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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**METHANOL TO AROMATICS CONVERSION OVER
MODIFIED HIGH SILICA ZEOLITES**

Speciality: 2307.01 – Physical Chemistry

Field of science: Chemistry

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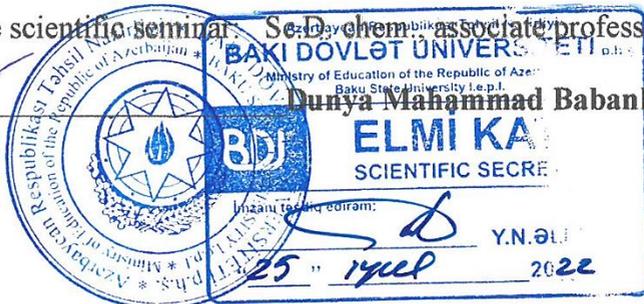


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GENERAL CHARACTERISTICS OF WORK

Relevance of the topic. The refineries have traditionally been a major source of many petrochemical products. The production of essential petrochemicals from alternative petroleum feedstocks such as natural and associated gases, methanol and bioethanol is one of the priority fields. However, the solution to the problem of the conversion of natural gas via methanol into aromatic hydrocarbons, intermediate organic synthesis products and high-octane components of engine fuels can be solved by developing high-performance catalysts.

Works of previous researchers (Khadzhiev S.N., Lapidus A.L., Gai G., Stöcker M., Zhang Y.K., Kedia A.O., Bleken F., etc.) revealed that the most promising catalysts for methanol conversion processes into olefins, aromatics and high-octane fuel components are molecular sieve SAPO and high silica zeolites of type ZSM-5. Although a considerable number of papers have been devoted to the preparation of catalysts for the conversion of methanol into aromatic hydrocarbons, there are a limited number of studies in the literature on the preparation of the most valuable product p-xylene from methanol. Insufficient attention has been dedicated to the study of the correlation between catalytic properties, especially para-selectivity, and the nature and concentration of promoters, acidic characteristics, and strength of active sites, their ratio and the microporous structure of zeolite.

With regard to above stated we consider that direction chosen by us to conduct research of catalytic properties of high silica zeolites modified by transition, rare-earth metals and nonmetals (P, B) for process of conversion of alternative raw material methanol to p-xylene is actual both in scientific and practical aspects.

The aims and objectives of research. The main purpose of the present work is to study the effect of nature, concentration and conditions of introduction of modifiers on physicochemical properties of zeolite catalyst for methanol into p-xylene conversion, to study the effect of changes in porous structure, acid properties, nature and strength of active centres on para-selectivity of catalyst based on ZSM-5 zeolite.

Methanol was used as the main feedstock, and high silica

zeolites such as ZSM-5, as well as their modified forms, were used as catalysts. The catalysts used were modified with rare earth and transition elements (Ba, Sr, Zn, Cr, Sc, Ga) and a non-metallic modifier. Deionised water, hydrochloric acid, nitric acid, dichloromethane and various gases (helium, nitrogen, oxygen) were used as supporting reagents.

In order to achieve the goal, the following main objectives were addressed:

- Study of the effect of the nature and concentration of rare earth and transition metals on the textural, acidic, physico-chemical and catalytic properties of zeolites;
- Study of effect of concentration of non-metallic modifier (P) on acidic and catalytic properties of ZSM-5 zeolite modified with rare-earth and transition metals
- Study of the effect of the nature and concentration of modifiers on the para-selectivity of the catalyst;
- Determination of the effect of the microporous zeolite structure and the strength distribution of the acid sites on the para-selectivity of the catalyst;
- Development of active and para-selective catalysts for the conversion of methanol to p-xylene with high performance stability.

The research methods. Modern physico-chemical methods of analysis were used in the delivery of the work for a comprehensive approach to the desired objectives. The synthesis of used catalysts, preparation of cationic forms of pentasil type of high silica zeolites and their modification were performed by ion exchange, impregnation and dry mixing methods. The heterogeneous gas-phase conversion of methanol into aromatic hydrocarbons was carried out in a continuous flow type catalytic unit.

The composition and physico-chemical properties of the synthesized catalyst samples were studied. The accuracy of the research results based on scientific provisions and outcomes was thoroughly studied by XRD, N₂ adsorption-desorption methods, scanning electron microscope (SEM), IR spectroscopy, gas chromatography (GC).

The main provisions of the defense.

- Study of the influence of the nature and concentration of rare earth and transition metals on the textural, acidic, physico-chemical and catalytic properties of zeolites;

- Concentration effect of non-metallic modifier on acidic and catalytic properties of ZSM-5 zeolite modified with rare-earth and transition metals;

- Study of the effect of the nature and concentration of modifiers on the para-selectivity of the catalyst;

- Determination of the effect of the microporous zeolite structure and the strength distribution of the acid sites on the para-selectivity of the catalyst;

- Development of active and para-selective catalysts for the conversion of methanol to p-xylene with high performance stability.

