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# EFFECT OF MODIFICATION OF ZEOLITE HZSM-5 WITH CERIUM OXIDE ON SELECTIVITY OF C<sub>2</sub>-C<sub>4</sub> OLEFINS FORMATION FROM METHANOL

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Catalytic compositions containing 2.0-5.0 wt.% of cerium oxide were prepared on the basis of zeolite HZSM-5 and cerium oxide in order to increase the selectivity for lower olefins, and their acid, textural and catalytic properties in the conversion of methanol to  $C_2$ - $C_4$  olefins in the temperature range  $250^{\circ}$ - $550^{\circ}C$  at atmospheric pressure were investigated. It was shown by XRD, low-temperature nitrogen adsorption and thermo-programmed ammonia adsorption methods that as a result of modification the zeolite structure is preserved, the modifier is dispersed on the outer surface and in the zeolite channels, and as a result of interaction of modifier nanoparticles with strong acid centres there is a decrease in the density of strong acid centres, an increase in the ratio of mesopores to total pore volume, which leads to an increase in selectivity for olefins  $C_2$ - $C_4$  and stability of the catalyst. High selectivity for propylene (39.7%) is achieved on the catalyst 4%CeO<sub>2</sub>/HZSM-5 at 550°C. Maximum selectivity for olefins (72.4%) and stability of operation (30 h) are achieved on the catalyst 5%CeO<sub>2</sub>/HZSM-5. at 450°C.

Keywords: conversion, methanol, light olefins, selectivity, zeolite ZSM-5, modification, serium oxide

### INTRODUCTION

Light olefins are important feedstocks in the petrochemical industry. Ethylene and propylene are mainly produced by thermal and catalytic cracking of hydrocarbon feedstocks, and much attention is also paid to alternative non-oil resources. The most promising way to produce light  $C_2$ - $C_4$  olefins is the conversion of methanol in the presence of catalysts based on molecular sieves [1-4].

Methanol is produced in large quantities from synthesis gas via natural gas. The methods of methanol conversion to olefins (MTO) and to petrol (MTG) can be used to produce light  $C_2$ - $C_4$  olefins and liquid fuels. Most of the literature data on MTO is devoted to the use of catalysts based on molecular sieves either SAPO-34 or ZSM-5 [4,5]. SAPO-34 is recognised as the best catalyst that gives up to 80%  $C_2$ - $C_4$  olefins with almost 100 % methanol conversion [5,6]. In the UOP/Norsk process, SAPO-34 based catalyst is used for selectivity in the production of light olefins from methanol [7]. However, SAPO-34 zeolite based catalysts are rapidly deactivated and, in addition, high propylene yields are not achieved.

For stable operation of zeolite catalyst in the conversion of methanol into olefins it is very important to create a stable acidity and reduce the residence time of olefins in the channels of zeolite, that is, to increase its mesoporosity, which can be achieved by modifying zeolite ZSM-5 [8]. For zeolite catalysts on the main parameters that affect the conversion of methanol into hydrocarbons are its acidity, structure, Si/AI ratio, textural characteristics [9].

To regulate the nature of the concentration of acid centres and the porous structure of zeolite ZSM-5 in order to increase the selectivity for light olefins, the method of chemical modification is widely used. Modification of HZSM-5 zeolite with phosphoric acid trimethyl phosphite improved the propylene yield to 47.01 %. The improvement of propylene selectivity on the catalyst containing 9% phosphorus was attributed by the authors [10-13] to a decrease in the concentration of strong acid centres as a result of the modification and a change in the porous structure of the zeolite as a result of the modification.

Catalysts based on zeolite of HZSM-5 type modified with Ca, Cr, Cu, Li, Mg, Ni, Fe, Mn and La show significant selectivity towards light olefins  $C_2$ - $C_4$  [14,15]. Among the modified catalysts, the highest selectivity towards propylene is achieved on the manganese modified sample [16].

This paper reports on the study of properties of the catalytic system based on zeolite HZSM-5 and cerium oxide obtained by solid-phase modification in the process of conversion of methanol to  $C_2$ - $C_4$  olefins.

