

UDC 544.47
AGRIS P33

https://doi.org/10.33619/2414-2948/85/08

CATALYTIC PROPERTIES STUDY OF MIXED MFI-MORD TYPE ZEOLITE IN BIOETHANOL TRANSFORMATION

©**Brovko R.**, ORCID: 0000-0001-9945-566X, SPIN-code: 1638-1220,
Scientific Technology University "Sirius", Tver State Technical University; Tver,
Federal territory "Sirius", Russia, romanvictorovich69@mail.ru

©**Lakina N.**, ORCID 0000-0002-7293-8781, SPIN-code: 3871-7341, Ph.D.,
Tver State Technical University, Tver, Russia, lakina@yandex.ru

©**Doluda V.**, ORCID: 0000-0002-2865-9945, SPIN-code: 8836-6137, Dr. habil.,
Tver State Technical University, Tver, Russia, doludav@yandex.ru

ИЗУЧЕНИЕ КАТАЛИТИЧЕСКИХ СВОЙСТВ СМЕШЕННОГО ЦЕОЛИТА MFI- MORD В РЕАКЦИИ КАТАЛИТИЧЕСКОЙ ТРАНСФОРМАЦИИ БИОЭТАНОЛА

©**Бровко Р. В.**, ORCID: 0000-0001-9945-566X, SPIN-код: 1638-1220, Тверской
государственный технический университет, Научно-технологический университет
«Сириус», федеральная территория «Сириус», г. Тверь, Россия, romanvictorovich69@mail.ru

©**Лакина Н. В.**, ORCID 0000-0002-7293-8781, SPIN-код: 3871-7341, канд. хим. наук, Тверской
государственный технический университет, г. Тверь, Россия, lakina@yandex.ru

©**Долуда В. Ю.**, ORCID: 0000-0002-2865-9945, SPIN-код: 8836-6137, д-р хим. наук,
Тверской государственный технический университет, г. Тверь, Россия, doludav@yandex.ru

Abstract. The decrease in stocks of traditional fossil fuels contributes to the widespread growth of interest in renewable sources of raw materials and energy. Bioethanol can become a serious alternative to traditional types of fossil raw materials and fuels due to the possibility of its widespread production from agricultural waste and wood processing. Bioethanol can be used directly as a fuel, or after transformation into hydrocarbons. The transformation of bioethanol into hydrocarbons is carried out using zeolites and zeotypes of various types, while the main problem encountered for these systems is deactivation during the catalytic transformation. In this case, one of the possible solutions to this problem is the regulation of the acidic and diffusion properties of the catalytic surface of zeolites. Changing the acidic properties can contribute to a significant increase in the stability and activity of zeolites. In this case, the variation of acidic properties is possible by combining different types of zeolites. The article presents the results of a study of a mixed zeolite of the MFI type and mordenite in the reaction of the transformation of ethanol into hydrocarbons. Zeolite synthesis was carried out by a sequential method using zeolite seed grains for the synthesis of MFI structures and n-butylamine for the synthesis of a mordenite layer. The synthesized sample was tested on a flow-type setup with a tubular reactor. The effect of temperature, specific ethanol feed rate, and total pressure in the system was investigated. An increase in the reaction temperature from 350 °C to 370 °C contributed to an increase in the rate of accumulation of liquid hydrocarbons from 0.52 to 0.64 g(HC)/(g(Cat)*h), while a further increase in temperature to 430 °C contributed to a decrease in the rate of formation of liquid hydrocarbons to 0.32 g(HC)/(g(Cat)*h). An increase in the specific feed rate of ethanol from 0.5 to 2 g(EtOH)/(g(Cat)*h) contributes to a decrease in the yield of liquid hydrocarbons. An increase in the total pressure in the system from 1 atm to 15 atm promotes an increase in the rate of accumulation of liquid hydrocarbons from 0.34 to 0.83 g(HC)/(g(Cat)*h).