Scientific innovation of the research. For the first time textural, acidic, physico-chemical and catalytic properties of high silica zeolites of pentasil type modified by methods of ionic exchange, impregnation with Ba, Sr, Zn, Cr, Sc, Ga, REE and by solid-phase mixing of H-ZSM-5 zeolite with Mo, W, Cr spinel structures containing cerium and gadolinium nanopowders in conversion of methanol into hydrocarbons have been systematically studied.

The mechanism of action of modifying additives was revealed, including reduction of pore volume, partial deactivation of acid sites inside the zeolite channels, and significant deactivation of acid sites on the outer surface of zeolite crystals, which promoted significant decrease of p-xylene isomerisation reaction contribution and enhancement of p-xylene selectivity. Highly efficient, selective and durable dual-modified (5%Ho-2%P-HZSM) and HZSM-5 – $Ce_xMg_{1-x}Al_2O_4$ ($Gd_xMg_{1-x}Al_2O_4$) catalysts for methanol into p-xylene conversion process have been developed.

Scientifically proved approaches to increase para-selectivity of catalysts in the process of conversion of methanol to p-xylene are presented.

Theoretical and practical significance of the research. The theoretical significance of the work lies in the scientific validation of the possibility of selective production of aromatic hydrocarbons,

especially p-xylene from non-oil feedstock methanol. The established patterns of modification of ZSM-5 zeolite by transition and rare earth metal nanoparticles permitted to increase the yield and selectivity towards p-xylene. The findings are of interest to specialists involved in the study of the behaviour of zeolite catalysts. The defined correlations between acidic, textural properties and catalytic activity open up wide possibilities for focused research and preparation of highly effective para-selective catalysts for aromatisation processes of alcohols, disproportionation and isomerisation of aromatic hydrocarbons. The designed bimetallic catalysts can be recommended for processes to produce p-xylene from non-oil feedstock - methanol.

Published works and approbation of the work. The most important achievements of this dissertation have been presented at local and international conferences: Materials of IX, X, XI, XII scientific conferences of postgraduates, masters and young researchers on “Actual problems of chemistry” dedicated to 92, 93, 94, 95th anniversaries of National Lider Heydar Aliyev, (Баку, 2015,2016,2017,2018); «Нагиевские чтения» посвященной 110 летию академика М.Нагиева (Ваку, 2018); XXI Менделеевский съезд по общей и прикладной химии (Санкт-Петербург, 2020); 7-ая Всероссийская цеолитная конференция (Звенигород, 2015); Материалы международной научно-практической конференции «Интеграция науки и образования в вузах нефтегазового профиля-2016» (Салават, 2016); Материалы II Всероссийской научной конференции «Актуальные проблемы адсорбции и катализа» (Плес-Иваново, 2019); II International scientific conference for students and young scientists (Vinnytsia, 2019); V Международная Бергмановская конференция «Физико-химический анализ в образовании, науке и технике (Махачкала, 2017); Актуальные проблемы естественных наук (Тамбов, 2015); II Международная конференция «Современные решения научных и производственных задач в химии и нефтехимии» (Казань, 2017); V Российская конференция. Актуальные проблемы Нефтехимии. Посвящена памяти академика В.Н. Ипатьева, (г.Звенигород, 2016); Сборник материалов IV Всероссийской студенческой конференции с международным участием, посвященной 220-

летию ФГБОУВО «Российский государственный педагогический университет им. А.И.Герцена» (Санкт-Петербург, 2017).

Affiliation. The research was performed at Baku State University, the department of Physical and Colloid Chemistry

The scope and structure of the work. The dissertation consists of an introduction (9737 pages) and four chapters (1st chapter 55491 symbols, 2nd chapter 18659 symbols, 3rd chapter 31651 symbols, 4th chapter 42615 symbols), main results (3.714), 174 cited references, in total has 161 pages, where, graphs (42), schemes (6) and tables (24) are shown.

Personal contribution of the author. The author's personal contribution includes the planning and organisation of the thesis work and the achievement of the main results. The applicant carried out all theoretical and experimental research, as well as the interpretation and synthesis of the results. The analysis and systematisation of the research results were prepared and formalised as scientific reports and articles with the active participation of the applicant.

CONTENT OF THE WORK

The **introduction** shows the relevance of the dissertation topic, the purpose of the substantiated work, the scientific innovation and practical significance of the results.

The first chapter deals with the structure, physico-chemical and catalytic properties of high silica zeolites type pentasil (ZSM-5) and zeolite-like materials in the conversion of methanol to hydrocarbons.

The second chapter outlines methods for the synthesis of zeolite catalysts, describes the experimental catalytic unit, the methodology of the experiments, the analysis of reaction products and methods of physico-chemical investigation of the catalysts.

The third chapter presents regularities of methanol conversion to hydrocarbons on different zeolite forms of ZSM-5 type, effect of nature and concentration of modifying metal on physico-chemical, acidic and catalytic properties of pentasil type zeolite in conversion of methanol to aromatic hydrocarbons.

