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CONVERSION OF METHANOL TO -OLEFINS IN THE PRESENCE OF CERIUM-MODIFIED ZSM-5 TYPE ZEOLITE CATALYSTS

Research article

Amirova G.A.[1], Mamedov S.E.[2], Mamedov E.S.[3], *
[1, 2, 3] Baku State University, Baku, Azerbaijan

* Corresponding author (g.amirova0803[at]gmail.com)

Abstract

In an effort to enhance selectivity towards light olefins, particularly propylene, ZSM-5 zeolite and cerium-based catalytic formulations were synthesized utilizing a solid phase modification approach, and their catalytic characteristics were examined in the methanol conversion process to -olefins. The conversion of methanol to hydrocarbons was conducted within a flow-type apparatus, utilizing a stationary layered catalyst, across a temperature spectrum of 250–550°C, with a methanol volumetric feed rate of 2.0 under atmospheric pressure and in the presence of nitrogen gas.

It has been demonstrated that, following the modification, cerium oxide nanoparticles exhibit a dispersed distribution on the external surface and within the pores of the zeolite, thereby interacting with its crystalline lattice, which results in a reduction of the density of strong acid centers. The density of strong acid centers within the zeolite is influenced by the concentration of cerium present. An increment in the cerium concentration within the zeolite up to 5.0 wt % leads to a decline in selectivity towards ethylene. Notably, a high selectivity for propylene (39.7%) is observed in 4% Ce-HZSM-5 at 550°C, while a substantial selectivity for butylenes (23.1–23.7%) is noted in 5% Ce-HZSM-5 at temperatures ranging from 400–450°C. Furthermore, a significant selectivity for -olefins (72.4%) is attained using the 4% Ce-HZSM-5 catalyst at 500°C. The observed enhancement in selectivity for both propylene and butylene can be attributed to the diminished density of strong acid centers resulting from the modification process.

Keywords: methanol conversion, selectivity of light olefins, zeolite ZSM-5, modification, cerium.

КОНВЕРСИЯ МЕТАНОЛА В -ОЛЕФИНЫ В ПРИСУТСТВИИ МОДИФИЦИРОВАННЫХ ЦЕРИЕМ ЦЕОЛИТНЫХ КАТАЛИЗАТОРОВ ТИПА ZSM-5

Научная статья

Амирова Г.А.[1], Мамедов С.Э.[2], Мамедов Э.С.[3], *
[1, 2, 3] Бакинский государственный университет, Баку, Азербайджан

* Корреспондирующий автор (g.amirova0803[at]gmail.com)

Аннотация

Для повышения селективности по отношению к легким олефинам, в частности пропилену, были синтезированы каталитические составы на основе цеолита ZSM-5 и церия с использованием метода твердофазной модификации, а их каталитические характеристики были исследованы в процессе конверсии метанола в олефины. Конверсию метанола в углеводороды проводили в аппарате проточного типа, используя стационарный слоистый катализатор, в температурном диапазоне 250–550°C, при объемной скорости подачи метанола 2,0 при атмосферном давлении и в присутствии газообразного азота.

Было продемонстрировано, что после модификации наночастицы оксида церия дисперсно распределяются на внешней поверхности и в порах цеолита, взаимодействуя с его кристаллической решеткой, что приводит к уменьшению плотности сильных кислотных центров. Плотность центров сильных кислот в цеолите зависит от концентрации церия. Увеличение концентрации церия в цеолите до 5,0 масс. % приводит к снижению селективности по отношению к этилену. Примечательно, что высокая селективность по пропилену (39,7%) наблюдается в 4%-ном Ce-HZSM-5 при 550 °C, в то время как значительная селективность по бутилену (23,1–23,7%) отмечается в 5%-ном Ce-HZSM-5 при температурах 400–450 °C. Кроме того, значительная селективность по -олефинам (72,4%) достигается при использовании катализатора 4% Ce-HZSM-5 при 500°C. Наблюдаемое увеличение селективности по пропилену и бутилену можно объяснить уменьшением плотности центров сильных кислот в результате процесса модификации.

Ключевые слова: конверсия метанола, селективность по легким олефинам, цеолит ZSM-5, модификация, церий.