### EXPERIMENTAL

Commercial zeolite ZSM-5 ( $SiO_2/Al_2O_3=40$ ;  $Na_2O<0.05$  wt.%) 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°C 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 oxide catalytic composition was 1.0-5.0 wt.% RFA of the syntesited catalysts was carried out using a RIGAKU "MINIFLEX" X-ray diffractometer with CuK<sub>a</sub> radiation according to the method described in [17].

The specific surface area, total pore volume, micro- and mesopore volumes of the catalysts were determined by the method of low-temperature nitrogen adsorption at 77 K on the ASAP-2010 unit of Micromeritics [18].

The acidic properties of the modified catalysts were determined on the sorption analyser USGA-101 (UNISIT, Russia) by temperature-programmed ammonia desorption (NH<sub>3</sub>-TPD) [17,18].

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<sub>3</sub>OH/N<sub>2</sub>=0.33 mol). The reaction products were analyzed on an Agilent GC782A gas chromatograph according to the procedure described in [18].

### **RESULTS AND DISCUSSION**

X-ray diffraction patterns of the original HZSM-5 and modified with cerium oxide show (Fig.1) that no structural changes in the zeolite framework occur after modification. The observed diffraction peaks for all the samples at 20 positions of 7.9°, 8.88°, 23.2°, 23.3°, and 24° are characteristic of ZSM-5 type zeolites (ICDD№0.1-0.86-1722). The characteristic peak related to cerium oxide is not observed in the X-ray diagram, indicating better dispersion of the modifier in the outer surface and channels of the zeolite.



Figure 1. X-ray patterns of unmodified ZSM-5 and 4% Ce<sub>2</sub>O<sub>3</sub> modified catalysts





Fig. 2 shows the dependences of methanol conversion in the presence of unmodified zeolite HZSM-5 and catalysts modified with cerium oxide.

On HZSM-5 already at temperature 300°C the methanol conversion reaches 98.6 %. The modified samples show different catalytic activity. On the modified samples high methanol conversion of 97-100 % is achieved in the temperature range of 400-450°C. The necessity of increasing the temperature to achieve high methanol conversion is obviously due to the decrease in the density of strong acid centres as a result of modification of HZSM-5 zeolite [19].

Table 1 shows that increasing the concentration of cerium oxide in the composition of zeolite HZSM-5 up to 5.0 wt.% leads to a decrease in the concentration of strong acid centres from 235  $\mu$ mol/g to 114  $\mu$ mol/g

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

Table 1. Acid characteristics of modified catalysts

Fig. 3 shows the temperature dependence of selectivity for ethylene and propylene in the presence of unmodified and modified samples.



Figure.3. Temperature dependence of selectivity for ethylene and propylene on HZSM-5 and modified samples

In the presence of HZSM-5 with increase of reaction temperature from 300°C to 550°C the growth of selectivity for ethylene from 9.6 to 30.6 % is observed. Modification of zeolite HZSM-5 with cerium oxide leads to a decrease in selectivity for ethylene, and the most significant decrease in selectivity for ethylene is observed at increasing the content of cerium oxide in the catalyst up to 5.0 wt.%. In contrast to ethylene with increasing cerium oxide content in the catalyst there is an increase in selectivity for propylene. Obviously, it is connected with the decrease in the density of strong acid centres, as well as with the increase in the ratio of the mesopore volume to the total pore volume (Table 2).

Catalyst	SBET	V <sub>total</sub>	V <sub>micro</sub>	V <sub>mezo</sub> /V <sub>total</sub>
-	(m²⋅g⁻¹)	(cm³·g⁻¹)	(cm³⋅g⁻¹)	
HZSM-5	266	0,24	0,062	25,8
2% CeO <sub>2</sub> -HZSM-5	255	0,22	0,064	29,0
4% CeO <sub>2</sub> -HZSM-5	236	0,18	0,067	37,2
5% CeO <sub>2</sub> -HZSM-5	227	0,17	00,69	40,5

 Table 2. Textural characteristics of modified catalysts

The maximum selectivity for propylene (39.7%) and C<sub>2</sub>-C<sub>4</sub> olefins (72.4%) is achieved with the 4% CeO<sub>2</sub>/HZSM-5 sample at  $500^{0}$ - $550^{0}$ C. Maximum selectivity for C<sub>2</sub>-C<sub>4</sub> olefins is achieved with 4% CeO<sub>2</sub>/HZSM-5 catalyst.