In the fourth chapter, the results on the conversion of methanol

to aromatic hydrocarbons on mono- and bimetallic zeolite catalysts obtained by solid-phase modification are discussed.

The conclusion summarises the results of the research carried out.

The thesis concludes with conclusions, a list of references and a list of abbreviations.

Summary of chapter 3

Effect of silicate modulus and running time on the catalytic, acidic and textural properties of zeolites.

Taking into account prospects of methanol conversion to olefine and aromatic hydrocarbons in the presence of high silica ZSM-5 type zeolites it was of great interest to study the effect of silicate module, running time, nature of modifying cation on its physico-chemical and catalytic behavior. Methanol conversion and yield selectivity are strongly dependent on the silicate modulus of the zeolite (figure 1).

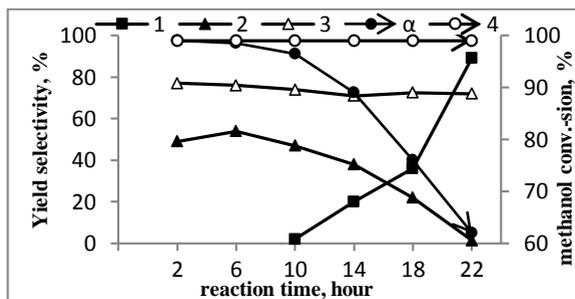


Figure 1: Relationship between methanol conversion, yield selectivity and reaction time on HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=61, 200$); $T=450^\circ\text{C}$, $v=4.0\text{h}^{-1}$, $\text{CH}_3\text{OH}:\text{N}_2=1:8$. \blacktriangle - C_2-C_4 ($\text{SiO}_2/\text{Al}_2\text{O}_3=61$); \triangle - C_2-C_4 ($\text{SiO}_2/\text{Al}_2\text{O}_3=200$); \blacksquare - DME ($\text{SiO}_2/\text{Al}_2\text{O}_3=61$); \square - DME ($\text{SiO}_2/\text{Al}_2\text{O}_3=200$); \bullet - methanol conversion ($\text{SiO}_2/\text{Al}_2\text{O}_3=61$); \circ - methanol conversion ($\text{SiO}_2/\text{Al}_2\text{O}_3=200$).

On a zeolite with silicate modulus 61, with increasing reaction time there is a significant decline in methanol conversion and $\text{C}_2\text{-C}_4$ selectivity. The strongest reduction in methanol conversion and $\text{C}_2\text{-C}_4$ selectivity is observed after a 10-hour reaction time. Whereas in 10-hour operation the DME selectivity is only 2.0%, in 22-hour work it reaches up to 89%. High methanol conversion and $\text{C}_2\text{-C}_4$ selectivity

are observed for HZSM-5 zeolite with a silicate module of 200 over the whole studied reaction time range. The reaction time of 22h resulted in a methanol conversion of 97.0 % and a C₂-C₄ selectivity of 72.0 %. As the silicate modulus grows, the stability of the zeolite obviously enhances. The change in the catalytic properties of zeolites as a function of running time is related to a variation in the acidic and textural properties of the zeolite during the conversion of methanol. By increasing the silicate, modulus of the zeolite a slight drop in the concentration of the strong acid sites can be observed. However, for zeolite with silicate modulus 61 the strong acid sites disappear after the reaction (22 hours of operation), and for zeolite with modulus 200 the acidity changes insignificantly. The loss of activity of HZSM(61) zeolite is also linked with a considerable reduction in its specific surface area (from 288 to 27 m²/g), total pore volume (from 0.24 to 0.03 cm³/g) and an increase in coke content (up to 11.5 wt.%). The acid and texture characteristics of HZSM (200) do not change significantly. The coke content is only 2.9 wt.%.

Thus, the decline of zeolite ZSM(61) activity depending on the running time is caused by blocking of acid sites and zeolite pores by coke deposits, leading to the loss of strong acid sites as active centres and blocking of zeolite surface and pores by coke.

As H-form zeolites are rapidly deactivated during methanol conversion, we modified the zeolites with transition and rare-earth metals using different modification methods.

Effect of modification method and concentration of modifiers on acidic and catalytic properties of ZSM-5 type zeolites.

The nature of the ion exchange cation significantly effects the yield of aromatic hydrocarbons in the conversion of methanol (figure 2). The cationic forms of the alkali earth metals (Sr and Ba) exhibit low activity (aromatic hydrocarbons (ArH) yields of 2.5-8.1 wt.% and 1.2-4.2 wt.% respectively). The replacement of Na cations with Zn, Sc and Gd cations leads to a significant enhancement of the aromatic activity. Among the cationic forms of zeolite type ZSM, the REE form of zeolite (Gd-ZSM) has the highest activity. The hydrogen form of zeolite (H-ZSM) has a low stability and the activity decreases

gradually with increasing running time.