Introduction

C_2_C_4 olefinic hydrocarbons are essential precursors in the petrochemical industry, primarily produced through the pyrolytic breakdown of oil fractions, thermal cracking, and the dehydrogenation of light alkanes using traditional methods. Recently, significant attention has been focused on the recovery of valuable olefins, aromatic compounds, and isoparaffins from alternative regenerated feedstocks, particularly in the presence of high-silica ZSM-5 type zeolite catalysts [1], [2], [3], [4]. The production of light C_2_C_4 olefins and hydrocarbons within the gasoline range from natural gas, which serves as a feasible alternative to petroleum, through synthetic gas and methanol derived from biomass, represents one of the most effective strategies. Currently, Mobil Oil Corporation has initiated the production of C_2_C_4 olefins utilizing catalysts based on SAPO-34 molecular sieves in the Methanol-to-Olefins (MTO) process. SAPO-34 has demonstrated efficacy as a catalyst for the selective conversion of methanol to ethylene, achieving a 100% conversion rate under mild operational conditions. However, achieving high yields of propylene remains a significant challenge [5], [6], [7], [8]. Among the various molecular sieves, the ZSM-5 type zeolite employed in the MTO reaction is characterized by its network of intersecting salt (0.51x0.53 nm) and sinusoidal (0.53x0.55 nm) nanoscale channels, along with a high specific surface area and remarkable resistance to acidic conditions and deactivation, making it particularly promising. Numerous studies have investigated the effects of different metallic species on the catalytic properties of ZSM-5 zeolite catalysts, aiming to enhance selectivity through variations in charge distributions. ZSM-5 zeolite catalysts modified with metals such as Ca, Cr, Cu, Li, Mg, Ni, and Cu show significant selectivity towards light olefins. Among the modified ZSM-5 zeolite variants with Mn, Cr, Fe, Ni, and Ag, the Mn/HZS variant has been noted for its performance [8], [9], [10], [12].

ZSM-5 zeolite can undergo modification using phosphorus compounds such as metaphosphoric acid, ammonium dihydrogen phosphate, and trimethyl phosphite to enhance its selectivity for light olefins. A notable yield of 47.01% propylene was achieved from methanol conversion when utilizing a ZSM-5 zeolite catalyst that had been modified with 90% phosphorus [13], [14], [15]. This zeolite effectively transforms methanol into light C_2-C_4 olefins and p-xylene with significant selectivity following solid-phase modification with Neodium oxide [16].

Furthermore, ZSM-5 zeolite catalysts that have been modified with non-transition elements (NTE), including La, Ce, Pr, Nd, Sn, and En, demonstrated considerable activity for producing C_2-C_4 olefins during butane cracking. In light of these findings, this study investigates the influence of cerium concentration on the catalytic performance of ZSM-5 zeolite in the methanol conversion process, particularly focusing on the production of light C_2-C_4 olefins, with an emphasis on propylene [17], [18].

Experimental part

Commercial zeolite ZSM-5 (SiO_2/Al_2O_3=40; Na_2O<0,05 wt.q) was used to prepare the catalysts. The catalytic compositions were prepared by solid-phase modification of cerium carbonate with HZSM-5 zeolite in a ball vibrating mill for 2 hours followed by calcination at 300° and 500°C for 4 hours respectively. All samples were pressed, and pulverized, then a 1,0–1,5 mm diameter fraction was selected for testing. The content of cerium catalytic composition was 1,0–5.0 wt.q RFA of the syntesited catalysts was carried out using a RIGAKU “MINIFLEX” X-ray diffractometer with CuKt radiation according to the method described in [19].

The catalytic experiments were carried out in a flow tubular quarts reactor (length 10 cm, inner diameter 1,0 cm) with a stationary bed loaded with 2.0 g of catalyst, a volumetric feed rate of methanol in the temperature range of 300°–550°C.

2.0 h^{-1} in the presence of nitrogen (CH_3OH/ N_2=0.33 mol). The reaction products were analyzed on an Agilent GC782A gas chromatograph according to the procedure described in [19].

Result and discussion

Figure 1 shows the X-ray diffraction images of HZSM-5 and Ce/HZSM-5 modified catalysts. When compared with the standard reference sample (ICDD No. 0.1-0.86-1722), there are noticeable peaks for all the samples at 2θ positions of 7.9°, 8.88°, 23.2°, 23.3°, and 24°, which are representative of the MFI framework zeolite crystals. This implies that there is no structural change in the zeolite framework after cerium metal is used in the modification. In addition, distinctive diffraction peaks for cerium oxide were not shown in this image (X-ray diffraction). This was probably because the high distribution of nanosized cerium oxide on zeolite surface and pore entrances. The relationship between temperature and methanol conversion rates for cerium-modified samples is as shown in Figure 2. For unmodified HZSM-5 zeolite, methanol conversion reaches 100% at temperatures greater than 306 °C. Samples that have been modified exhibit catalytic activity that quite variably depends on how much cerium is in the sample. The more cerium that is in the sample, the more cerium is in the zeolite matrix, the warmer the sample has to get before methanol is completely converted to something else.

