considerable increase in reaction rates and process selectivity [3, 7]. However, microreactor application for basic organic synthesis is controversial issue due to microreactor high cost and difficulties of its fabrication [10]. One possible solution to overcome these disadvantages is an application of microchannel monolith [12] reactor that can be easily fabricated compared to a staleness steal reactor [13] and applied in high throughput industrial production systems. Methanol [14] to hydrocarbons catalytic transformation is a possible way for the production of synthetic hydrocarbons [15, 16], including aromatic hydrocarbons, olefins, and aliphatic hydrocarbons [17, 18]. Typically, methanol to hydrocarbons transformation process accompanies by rapid catalytic activity decrease due to active surface carbonization [19, 20]. However, this issue can be partly reduced by catalyst mass transfer intensification [21, 22] in the case of a thin catalyst layer in a microfluidic reactor [7, 21, 23]. The article is devoted to the study of methanol to hydrocarbons transformation process in microfluidic conditions.

MATERIALS AND METHODS

For providing experiments, chemical purity grade NaOH (99 wt.%), NH_4NO_3 (99 wt.%), SiO_2 (99 wt.%), Al_2O_3 (99 wt.%), H-ZSM-5 (98 wt.%, CVM, Si/Al = 40, Nizhny Novgorod sorbents), tetrapropilammonium bromide (98 wt.%) were purchased from a local supplier and used without further purification. Monolith chip for microreactor was formed using

90 wt.% alumina powder mixed with 10 wt.% of H-ZSM-5 powder. The composition was pressed in a mold, followed by handling in water solution of 0.1M of sodium hydroxide for 3 h followed by drying at 105 °C for 2 h and calcination at 600 °C. Synthesized cylindrical monolith chip was 20 mm in diameter and 50 mm in length, internal cylindrical channels have 1 mm in diameter. Then, secondary growth of H-ZSM was performed on the monolith surface. Monolith was placed in 5 wt. % tetrapropilammonium bromide water solution and stored for half an hour than monolith was mounted in autoclave filled with precursors solution characterized by molar composition $7Na_2O:0.25Al_2O_3:100SiO_2:3500H_2O$. The autoclave was heated up to 140 °C and monolith was stored in this solution for 65 h under soft stirring 120 rpm. Then monolith was washed with distillate water and placed in 1M solution of ammonia nitrate for 3 h, followed by washing with distillate water, filtration, drying, and calcination. Finally, after the H-ZSM-5 deposition process internal channels effective diameter was found to be 0.9 mm. For the determination of monolith surface acidity, ammonia chemosorption was performed using AutoChem HP 2950 analyzer. For analysis sample was placed in a quartz cuvette purged with helium under heating to 600 °C, cooled to ambient temperature, purged with ammonia (10 wt.%) mixture in helium for 1 h and then heated in helium to 600 °C. The internal and external surface area were determined using Beckman coulter SA 3100 nitrogen analyzer, and a t-plot model was applied. The Si and Al concentrations were analyzed gravimetrically according to ISO 2598-1:1992 standard method.

Methanol to hydrocarbons transformation reactor was studied in reactor set up showed on Fig. 1, consist of a flask with methanol, high-pressure pump for methanol supply, heater, microreactor for monolith catalyst and condenser.

In typical experiment, monolith catalysts placed in holder, methanol was pumped through the heater and reactor. Methanol weight hourly space velocity (WHSV) was 4 kg(MeOH)/((kg(Cat)×h), reactor temperature was 450 °C, overall pressure in the reactor was 0.11 MPa. Catalyst activation and regeneration process was performed in a muffle furnace in the air by heating monolith up to 600 °C for 3 h. After reaction catalyst samples were dried at 105 °C for 2 h and calcined in air at 600 °C for gravimetric carbon depositions determination.

RESULTS AND DISCUSSIONS

Determined physicochemical properties of produced catalysts are presented in table 1, Si/Al ratio values are close for both samples and typical for H-ZSM-5 [17, 19]. Synthesized monolith sample characterized by higher acids sites concentration micro and mesopore surface area compare to powdered H-ZSM-5 sample, therefore monolith sample should have higher catalytic activity.