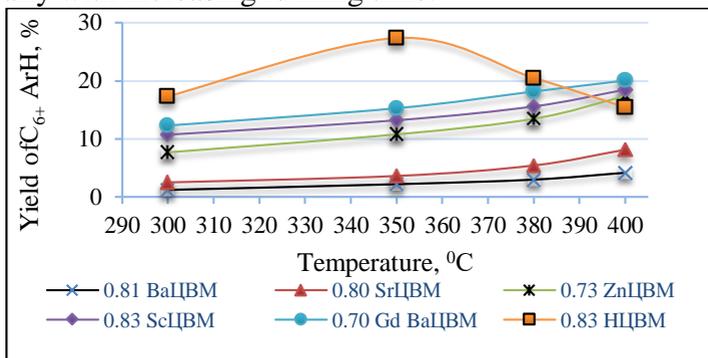


Figure 2: Dependence of aromatic hydrocarbon yield on the nature of the cation at different temperatures ($T=400^{\circ}\text{C}$, $v=2\text{h}^{-1}$)

By increasing the temperature from 300°C to 400°C the yield of aromatic hydrocarbons decreases from 17,3 to 15,4 wt.%. The cationic forms of ZSM (IIBM) type of zeolite are arranged in a series according to increasing yield of aromatic hydrocarbons:

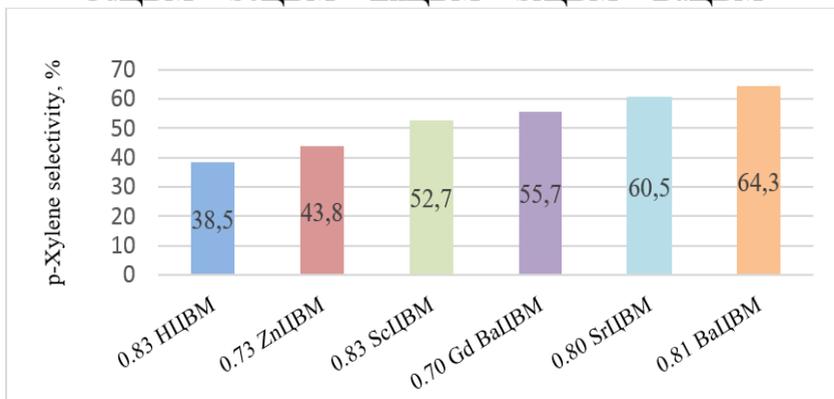


Figure 3: Dependence of p-xylene selectivity on the nature of the exchange cation ($T=400^{\circ}\text{C}$, $v=2\text{h}^{-1}$)

The nature of the cation also significantly alters the distribution of the p-isomer in the xylene fraction. The H-form of zeolite has the lowest p-xylene selectivity (38.5%). An increase in p-xylene

selectivity occurs when moving from Zn²⁺ to Gd³⁺. For example, on ZnZSM and GdZSM the p-xylene selectivity is 43.8% and 55.7% (figure 3). Among the cationic forms of zeolites, the Ba-form of zeolite has the highest para-selectivity (64.3%). However, the yield of aromatic hydrocarbons of Ba-form is considerably lower than that of Sc- and Gd-forms of zeolite. The higher activity of Sc and Gd forms of zeolite can be explained by the high polarising capacity of scandium and gadolinium cations. The concentration of the strongly acidic sites on HZSM is significantly higher than on the investigated cationic forms (Table 1). The ratio of strong proton-donating centres on Sr-ZSM and Ba-ZSM is insignificant and amounts only to 18.3 and 10.7 $\mu\text{mol}\cdot\text{g}^{-1}$. As a result of ion exchange, the concentration of weak ($E < 95\text{kJ/mol}$) and strong acid sites ($E > 130\text{kJ/mol}$) declines. It should be noted that the modification of zeolite with multicharged cations (Zn²⁺, Sc³⁺, Gd³⁺) results in the formation of new, stronger aprotion sites. The concentration of the aprotion sites on Zn-ZSM, Sc-ZSM and Gd-ZSM is 117.5-124.6 $\mu\text{mol}\cdot\text{g}^{-1}$.

Table 1.
Effect of the nature of the cation on the distribution of the acid sites by activation energy (E, kJ/mol)

Catalysts	E<95	95<E<130	E>130	High-temperature shoulder	130<E<(160-175)
0,83HZSM	618	212.6	329.4	-	-
0,81BaZSM	370.6	196.5	10.7	-	-
0.80SrZSM	347.7	220.3	18.3	-	-
0.73ZnZSM	190.4	228.4	194.4	75.5(>165°C)	118.9
0.83ScZSM	192.6	232.6	198.7	77.4(>165°C)	121.3
0.70GdZSM	198.8	239.2	202.3	80.2(>165°C)	122.1

Thus, the catalytic properties of cationic forms of pentasyls in the conversion of methanol to ArH depend on the nature, charge, size of cations and concentration of proton and aprotion sites.