Аннотация. Уменьшение запасов традиционного ископаемого топлива способствует повсеместному росту интереса к возобновляемым источникам сырья и энергии. Биоэтанол может стать серьезной альтернативой традиционным видам ископаемого сырья и топлива в связи с возможностью его широкого получения из отходов сельского хозяйства и деревопереработки. Биоэтанол может использоваться непосредственно в качестве топлива, или после трансформации в углеводороды. Трансформация биоэтанола в углеводороды проводится с использованием цеолитов и цеотипов различных видов, при этом основной встречающейся проблемой для этих систем является дезактивация в процессе каталитической трансформации. При этом одним из возможных решений этой проблемы является регулирование кислотных и диффузионных свойств каталитической поверхности цеолитов. Изменение кислотных свойств может способствовать существенному увеличению стабильности и активности цеолитов. При этом варьирование кислотных свойств возможно путем совмещения различных типов цеолита. В статье приводятся результаты исследования смешенного цеолита типа MFI и морденита в реакции трансформации этанола в углеводороды. Синтез цеолита производился последовательным методом с использованием затравочных зерен цеолита для синтеза MFI структур и н-бутиламина для синтеза слоя морденита. Тестирование синтезированного образца проводилось на установке проточного типа с трубчатым реактором. Было исследовано влияние температуры, удельной скорости подачи этанола и общего давления в системе. Увеличение температуры протекания реакции с 350 °C до 370 °C способствовало увеличению скорости накопления жидких углеводородов с 0,52 до 0,64 г(УВ)/(г(Кат)*ч), при этом дальнейшее увеличение температуры до 430 °C способствовало снижению скорости образования жидких углеводородов до 0,32 г(УВ)/(г(Кат)*ч). Увеличение удельной скорости подачи этанола с 0,5 до 2 г(ЭтОН)/(г(Кат)*ч) способствует уменьшению выхода жидких углеводородов. Увеличение общего давления в системе с 1 атм до 15 атм способствует росту скорости накопления жидких углеводородов с 0,34 до 0,83 г(УВ)/(г(Кат)*ч).

Keywords: zeolites, synthesis, acidity.

Ключевые слова: цеолиты, синтез, кислотность.

Introduction

Decreasing of fossil fuel production and annual growth of energy demand needs to develop sustainable methods of synthetic hydrocarbons production from renewable materials [1-4]. Bioethanol can be considered as sustainable material widely acceptable and easy producing through biofermentation of agriculture and wood processing residuals [4-6]. However direct application of bioethanol is problematic due to technical issues and in some countries because of social problems of bioethanol applications for beverage production. Therefore bioethanol needs to be transferred to some valuable product prior to its direct application. Catalytic bioethanol transformation is a process of special interest due to its industrial value for synthetic hydrocarbons synthesis for energy and transport demand. Bioethanol can be easily transferred to synthetic hydrocarbons applicable for transport application [7-11].

Typically, different zeolites and zeotypes are used as catalysts for bioethanol transformation. The main problem of zeolites application for bioethanol transformation is rapid deactivation of synthesized zeolites due to active sites carbonization. One possible solution to solve this problem can be application of mixed zeolite systems with mixed structure for better hydrocarbons diffusion and catalytic transformation [12-14].

MFI type zeolites are characterized by three-dimensional structure of straight channels connected to one another via the sinusoidal channels with diameter 5.1-5.6 Å. Morденite is characterized by two-dimensional channels structure with six ring pores opening acceptable for molecules diffusion with following dimensional parameters a: 1.57 Å, b: 2.95 Å, c: 6.45 Å. The article is devoted to MFI-mordenite catalytic properties study.