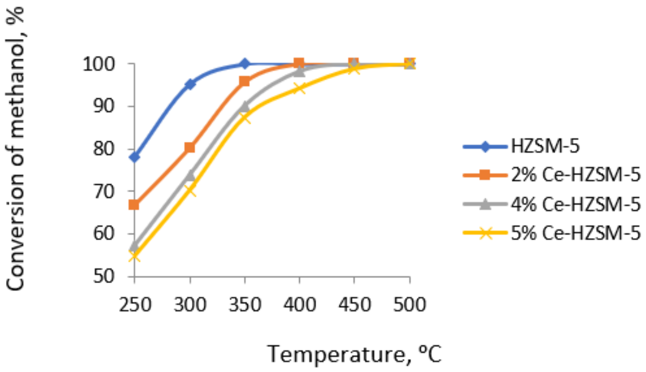

Figure 1 - Temperature dependence of methanol conversion on HZSM-5 and modified samples
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There are two instances of this: 2.0 wt % and 5.0 wt %. They give two different temperatures before methanol is completely converted: 400°C and 500°C. In between these two events, we can assume that there are some molecules that have converted and some molecules that haven't. Table 1 suggests that these events may be caused by reducing the amount of Brønsted acid present in the reheated samples that were heated before methanol was added.

It is evident that an increase in cerium concentration within HZSM-5 zeolite to 5.0 wt% corresponds with a decline in the concentration of robust acid sites, decreasing from 235 μmol/g to 114 μmol/g.

Between these two states, in going from HZSM-5 to cerium-modified HZSM-5, we should expect a decrease in ethylene selectivity, given the observation that robust acid sites promote it.

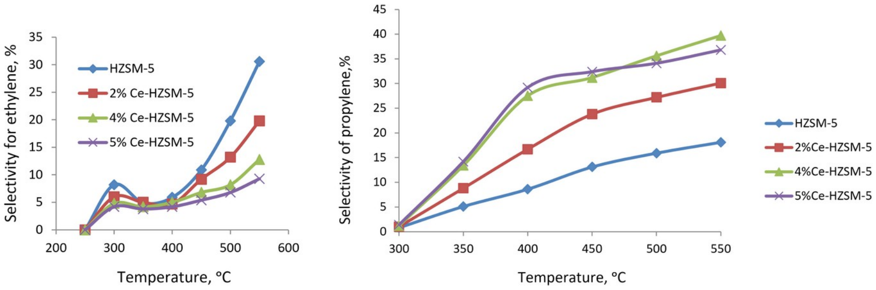

Figure 2 - Temperature dependence of selectivity for ethylene and propylene on HZSM-5 and modified samples
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An elevated selectivity (30.6%) for ethylene is attained utilizing HSZM-5 zeolite. The 5.0% HZSM-5 catalyst, characterized by diminished acid sites (114 µmol/g), demonstrates a reduced selectivity (9.3%) for ethylene. The selectivity towards ethylene and propylene exhibits an upward trend correlating with increasing temperature across all samples. Upon augmenting the cerium content in HZSM-5 zeolite to 4.0 wt %, the selectivity for propylene enhances, culminating in a peak value.

Table 1 - Data table

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Type of catalyst	Weak acid sites, µmol/g (100-300°C)	Strong acid sites, µmol/g (300-600°C)	Total concentration of acid sites µmol/g
HZSM-5	394	235	629
2% B-HZSM-5	316	182	498
4% B-HZSM-5	267	138	405
5% B-HZSM-5	246	114	350

In the context of 4% HZSM-5 zeolite, the selectivity for propylene attains values between 35.6-39.7% within the temperature spectrum of 500–550°C. When the cerium concentration in HZSM-5 zeolite is escalated to 5.0% by mass, no discernible enhancement in the selectivity of propylene is noted, with the selectivity for propylene under such conditions ranging from 34.1–36.8%