The effect of the nature of metals on the catalytic properties of pentasil was studied on HZSM zeolite samples containing 1.0 wt. % of the modifier.

As temperature increases, the activity of unmodified zeolite drops, which is due to the deactivation of H-ZSM as a result of the coke formation process (Figure 4).

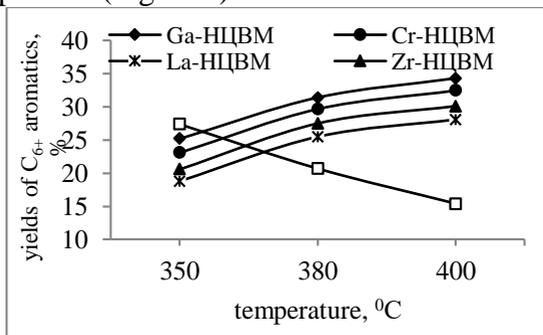


Figure 4: Temperature dependence of the yield of C₆₊ ArH on the modified catalysts. (T=400°C, v=2h-1)

The modification of H-CVM with metals (Ga, Cr, La, Zr) in an amount of 1.0 wt.% enhances the activity in the formation of aromatic hydrocarbons. The yield of C₆₊ aromatic hydrocarbons rises with increasing temperature. The highest yield of C₆₊ aromatic hydrocarbons at 400°C is achieved with Ga-ZSM catalyst (34.3 wt.%). The catalysts are ordered in ascending C₆₊ aromatic hydrocarbon yields in the series Ga-HZSM>Cr-HZSM>Zr-HZSM>La-HZSM>H-HZSM. The xylene fraction yield was 20,8 wt.% at 350°C on the H-ZSM. However, in the temperature range 380-400 °C the yield of the xylene fraction reduces and comes to 13.4-15.8 wt.%. In this temperature range, the modification of H-pentasil promotes an increase in the yield of the xylene fraction. At 400°C the yield of the xylene fraction on the modified samples ranges between 15.4 and 18.8 wt.%. The highest yield of the xylene fraction is achieved at Ga-HZSM (18.8 wt.%) and the least ones at La-HZSM (15.4 wt.%).

The p-xylene selectivity strongly depends on the nature of the modifying metal (figure 5). A modification of HZSM with metals (Ga, Cr, La, Zr) leads to a considerable enhancement of the p-xylene content in the xylene fraction. Para-selectivity at 400°C on H-form zeolite is only 35.8%, while on the modified ones it ranges from 49.5

to 56.8%. The highest para-selectivity is shown by La and Zr modified samples, 53.6 and 56.8% respectively (Figure 5).

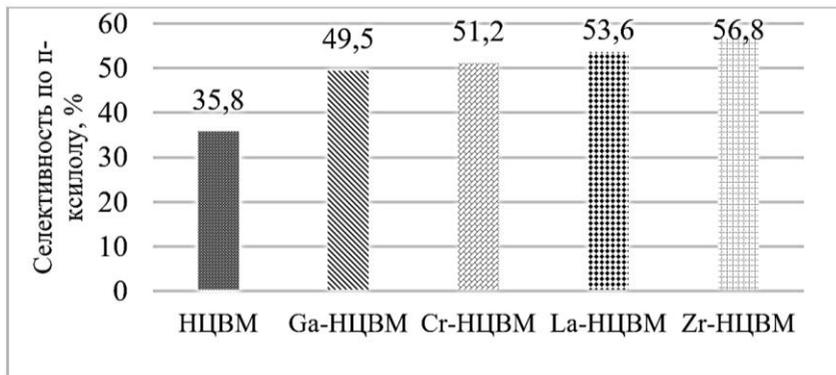


Figure 5. Effect of the nature of the modifying metal on the p-xylene selectivity ($T=400^{\circ}\text{C}$, $v=2.0\text{ h}^{-1}$).

Variations in HZSM activity and para-selectivity can be caused by changes in acid site concentration. The introduction of 1.0 wt.% modifier in the HZSM composition considerably effects the concentration of strong acid sites. The most significant reduction in the concentration of strong acid centres is observed when HZSM is modified with lanthanum and zirconium. Whereas, the concentration of strong acid sites drops from 542 to 308-312 $\mu\text{mol}\cdot\text{g}^{-1}$. A reduction in the concentration of the strong Brandsted acid sites of the zeolite dramatically slows down the by-product reactions and thereby contributes to an enhancement of the catalyst's para-selectivity.

Thus, the nature of the modifying metal significantly affects the yield of C_{6+} aromatic hydrocarbons and the p-xylene selectivity, which can be explained by the change in the acidic properties of the catalyst resulting due to the modification. La and Zr modified catalysts perform higher para-selectivity in the conversion of methanol to p-xylene.