Materials and Methods

For obtaining mixed structure material consecutive MFI-mordenite synthesis was provided. For obtaining initial MFI zeolite chemical grade sodium hydroxide, sodium aluminate, silica gel and MFI zeolite seeds with purity not less than 99% were purchased from local supplier. Distillate water was purified using DE-25 aqua distillation system. Prior to synthesis silica gel was crashed in laboratory milling machine to obtained 10-100 µm particles fraction. In initial zeolite synthesis 9.54 g of sodium hydroxide 0.6 g of sodium aluminate 21.8 g of silica powder were dissolved in 250 ml of water in autoclave at 600 rpm and 70°C for one hour. Then temperature was set to 240°C for 72 hours. Reaction mixture was placed in IEC HN-SII centrifuge and initial zeolite was separated from reaction solution. Zeolite was washed with distillate water three times and dried in laboratory drier at 140°C. For mordenite synthesis ten grams of dried MFI zeolite samples were placed in autoclave and treated with two hundred milliliters of 0.1M solution of sodium hydroxide for one hour at 50°C for desoldering initial zeolite surface structure. Then suspension was placed on shell for sedimentation for two hours and solution was decanted and twenty milliliters of n-butylamine was added and stirred for three hours. Then mixture of reagents was added to gel consist of 1.6 g of sodium hydroxide, 1 g of sodium aluminate and 9.1 g of silica dissolved in 150 ml of distilled water. Then suspension was sealed in autoclave equipped with impeller and heated to 240°C for 72 hours. Then reaction mixture was placed in IEC HN-SII centrifuge and mixed zeolite was separated from reaction solution. Zeolite was washed with distillate water three times and dried in laboratory drier at 140°C. Synthesized MFI mordenite samples were designated according to synthesis procedure MFI-MORD. Mixed MFI mordenite sample was tested in ethanol catalytic process in tube reactor systems. Quantity of formed liquid hydrocarbons was calculated due to gravimetric data.

Results and Discussions

Reaction temperature is of great importance for catalytic performance in ethanol to hydrocarbons transformation process. Increasing of reaction temperature (Figure 1) from 350°C to 370°C results in appropriate increase of liquid hydrocarbons transformation rate from 0.52 g(HC)/(g(Cat)*h) up to 0.64 g(HC)/(g(Cat)*h), that can be explained by increase of hydrocarbons formation reactions rate.

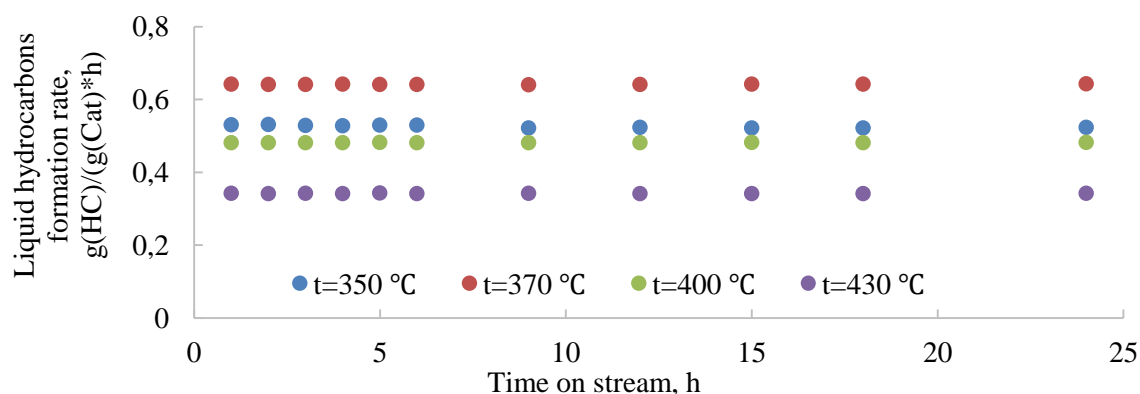


Figure 1. Influence of reaction temperature on liquid hydrocarbons formation rate (reaction temperature 350-430°C, ethanol liquid hourly space velocity 1 g(EtOH)/(g(Cat)*h))

Further increase of reaction temperature up to 430°C results in decrease of liquid hydrocarbons formation rate down to 0.32 g(HC)/(g(Cat)*h) that can be explained by increasing of liquid hydrocarbons destruction rate to gaseous hydrocarbons.

Increase of ethanol weight hourly space velocity (Figure 2) from 0.5 g(EtOH)/(g(Cat)*h) to 2 g(EtOH)/(g(Cat)*h) results in appropriate decrease of liquid ethanol formation rate that can be explained by decreasing of hydrocarbons chain growth rate.