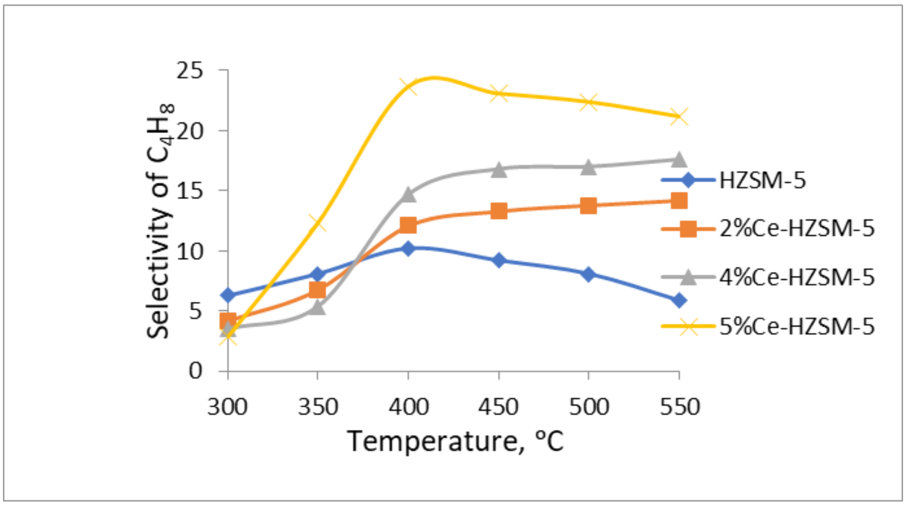

Figure 3 - Temperature dependence of selectivity for butylene on Ce/HZSM-5 and modified samples
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The peak selectivity for butylene (23.1%) is attained at a temperature of 450°C within this specific sample.

Analogously, an increase in the cerium content within HZSM-5 zeolite correlates with a higher selectivity for butylene. A heightened selectivity (30.6%) for ethylene is observed. The specimen modified with 5.0 wt % cerium demonstrates an elevated selectivity for butylene.

Conclusion

1. Catalytic systems were obtained by solid-phase modification of zeolite HZSM-5 with cerium oxide in order to study the effect of cerium oxide concentration on the selectivity of C_2-C_4 olefins formation from methanol.

2. It was found that the selectivity for C_2-C_4 olefins in methanol conversion in the presence of CeO_2/HZSM-5 is determined by the concentration of cerium oxide in the catalyst and the density of acid centres of the zeolite.

3. The optimal compositions of catalysts in the presence of which high yields of propylene and C2-C4 olefins are achieved were revealed. The catalyst containing 4% CeO2 provides maximum selectivity (39.7%) for propylene at 500°C, and on the catalyst of 5%CeO2/HZSM-5 composition at 450°C maximum selectivity (72.4%) for C2-C4 olefins is achieved.

Конфликт интересов

Не указан.

Рецензия

Все статьи проходят рецензирование. Но рецензент или автор статьи предпочли не публиковать рецензию к этой статье в открытом доступе. Рецензия может быть предоставлена компетентным органам по запросу.

Conflict of Interest

None declared.

Review

All articles are peer-reviewed. But the reviewer or the author of the article chose not to publish a review of this article in the public domain. The review can be provided to the competent authorities upon request.

Список литературы на английском языке / References in English

1. Li Y. Recent Progress of Ga-Based Catalysts for Catalytic Conversion of Light Alkanes / Y. Li, Sh. Fu, Q. Zhang [et al.] // Catalysts. — 2022. — Vol. 12 (11). — P. 1371. — DOI: 10.3390/catal12111371.

2. Chakraborty J.P. Chapter 6- Advances in the conversion of methanol to gasoline. Hydrocarbon Biorefinery / J.P. Chakraborty, S. Singh, S.K. Maity // Sustainable Processing of Biomass for Hydrocarbon Biofuels. — 2022. — P. 177–200. — DOI: 10.1016/B978-0-12-823306-1.00008-X.

3. Chen Z. Decentralized methanol feed in a two-stage fluidized bed for process intensification of methanol to aromatics / Z. Chen, H. Wang, W. Song [et al.] // Chemical Engineering and Processing — Process Intensificat ion. — 2020. — Vol. 154. — P. 108049.

4. Liu Z. Fundamentals of the catalytic conversion of methanol to hydrocarbons / Z. Liu, J. Huang // Chem. Synth. — 2022. — Vol. 2 (4). — P. 21.

5. Stöcker M. Methanol-to-hydrocarbons: catalytic materials and their behavior / M. Stöcker // Microporous and Mesoporous Materials. — 1999. — Vol. 29. — Iss. 1–2. — P. 3–48. — DOI: 10.1016/S1387-1811(98)00319-9.