Study of effect of Zr concentration (from 1.0 to 10.0 wt. %) demonstrated that by growth of zirconium concentration in HZSM from 1.0 to 5.0 wt. % an upward trend in yield of xylene fraction (from 16.5 wt. % to 22.5 wt. %), and C_{6+} aromatic hydrocarbons (from 30.1

to 35.3 wt. %), while further increase of zirconium content to 10.0 wt. % results in significant reduction of yield of xylene fraction (to 15.7 wt. %) and C_{6+} ArH (up to 27.2 wt.%). An increase of the zirconium concentration in HZSM from 1.0 wt.% to 5.0 wt.% leads to a sharp enhancement of the p-xylene selectivity (from 56.8 to 73.0%). A further increase in para-selectivity (77.8%) occurs when the content of the modifier is raised to 10.0 wt.%. High selectivity for p-xylene is also exhibited by pentasils like Ultrasil (US) and IQBH (analogues of ZSM-5 zeolite). The appearance of high para-selectivity of modified pentasils is due to the interaction of the modifier with the crystal structure, accompanied by a change in the acidic properties and porous structure of the zeolite. A gradual decline in the concentration of strong acid centres and a drop in the sorption capacity of the catalyst occurs as the concentration of Zr increases. For example, by increasing the Zr concentration in the catalyst to 5.0 wt.% the sorption capacity for n-heptane reduces from 0.167 to 0.098 cm³/g and for benzene from 0.080 to 0.054 cm³/g. The data proves enough that the modifier penetrates the channels of the zeolite, leading to a reduction in pore volume.

Thus, the chemical modification of H-pentasil by zirconium results in redistribution of acid centres: reduction of strong acid centres, formation of acid centres of medium strength, as well as changes in the porous structure of zeolite. All these factors ultimately contribute to an overall increase in the para-selectivity of the catalyst.

The effect of the nature and concentration of rare earth elements on the physico-chemical and catalytic properties of MWC zeolite in the conversion of methanol into C₂-C₃ olefins.

Loading of REE metals (La, Pr, Yb) into pentasil type zeolite by impregnation using aqueous solutions of corresponding metal nitrates with subsequent salt decomposition at 550 °C leads to significant changes in its physico-chemical properties and catalytic activity in conversion of methanol into C₂-C₃ olefins and aromatic hydrocarbons. The H-form of ZSM exhibits low activity on C₂-C₃ olefins.

Modification of HZSM leads to a change of catalytic properties of the catalyst. In contrast to HZSM, the modified catalysts display high selectivity for the synthesis of C₂-C₃ alkenes in the temperature

range 300-350°C. In the presence of the modified catalysts the ethylene and propylene content of the gas has been found to be 21.2-29.8 and 25.8-31.8 wt.%. The lanthanum-modified sample shows the highest activity. The yields of ethylene and propylene in this sample at 300°C represent 29.8 wt.% and 26.4 wt.%.

Effect of the nature and concentration of REE in pentasil on methanol conversion to hydrocarbons and p-xylene selectivity

The modification of the REE zeolite also leads to an increase in the para-selectivity of the catalyst (Figure 6 b). A significant enhancement of methanol conversion to hydrocarbons (Figure 6a) and p-xylene selectivity is observed at 400°C on all modified catalysts.

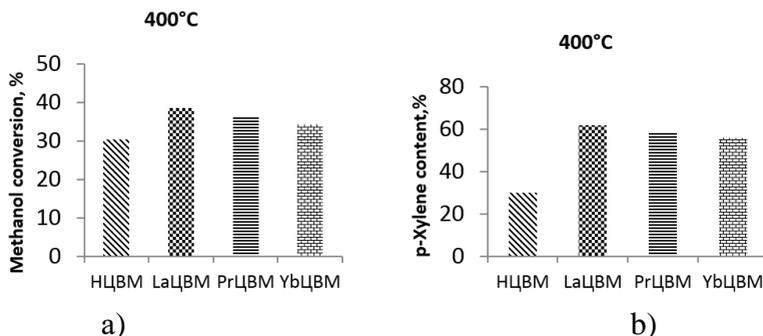


Figure 6. Effect of the nature of the modifying metal on the conversion of methanol to hydrocarbons (a) and on the p-xylene content in the xylene mixture (b) ($T=400^{\circ}\text{C}$, $v=2.0\text{h}^{-1}$).

Moreover, the p-xylene selectivity on catalysts modified with REE metals significantly depends on the nature of the loaded element. The maximum p-xylene selectivity is achieved at La-HZSM and amounted to 62.3% (Figure 6 b). The catalysts are listed in order of their p-xylene selectivity depending on the loaded metal:

La-HZSM > Pr-HZSM > Yb-HZSM > HZSM

Porometric studies have proven that modifying zeolite with metals results in a reduction of the specific surface area, pore volume and pore radius of the zeolite. Apparently, it can be explained by the fact that as a result of modification the exchange of part of H^+ in zeolite for metal cations takes place, as well as loading of metal oxides on the

surface and in zeolite channels, leading to reduction of specific surface area from 288.5m²/g to 256.3 m²/g, pore volume from 0.24 cm³/g to 0.19 cm³/g and effective pore radius from 10-110 to 8-80 Å. The loading of REE into the HZSM also effects the concentration of acid sites.