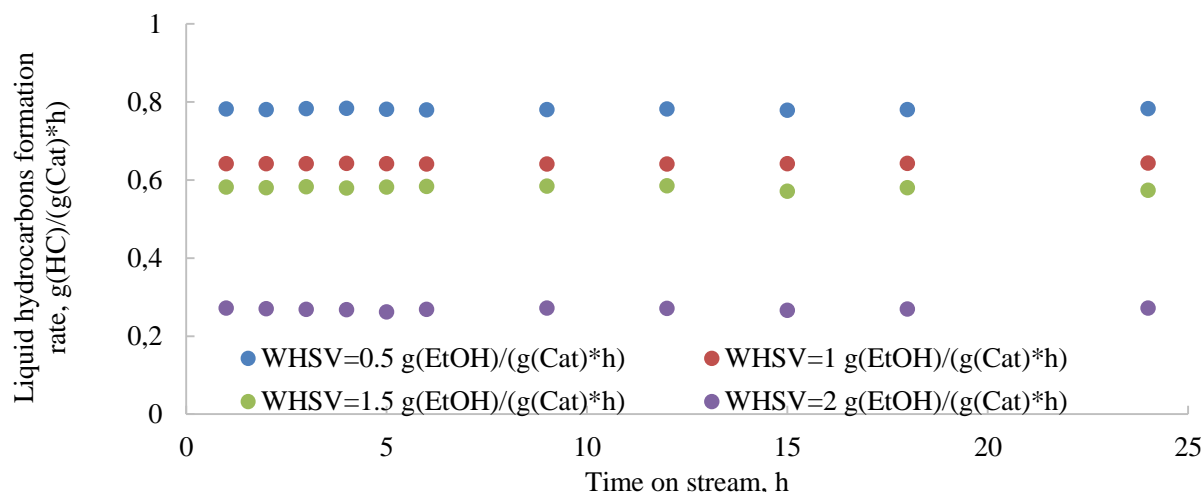


Figure 2. Influence of ethanol weight hourly space velocity on liquid hydrocarbons formation rate (reaction temperature 370°C, ethanol liquid hourly space velocity 0.5-2 g(EtOH)/(g(Cat)*h))

Pressure influence is of great importance on ethanol to hydrocarbons transformation rate (Figure 3). Increasing of system pressure from 1 to 15 Bars results in appropriate increase of hydrocarbons formation rate from 0.34 to 0.83 g(HC)/(g(Cat)*h).