Figure 3. Temperature dependence of selectivity for butylene on CeO<sub>2</sub>/HZSM-5 and modified samples

Similarly, the increase of cerium content in zeolite HZSM-5 leads to an increase in selectivity for butylenes (Fig. 4). On the sample containing 5.0 wt.% of cerium oxide, the maximum selectivity for butylenes (23.1%) is reached at 425°C

Thus, as a result of modification of HZSM-5 with cerium oxide, there is a decrease in the density of strong acid centres, as well as a decrease in the total pore volume and an increase in the ratio of mesopore volume to total pore volume, which leads to an increase in selectivity for propylene and butylenes.

Decrease in the density of strong acid centres, increase in the ratio of mesopore volume to total pore volume, i.e. increase in mesoporosity as a result of modification contributes to the increase in the stability of the catalyst operation.



Figure 4. Dependence of methanol conversion on time

Fig.4 shows that compared to unmodified zeolite HZSM-5, modified zeolite CeO<sub>2</sub>/HZSM-5 during 30 hours of operation maintains stability of operation.

### CONCLUSIONS

Solid-phase modification of zeolite HZSM-5 with cerium oxide reduces the density of strong acid centres, the volume of micropores and increases the volume of mesopores, which play a major role in increasing the selectivity for  $C_2$ - $C_4$  olefins from methanol. At 500  $^{\circ}$ C, the catalyst 4% CeO<sub>2</sub>/HZSM-5 shows high activity for  $C_2$ - $C_4$  olefins (72,4%) and propylene (39,7%)

## REFERENCES

- [1] Li, Y.; Fu, Sh.; Zhang, Q.; Liu, H. andWang, Y. Recent Progress of Ga-Based Catalysts for Catalytic Conversion of Light Alkanes. *Catalysts*, **2022**, *12*(11), pp. 1371-1382; <u>https://doi.org/10.3390/catal12111371</u>
- [2] Chakraborty, J.P. and Singh, S.; Maity, S.K. Chapter 6- Advances in the conversion of methanol to gasoline. Hydrocarbon Biorefinery. Sustainable Processing of Biomass for Hydrocarbon. *Biofuels*, **2022**, pp .177-200, <u>https://doi.org/10.1016/B978-0-12-823306-1.00008-X</u>
- [3] Chen, Z.; Wang, H.; Song, W.; Hou, Y. and Qian, W. Decentralized methanol feed in a two-stage fluidized bed for process intensification of methanol to aromatics. *Chemical Engineering and Processing - Process Intensification*, **2020**, 154, pp.108049-108056, <u>https://doi.org/10.1016/j.cep.2020.108049</u>
- [4] Liu, Z. and Huang, J. Fundamentals of the catalytic conversion of methanol to hydrocarbons, *Chem. Synth.*, **2022**, 2(4), pp.21-28, <u>http://dx.doi.org/10.20517/cs.2022</u>
- [5] Stöcker, M. Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous and Mesoporous Materials*, **1999**, 29(1–2), pp. 3-48, <u>https://doi.org/10.1016/S1387-1811(98)00319-9</u>
- [6] Chen, J.Q.; Bozzano, A.; Glover, B.; Fuglerud, T. and Kvisle, S. Recent advancements in ethylene and propylene production using the UOP/hydro MTO process. *Catal. Today*, 2005, 106(1–4), pp. 103-107, <u>https://doi.org/10.1016/j.cattod.2005.07.178</u>
- [7] Teketel, Sh.; Erichsen, M.W.; Bleken, F.L.; Svelle, S.; Lillerud, K.P. and Olsbye, U. Shape selectivity in zeolite catalysis. The methanol to hydrocarbons (MTH) reaction. *Catalysis*, **2014**, 26, pp.179-217. <u>http://dx.doi.org/10.1039/9781782620037-00179</u>
- [8] Tian, P.; Wei, Y.; Ye M.; Liu, Z. Methanol to Olefins (MTO): From Fundamentals to Commercialization. ACS Catal. 2015, 5(3), pp. 1922-1938. <u>https://doi.org/10.1021/acscatal.5b00007</u>
- [9] Zhang, C.; Kwak, G.; Lee, Y.J.; Jun, K.W.; Gao, R.; Park, H.G., Kim, S., Min, J.E., Kang, S.C. and Guan, G. Light hydrocarbons to BTEX aromatics over Zn-modified hierarchical ZSM-5 combined with enhanced catalytic activity and stability. *Microporous and Mesoporous Materials*, **2019**, 284, pp.316-326. https://doi.org/10.1016/j.micromeso.2019.04.041
- [10] Kaarsholm, M.; Joensen, F.; Nerlov, J.; Cenni, R., Chaouki, J., Patience, G.S. Phosphorous modified ZSM-5: Deactivation and product distribution for MTO, *Chemical Engineering Science*, **2007**, 62(18–20), pp. 5527-5532. https://doi.org/10.1016/j.ces.2006.12.076
- [11] Tynjälä, P., Pakkanen, T.T. Modification of zsm-5 zeolite with trimethyl phosphite part 1. structure and acidity, *Microporous and Mesoporous Materials*, **1998**, 20(4–6), pp. 363-369. <u>https://doi.org/10.1016/S1387-1811(97)00050-4</u>
- [12] Li, P., Zhang, W., Han, X. Conversion of methanol to hydrocarbons over phosphorus modified ZSM-5/ZSM-11 intergrowth zeolites. *Catalysis Letter*, **2010**, 134, pp.124-130, <u>https://doi.org/10.1007/s10562-009-0214-6</u>
- [13] Tian, Sh.X., Ji, Sh.F., Sun, Q. Preparation of phosphorus modified HZSM-5 zeolite catalysts and their catalytic performances of methanol to olefins. Advanced Materials Research, 2014, Vol. 875-877, pp.295-299, <u>10.4028/www.scientific.net/AMR.875-877.295</u>
- [14] Liu, J., Zhang, Ch., Shen, Zh., Hua, W., Tang, Y., Shen, W., Yue, Y., Xu, H. Methanol to propylene: Effect of phosphorus on a high silica HZSM-5 catalyst. *Catalysis Communications.* 2009. 10(11), pp. 1506-1509. https://doi.org/10.1016/j.catcom.2009.04.004
- [15] Mammadov, E.S., Makhmudova, N.I., Babayeva, T.A., Mammadov, S.E., Akhmadov, E.I., Mammadova, A.Z. Effect of solid-phase modification of zeolite tsvn with neodymium oxide in the conversion of methanol to  $C_2$ - $C_4$  alkenes hydrocarbons and p-xylene. *PPOR*, **2024**, 25 (2), pp. 548-556.