Thus, the nature of REE (La, Pr, Yb) in ZSM zeolite plays a crucial role in its selectivity and catalytic activity, associated with changes in acidic and textural properties of catalysts as a result of chemical modification. The nature of REE significantly changes the distribution of the xylenes in the xylene mixture. The loading of 2.5% REE into the HZSM leads to an enhancement of the p-xylene selectivity up to 62.3 % from 30.2 %.

Conversion of methanol to hydrocarbons using bimetallic catalysts based on ZSM-5 type zeolite.

The double modification of HZSM-5 zeolite with modifiers (Zn-La, Zn-Zr, La-Zr) leads to further enhancement of the xylene fraction yield and the p-xylene selectivity (figure 7).

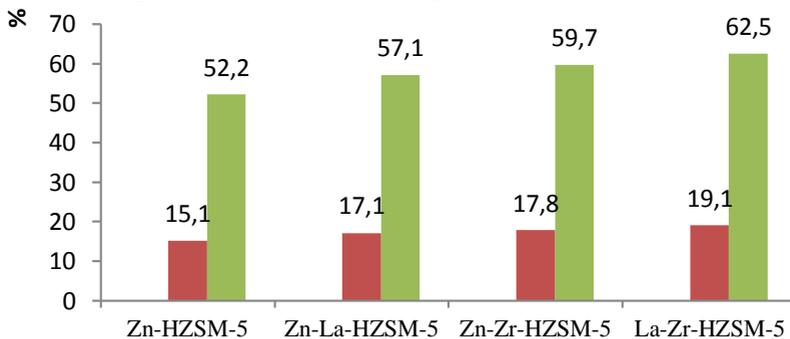


Figure 7. Effect of double modification on xylene yield and p-xylene selectivity (400°C, $v=2.0h^{-1}$ modifier content 1.0 wt. %).

The highest yield of the xylene fraction is observed with a catalyst modified with 1.0 wt.% La and 1.0 wt.% Zr.

Effect of holmium and phosphorus concentrations in H-pentasil zeolite on the selectivity for xylenes and C₂-C₄ olefins in the conversion of methanol.

The modification of H-pentasil by the consequent addition of REE and phosphorus considerably changes its properties. The loading

of holmium (figure 8) into H-pentasil leads to a remarkable change in its selectivity for xylenes and C₂-C₄ olefins.

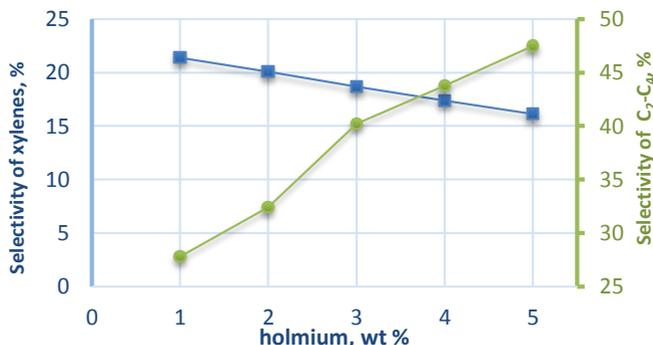


Figure 8. Effect of holmium concentration in Ho-pentasil catalyst on selectivity for xylenes and C₂-C₄ olefins (T=400°C, v=2.0h⁻¹).

An increase of Ho content in H-pentasil from 1.0 wt.% to 5.0 wt.% reduces the yield of xylenes (from 21.4 to 16.1 wt.%) and enhances the selectivity for C₂-C₄ olefins. However, a considerable rise in the p-xylene selectivity occurs. As the Holmium concentration in the catalyst increased from 1.0 wt.% to 5.0 wt.%, an upward rise in the p-xylene selectivity from 62.1 to 76.6% was observed. Further modification of the catalyst with 5%Ho-H-pentasil ammonium hydrophosphate markedly improves the yield of C₂-C₄ olefins and reduces the selectivity for xylenes. Increasing the phosphorus content of the Ho-loaded catalyst to 4.0 wt.% enhances the olefin selectivity up to 59.3% and decreases the xylene yield to 9.8 wt.%. Here the p-xylene selectivity goes up to 94.2%. An optimum content of phosphorus in the Ho-loaded catalyst can be taken as 2.0 wt.%, resulting in 14.5% yield of xylenes, 85.7% selectivity for p-xylenes and 53.4% selectivity for C₂-C₄ olefins (figure 9).

It was found that the modification results in a reduction in the concentration of strong Bronsted acid sites, the formation of new Lewis acid sites and a decrease in the pore volume of the zeolite. These factors are the main reason for the increased para-selectivity of the catalysts.