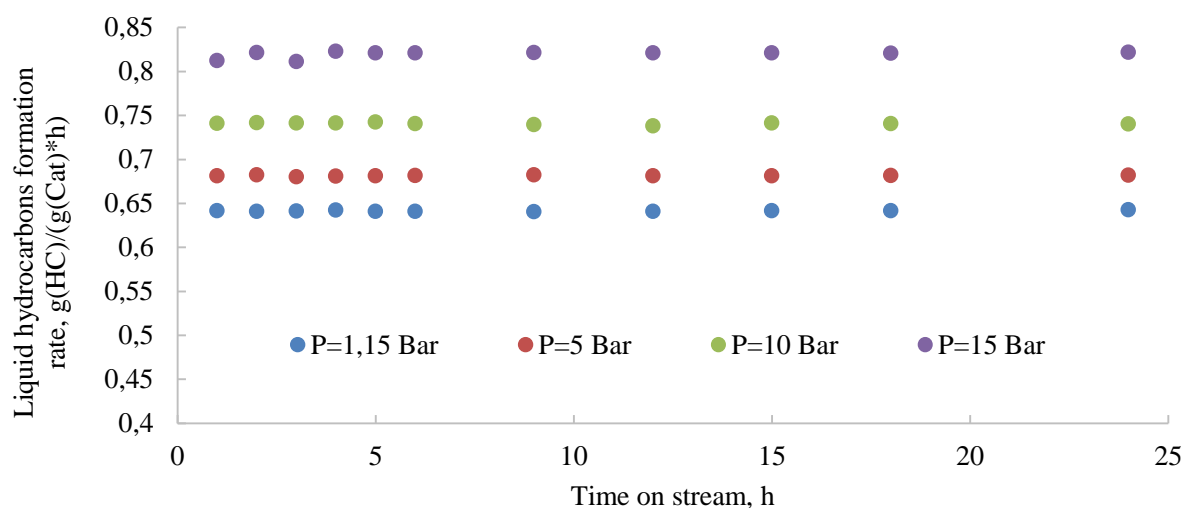


Figure 3. Influence of system pressure on liquid hydrocarbons formation rate (reaction temperature 370°C, ethanol liquid hourly space velocity 1 g(EtOH)/(g(Cat)*h))

However, increase of system pressure results in shift of formed hydrocarbons to heavy products due to enhanced hydrocarbons chain grows under high pressure.

Conclusions

Ethanol to hydrocarbons transformation rate strongly influenced by process conditions. Increasing of reaction temperature from 350°C to 370°C results in appropriate increase of liquid hydrocarbons transformation rate from 0.52 g(HC)/(g(Cat)*h) up to 0.64 g(HC)/(g(Cat)*h), that can be explained by increase of hydrocarbons formation reactions rate. Further increase of reaction temperature up to 430°C results in decrease of liquid hydrocarbons formation rate down to 0.32 g(HC)/(g(Cat)*h) that can be explained by increasing of liquid hydrocarbons destruction rate to gaseous hydrocarbons. Increase of ethanol weight hourly space velocity from 0.5 g(EtOH)/(g(Cat)*h) to 2 g(EtOH)/(g(Cat)*h) results in appropriate decrease of liquid ethanol formation rate that can be explained by decreasing of hydrocarbons chain growth rate. Increase of system pressure from 1 to 15 Bars results in appropriate increase of hydrocarbons formation rate from 0.34 to 0.83 g(HC)/(g(Cat)*h).

Acknowledgments: The reported study was funded by Russian Foundation for Basic Research (RFBR), project number 20-08-00191.

References:

1. Madhuvanthi, S., Jayanthi, S., Suresh, S., & Pugazhendhi, A. (2022). Optimization of consolidated bioprocessing by response surface methodology in the conversion of corn stover to bioethanol by thermophilic *Geobacillus thermoglucosidasius*. *Chemosphere*, 135242. <https://doi.org/10.1016/j.chemosphere.2022.135242>
2. Singh, A., Singhanian, R. R., Soam, S., Chen, C. W., Haldar, D., Varjani, S., ... & Patel, A. K. (2022). Production of bioethanol from food waste: Status and perspectives. *Bioresource Technology*, 127651. <https://doi.org/10.1016/j.biortech.2022.127651>
3. Li, J., Xiong, F., Fan, M., & Chen, Z. (2022). The role of nonfood bioethanol production in neutralizing China's transport carbon emissions: An integrated life cycle environmental-economic assessment. *Energy for Sustainable Development*, 70, 68-77. <https://doi.org/10.1016/j.esd.2022.06.002>
4. Lee, J., Kim, S., Lee, K. H., Lee, S. K., Chun, Y., Kim, S. W., ... & Yoo, H. Y. (2022). A design based on glucose conversion from waste chestnut shells has successfully improved glucose recovery and can contribute to a sustainable society through bioethanol production. *Environmental Technology & Innovation*, 102955. <https://doi.org/10.1016/j.eti.2022.102955>
5. Santoyo-Castelazo, E., Santoyo, E., Zurita-García, L., Luengas, D. C., & Solano-Olivares, K. (2023). Life cycle assessment of bioethanol production from sugarcane bagasse using a gasification conversion Process: Bibliometric analysis, systematic literature review and a case study. *Applied Thermal Engineering*, 219, 119414. <https://doi.org/10.1016/j.applthermaleng.2022.119414>
6. Zhang, J., Rentizelas, A., Zhang, X., & Li, J. (2022). Sustainable production of lignocellulosic bioethanol towards zero waste biorefinery. *Sustainable Energy Technologies and Assessments*, 53, 102627. <https://doi.org/10.1016/j.seta.2022.102627>
7. Periyasamy, S., Isabel, J. B., Kavitha, S., Karthik, V., Mohamed, B. A., Gizaw, D. G., ... & Aminabhavi, T. M. (2022). Recent Advances in Consolidated Bioprocessing for Conversion of Lignocellulosic Biomass into Bioethanol-A Review. *Chemical Engineering Journal*, 139783. <https://doi.org/10.1016/j.cej.2022.139783>
8. Bender, L. E., Lopes, S. T., Gomes, K. S., Devos, R. J. B., & Colla, L. M. (2022). Challenges in bioethanol production from food residues. *Bioresource Technology Reports*, 101171. <https://doi.org/10.1016/j.biteb.2022.101171>