https://doi.org/10.62972/1726-4685.2024.2.548

- [16] Hadi, N., Niaei, A., Nabavi S.R., Farzi A., Shirazi M.N. Development of a New Kinetic Model for Methanol to Propylene Process on Mn/H-ZSM-5 Catalyst. *Chemical and Biochemical Engineering Quarterly*. 2014, 28 (1), pp. 53-63, http://silverstripe.fkit.hr/cabeg/assets/Uploads/Cabeg-2014-01-05.pdf
- [17] Makhmudova, N.I., Verdiyeva, L.R., Ilyasly, T.M., Babayeva, T.A, Mammadov, E.S. Synthesis of Ce<sub>x</sub>Mg<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> Nano Parts and the Study of Their Physico Chemical and Catalytic Properties in Composition with Zeolite ZSM-5 in Conversion of Methanol into p-Xylol. *Fundamental Research*, **2017**, 10(3), pp. 483-491, <u>https://fundamental-research.ru/en/article/view?id=41862</u>
- [18] Kerimli, F.Sh.; Ilyasli, T.M.; Mammadov, E.S, Akhmedova, N.F., Mammadov, E.S, Makhmudova, N.I.; Akhmedov, E.I. Evaluation of the Properties of ZSM-5 Type Zeolites Modified with Ce<sub>x</sub>Mg<sub>1-x</sub>Al<sub>2</sub>O<sub>4</sub> Na nopowders in the Toluene Disproportionation Reaction. *Petroleum Chemistry*, **2021**, 61, pp. 895-900. https://doi.org/10.1134/S0965544121080041
- [19] Bjørgen, M.; Joensen, F.; Lillerud K.-P., Olsbye, U., Svelle, S. The mechanisms of ethene and propene formation from methanol over high silica H-ZSM-5 and H-beta. *Catalysis Today*, **2009**, 142(1–2), pp. 90-97, <u>https://doi.org/10.1016/j.cattod.2009.01.015</u>

[1]