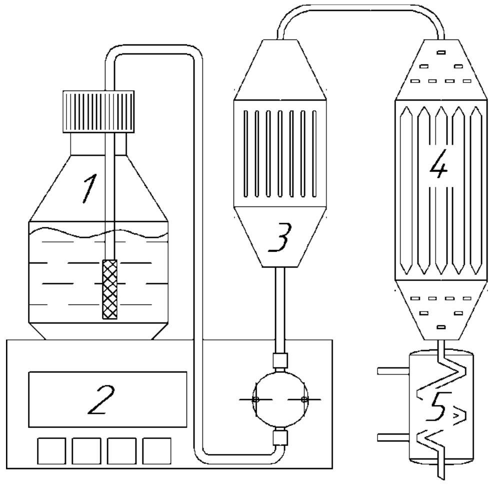

Fig. 1. Scheme of microfluidic set up for methanol to hydrocarbons catalytic transformation (1 – flask with methanol, 2 – high-pressure pump, 3 – microfluidic heater, 4 – microfluidic reactor for methanol to hydrocarbons transformation, 5 - condenser)
Рис. 1. Схема каталитической микрофлюидной установки для проведения каталитического процесса трансформации метанола в углеводороды (1 - емкость для метанола, 2 – насос высокого давления, 3 – микрофлюидный подогреватель, 4 – микрофлюидный реактор трансформации метанола в углеводороды, 5 - конденсатор).

Table 1

Physicochemical properties of developed H-ZSM-5 catalyst

***Таблица 1.* Физико-химические свойства синтезированных катализаторов**

Sample	$\frac{Si}{Al}$	NH_3 mmol/g	t-plot surface area, m^2/g	
			micropores	mesopores
Powder	40	1.2	218	41
Monolith	36	1.4	232	82

For comparison of methanol transformation in microchannel monolith reactor and fixed bed reactor experiments with powdered H-ZSM-5 diluted with silica was performed with WHSV equal to 4 kg(MeOH)/((kg(Cat)×h). The results of methanol conversion rate correlation on time on stream are presented in Fig. 2. The initial methanol transformation rate for reaction provided in microfluidic conditions is higher by 15% compared to reaction provided in fixed bed mode. Besides, drastic decrease in methanol transformation rate for 35% is noticeable for methanol transformation proses in fixed bed reactor to the end of 24 h on stream while for reaction provided in microflow conditions, there was not any decrease in catalytic activity.

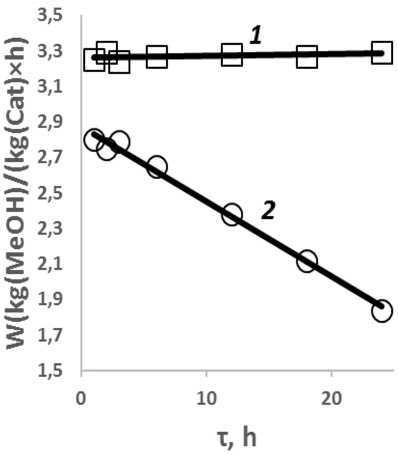

Fig. 2. Dependence of methanol transformation rate on zeolite H-ZSM-5 on the time of catalyst use (1 – methanol transformation in microfluidic conditions, 2 – for methanol transformation with fixed bed catalyst layer)

Рис. 2. Зависимость скорости трансформации метанола на цеолите H-ZSM-5 от времени использования катализатора (1-при проведении реакции в условиях микропотоков, 2 – при проведении реакции в закрепленном слое катализатора)

Identified reaction products include alkanes, olefins, and aromatic hydrocarbons. The considerable differences can be noticed in hydrocarbons composition for methanol to hydrocarbons transformation in microfluidic and fixed bed conditions in Fig. 3. Microfluidic conditions favor increase in ethylene and propylene concentration up to 8 wt.% and 18 wt.% respectively, while for methanol transformation process in fixed bed conditions ethylene and propylene concentration was found to be only 0.5 wt.% and 1.6 wt.%. Besides, some increase in aliphatic hydrocarbons concentration for 5 wt.% and drastic decrease in aromatic hydrocarbons concentration for 18 wt.% is noticeable for the microfluidic catalytic process.

Difference in reaction mixture hydrocarbons composition can be subscribed to better reaction products and initial substances diffusion conditions and better release of light reaction products in case of microfluidic conditions. While for fixed bed process due to diffusion limitations, light olefins take part in series of consecutive reactions with the final formation of different aromatic hydrocarbons.

Carbon deposition is the main reason for zeolite deactivation during methanol to hydrocarbons transformation process [18]. Increasing in carbon concentration in zeolite results in an appropriate decrease in catalytic activity. In the case of methanol transformation in microflow conditions, carbon concentration increases much slowly compares to methanol transformation process in fixed bed conditions, Fig. 4.