6. Chen J.Q. Recent advancements in ethylene and propylene production using the UOP/hydro MTO process / J.Q. Chen, A. Bozzano, B. Glover [et al.] // Catal. Today. — 2005. — Vol. 10 (1–4). — P. 103–107. — DOI: 10.1016/j.cattod.2005.07.178

7. Teketel Sh. Shape selectivity in zeolite catalysis. The methanol to hydrocarbons (MTH) reaction / Sh. Teketel, M.W. Erichsen, F.L. Bleken [et al.] // Catalysis. — 2014. — Vol. 26. — P. 179–217. — DOI: 10.1039/9781782620037-00179.

8. Tian P. Methanol to Olefins (MTO): From Fundamentals to Commercialization / P. Tian, Y. Wei, M. Ye [et al.] // ACS Catal. — 2015. — № 5. — Vol. 3. — P. 1922–1938. — DOI: 10.1021/acscatal.5b00007.

9. Zhang C. Light hydrocarbons to BTEX aromatics over Zn-modified hierarchical ZSM-5 combined with enhanced catalytic activity and stability / C. Zhang, G. Kwak, Y.J. Lee [et al.] // Microporous and Mesoporous Materials. — 2019. — Vol. 284. — P. 316–326.

10. Kaarsholm M. Phosphorous modified ZSM-5: Deactivation and product distribution for MTO / M. Kaarsholm, F. Joensen, J. Nerlov [et al.] // Chemical Engineering Science. — 2007. — Vol. 62. — Iss. 18–20. — P. 5527–5532. — DOI: 10.1016/j.ces.2006.12.076.

11. Hadi N. Development of a New Kinetic Model for Methanol to Propylene Process on Mn/H-ZSM-5 Catalyst / N.A. Hadi, S.R. Niaei, A. Nabavi [et al.] // Chemical and Biochemical Engineering Quarterly. — 2014. — Vol. 28 (1). — P. 53–63.

12. Xiaoning W.Z. Effects of Light Rare Earth on ' Acidity and Catalytic Performance of HZSM-5 Zeolite for Catalytic Cracking of Butane to Light Olefins / W.Z. Xiaoning, X. Zhen, D. Chunming [et al.] // Journal of Rare Earths. — 2007. — Vol. 25 (3). — P. 321–328.

13. Tynjälä P. Modification of zsm-5 zeolite with trimethyl phosphite part 1. structure and acidity / P. Tynjälä, T.T. Pakkanen // Microporous and Mesoporous Materials. — 1998. — Vol. 20. — Iss. 4–6. — P. 363–369. — DOI: 10.1016/S1387-1811(97)00050-4

14. Li P. Conversion of methanol to hydrocarbons over phosphorus — modified ZSM-5 / ZSM-11 intergrowth zeolites / P. Li, W. Zhang, X. Han // Catalysis Letter. — 2010. — Vol. 134. — P. 124–130.

15. Tian Sh.X. Preparation of phosphorus modified HZSM-5 zeolite catalysts and their catalytic performances of methanol to olefins / Sh.X. Tian, Sh.F. Ji, Q. Sun // Advanced Materials Research. — 2014. — Vol. 875–877. — P. 295–299.

16. Mammadov E.S. Effect of solid-phase modification of zeolite tsvn with neodymium oxide in the conversion of methanol to C_2-C_4alkenes hydrocarbons and p-xylene / E.S. Mammadov, N.I. Makhmudova, T.A. Babayeva [et al.] // PPOR. — 2024. — Vol. 25 (2). — P. 548–556.

17. Bjørgen M. The mechanisms of ethene and propene formation from methanol over high silica H-ZSM-5 and H-beta / M. Bjørgen, F. Joensen, K.-P. Lillerud [et al.] // Catalysis Today. — 2009. — Vol. 142 (1–2). — P. 90–97. — DOI: 10.1016/j.cattod.2009.01.015.

18. Kerimli F.Sh. Evaluation of the Properties of ZSM-5 Type Zeolites Modified with CexMg1—xAl2O4 Na nopowders in the Toluene Disproportionation Reaction / F.Sh. Kerimli, T.M. Ilyasli, E.S. Mammadov [et al.] // Petroleum Chemistry. — 2021. — Vol. 61. — P. 895–900. — DOI: 10.1134/S0965544121080041.

19. Makhmudova N.I. Synthesis of CexMg1-xAl2O4 Nano Parts and the Study of Their Physico Chemical and Catalytic Properties in Compo sition with Zeolite ZSM-5 in Conversion of Methanol into p-Xylol / N.I. Makhmudova, L.R. Verdiyeva, T.M. Ilyasly [et al.] // Fundamental Re search. — 2017. — Vol. 10 (3). — P. 483–491.