9. Papadopoulos, K. P., Economou, C. N., Stefanidou, N., Moustaka-Gouni, M., Genitsaris, S., Aggelis, G., ... & Vayenas, D. V. (2023). A semi-continuous algal-bacterial wastewater treatment process coupled with bioethanol production. *Journal of Environmental Management*, 326, 116717. <https://doi.org/10.1016/j.jenvman.2022.116717>
10. Rico, X., Yáñez, R., & Gullón, B. (2023). Evaluation of strategies for enhanced bioethanol production from melon peel waste. *Fuel*, 334, 126710. <https://doi.org/10.1016/j.fuel.2022.126710>
11. Maity, S., & Mallick, N. (2022). Bioprospecting marine microalgae and cyanobacteria as alternative feedstocks for bioethanol production. *Sustainable Chemistry and Pharmacy*, 29, 100798. <https://doi.org/10.1016/j.scp.2022.100798>
12. Pilar, R., Moravkova, J., Sadovska, G., Sklenak, S., Brabec, L., Pastvova, J., & Sazama, P. (2022). Controlling the competitive growth of zeolite phases without using an organic structure-directing agent. Synthesis of Al-rich* BEA. *Microporous and Mesoporous Materials*, 333, 111726. <https://doi.org/10.1016/j.micromeso.2022.111726>
13. Yu, Q., Cheng, H., Tang, X., Yi, H., Ren, X., & Li, Z. (2022). Progress in the synthesis of small-pore zeolites for purifying NOx from motor vehicle exhaust. *Journal of Cleaner Production*, 135119. <https://doi.org/10.1016/j.jclepro.2022.135119>
14. Li, Z., Liu, Y., Dou, T., Li, X., Di, C., & Chen, S. L. (2022). Sustainable synthesis of AEI/CHA intergrowth zeolites for methanol-to-olefins conversion. *Microporous and Mesoporous Materials*, 344, 112201. <https://doi.org/10.1016/j.micromeso.2022.112201>

Список литературы:

1. Madhuvanthi S., Jayanthi S., Suresh S., Pugazhendhi A. Optimization of consolidated bioprocessing by response surface methodology in the conversion of corn stover to bioethanol by thermophilic *Geobacillus thermoglucosidasius* // *Chemosphere*. 2022. P. 135242. <https://doi.org/10.1016/j.chemosphere.2022.135242>
2. Singh A., Singhania R. R., Soam S., Chen C. W., Haldar D., Varjani S., Patel A. K. Production of bioethanol from food waste: Status and perspectives // *Bioresource Technology*. 2022. P. 127651. <https://doi.org/10.1016/j.biortech.2022.127651>
3. Li J., Xiong F., Fan M., Chen Z. The role of nonfood bioethanol production in neutralizing China's transport carbon emissions: An integrated life cycle environmental-economic assessment // *Energy for Sustainable Development*. 2022. V. 70. P. 68-77. <https://doi.org/10.1016/j.esd.2022.06.002>
4. Lee J., Kim S., Lee K. H., Lee S. K., Chun Y., Kim S. W., Yoo H. Y. A design based on glucose conversion from waste chestnut shells has successfully improved glucose recovery and can contribute to a sustainable society through bioethanol production // *Environmental Technology & Innovation*. 2022. P. 102955. <https://doi.org/10.1016/j.eti.2022.102955>
5. Santoyo-Castelazo E., Santoyo E., Zurita-García L., Luengas D. C., Solano-Olivares K. Life cycle assessment of bioethanol production from sugarcane bagasse using a gasification conversion Process: Bibliometric analysis, systematic literature review and a case study // *Applied Thermal Engineering*. 2023. V. 219. P. 119414. <https://doi.org/10.1016/j.applthermaleng.2022.119414>
6. Zhang J., Rentizelas A., Zhang X., Li J. Sustainable production of lignocellulosic bioethanol towards zero waste biorefinery // *Sustainable Energy Technologies and Assessments*. 2022. V. 53. P. 102627. <https://doi.org/10.1016/j.seta.2022.102627>
7. Periyasamy S., Isabel J. B., Kavitha S., Karthik V., Mohamed B. A., Gizaw D. G., Aminabhavi T. M. Recent Advances in Consolidated Bioprocessing for Conversion of