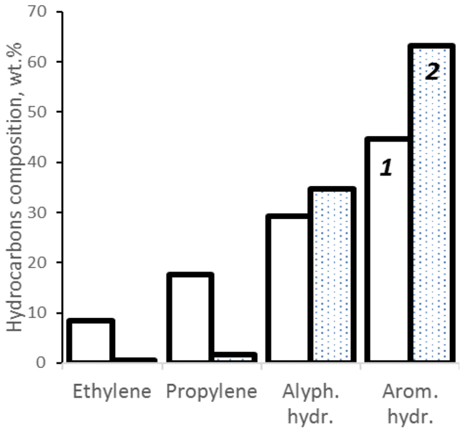

Fig. 3. Hydrocarbons composition in methanol to hydrocarbons catalytic transformation process over H-ZSM-5 zeolite (1 – methanol transformation in microfluidic conditions, 2 – for methanol transformation with fixed bed catalyst layer)

Рис. 3. Зависимость состава углеводородов, образующихся в результате каталитической трансформации метанола на цеолите H-ZSM-5 (1-при проведении реакции в условиях микропотоков, 2 – при проведении реакции в закрепленном слое катализатора)

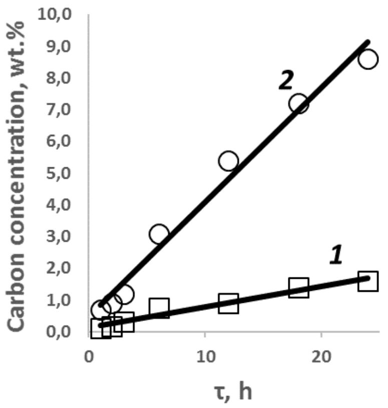

Fig. 4. Changes in carbon concentration during the catalytic transformation of methanol into hydrocarbons on zeolite H-ZSM-5 (1 – methanol transformation in microfluidic conditions, 2 – for methanol transformation with fixed bed catalyst layer)

Рис. 4. Изменение концентрации углерода в процессе каталитической трансформации метанола в углеводороды на цеолите H-ZSM-5 (1-при проведении реакции в условиях микропотоков, 2 – при проведении реакции в закрепленном слое катализатора)

Significant decrease in carbon deposits formation rate in case of microflow conditions can be subscribed to decrease in diffusion limitations, favor good transport of light hydrocarbons that slow down formation of heavy hydrocarbons responsible for carbon deposits formation and overall catalyst activity decrease.

Physicochemical properties of used H-ZSM-5 samples are presented in Table 2, Si/Al ratios values are close to initial samples values. Used powdered sample applied for methanol to hydrocarbons transformation in fixed bed reactor showed a considerable decrease in micropores surface area and zeolite acidity while mesopores surface area decrease not so with that can be explained by carbon deposition over catalysts surface, mainly in micropores of H-ZSM-5 zeolite. On the other side, monolith sample showed a decrease in acidity only for 15% and a decrease in micro and mesopores surface area for 3% and 5%, which can be explained by better mass transfer of reaction substrates and products in microfluidic conditions.

Table 2

Physicochemical properties of developed H-ZSM-5 catalysts after methanol to hydrocarbons transformation process*

***Таблица 2.* Физико-химические свойства использованных катализаторов**

Sample	Si/Al	NH_3 mmol/g	t-plot surface area, m^2/g	
			micropores	mesopores
Powder	38	0.6	114	36
Monolith	36	1.2	224	78

Note: * - reaction conditions WHSV - 4 kg(MeOH)/((kg(Cat)×h), reactor temperature – 450 °C, overall pressure in reactor was 0.11 MPa, time on stream 24 h

Примечание: * - условия реакции WHSV - 4 кг(MeOH)/ /((кг(Cat)×ч), температура реактора - 450 °C, общее давление в реакторе 0,11 МПа, время работы 24 ч.

CONCLUSION

Methanol to hydrocarbons transformation proses is a perspective method for obtaining synthetic hydrocarbons, including alkanes, olefins, and aromatic hydrocarbons as from traditional oil-based resources and from bio renewable resources. However, some technological issues, including low catalytic stability are still hindering the widespread application of this process in the industry. Methanol to hydrocarbons catalytic transformation in microfluidic conditions using monolith catalyst is a perspective way for solving these problems. Synthesis of monolith H-ZSM-5 on alumina support showed the possibility to obtain catalysts with practically the same physicochemical properties compare to powdered commercial H-ZSM-5 sample. Application of monolith microchannel catalyst showed a considerable increase in process selectivity to small olefins including ethylene and propylene. Besides, methanol transformation rate rose from 2.8 kg(MeOH)/((kg(Cat)×h) to 3.3 kg(MeOH)/((kg(Cat)×h) and catalyst deactivation was not noticed for 24 h on stream. Gravimetric determination of carbon depositions over H-ZSM-5 catalyst showed a decrease in carbon concentration from 9 wt.% down to 1.4 wt.% in case of methanol transformation in microfluidic operation mode. Physicochemical properties study monolith H-ZSM-5 zeolite showed a lower decrease in surface acidity and micropore surface area compared to the powdered sample. The increase in methanol to hydrocarbons transformation process selectivity to olefins catalysts activity and stability can be subscribed to enhanced mass transfer of reaction substances, intermediates, and products.

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

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