Lignocellulosic Biomass into Bioethanol-A Review // Chemical Engineering Journal. 2022. P. 139783. <https://doi.org/10.1016/j.cej.2022.139783>

8. Bender L. E., Lopes S. T., Gomes K. S., Devos R. J. B., Colla L. M. Challenges in bioethanol production from food residues // Bioresource Technology Reports. 2022. P. 101171. <https://doi.org/10.1016/j.biteb.2022.101171>

9. Papadopoulou K. P., Economou C. N., Stefanidou N., Moustaka-Gouni M., Genitsaris S., Aggelis G., Vayenas D. V. A semi-continuous algal-bacterial wastewater treatment process coupled with bioethanol production // Journal of Environmental Management. 2023. V. 326. P. 116717. <https://doi.org/10.1016/j.jenvman.2022.116717>

10. Rico X., Yáñez R., Gullón B. Evaluation of strategies for enhanced bioethanol production from melon peel waste // Fuel. 2023. V. 334. P. 126710. <https://doi.org/10.1016/j.fuel.2022.126710>

11. Maity S., Mallick N. Bioprospecting marine microalgae and cyanobacteria as alternative feedstocks for bioethanol production // Sustainable Chemistry and Pharmacy. – 2022. – T. 29. – С. 100798. <https://doi.org/10.1016/j.scp.2022.100798>

12. Pilar R., Moravkova J., Sadovska G., Sklenak S., Brabec L., Pastvova J., Sazama P. Controlling the competitive growth of zeolite phases without using an organic structure-directing agent. Synthesis of Al-rich* BEA // Microporous and Mesoporous Materials. 2022. V. 333. P. 111726. <https://doi.org/10.1016/j.micromeso.2022.111726>

13. Yu Q., Cheng H., Tang X., Yi H., Ren X., Li Z. Progress in the synthesis of small-pore zeolites for purifying NOx from motor vehicle exhaust // Journal of Cleaner Production. 2022. P. 135119. <https://doi.org/10.1016/j.jclepro.2022.135119>

14. Li Z., Liu Y., Dou T., Li X., Di C., Chen S. L. Sustainable synthesis of AEI/CHA intergrowth zeolites for methanol-to-olefins conversion // Microporous and Mesoporous Materials. 2022. V. 344. P. 112201. <https://doi.org/10.1016/j.micromeso.2022.112201>

*Работа поступила
в редакцию 10.11.2022 г.*

*Принята к публикации
19.11.2022 г.*

Ссылка для цитирования:

Brovko R., Lakina N., Doluda V. Catalytic Properties Study of Mixed MFI-MORD Type Zeolite in Bioethanol Transformation // Бюллетень науки и практики. 2022. Т. 8. №12. С. 67-73. <https://doi.org/10.33619/2414-2948/85/08>

Cite as (APA):

Brovko R., Lakina N., Doluda V. (2022). Catalytic Properties Study of Mixed MFI-MORD Type Zeolite in Bioethanol Transformation. *Bulletin of Science and Practice*, 8(12), 67-73. <https://doi.org/10.33619/2414-2948/85/08>