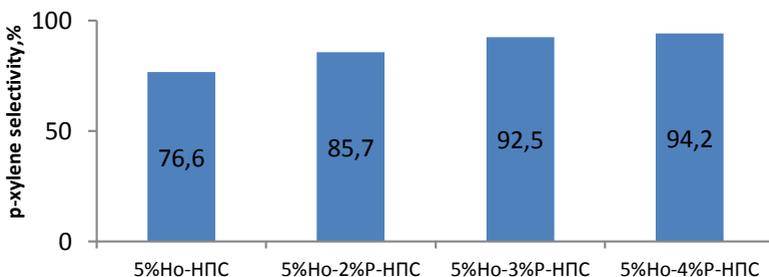


Figure 9. Effect of phosphorus concentration on the p-xylene selectivity. ($T=400^{\circ}\text{C}$, $v=2.0\text{h}^{-1}$)

Summary of chapter 4

Effect of mono (Zr, Mo, W, Cr and Ni) and bimetallic (Zr-Mo, Zr-W) modification of ZSM-5 based catalysts on the physico-chemical and catalytic properties of pentasils in the conversion of methanol to aromatic hydrocarbons and para-selectivity of the catalyst.

The nature and concentration of nanopowders of metals (Zr, Mo, W) in mono- and bimetallic catalysts based on pentasil prepared by solid-phase modification considerably influences its physico-chemical, catalytic properties in comparison with yield of xylene fraction and selectivity for p-xylene (figure 10).

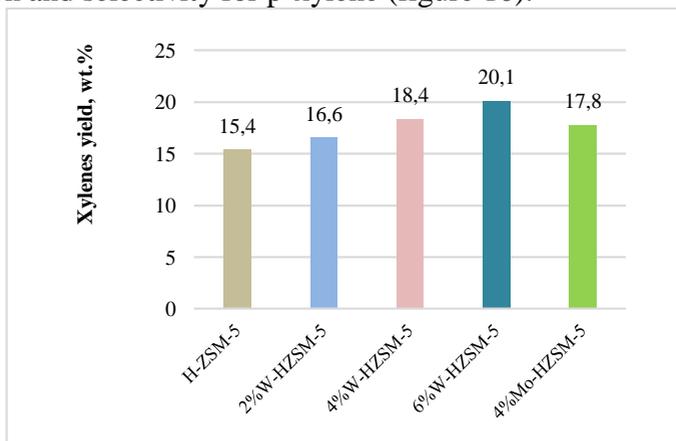


Figure 10. Xylene yield dependence on the nature and concentration of the modifying metal ($T=400^{\circ}\text{C}$, $v=2.0\text{h}^{-1}$)

The introduction of modifiers into the HZSM-5 zeolite leads to an increase in the yield of the xylene fraction (figure 10). For example, raising the content of tungsten nanopowder in zeolite leads to an increase in the xylene fraction from 15.4 wt.% to 20.1 wt.%.

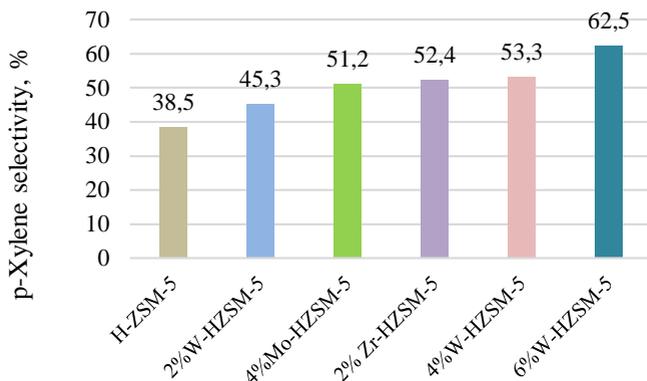


Figure 11. Dependence of p-xylene selectivity on concentration and nature of the modifying metal ($T=400\text{ }^{\circ}\text{C}$, $v=2.0\text{h}^{-1}$)

The activity of the zeolite catalysts modified with Mo and W nanopowders does not significantly differ from each other. The Zr-containing catalyst shows a higher selectivity for p-xylene (52.4%) than the W-containing catalyst (45.3%) for the same amount (2.0 wt.%). Once the W content in the catalyst is up to 6.0 wt%, the p-xylene selectivity achieves up to 62.5% (figure 11).

The loading of 0.5-1.5 wt.% Zr into 6% W-HZSM-5 catalyst has a slight effect on the yield of xylene fraction, but the selectivity for p-xylene is noticeably increased (figure 12). If the Zr content in the bimetallic catalyst is equal to 1.5 wt.%, the p-xylene selectivity grows to 68.0 %. Continuous increase of Zr content (2,5-3 mas.%) significantly decreases the yield of xylene fraction (up to 15,8 %), but leads to further increase of p-xylene selectivity (up to 71,6 %). Because of the modification, the modifier interacts with the acid sites of the initial zeolite and thereby alters the strength distribution of the acid sites. Raising the W content to 6.0 wt.% reduces the concentration of strong acid sites from 542 to 201 $\mu\text{mol}\cdot\text{g}^{-1}$, and the total acid site concentration to 528 $\mu\text{mol}\cdot\text{g}^{-1}$.

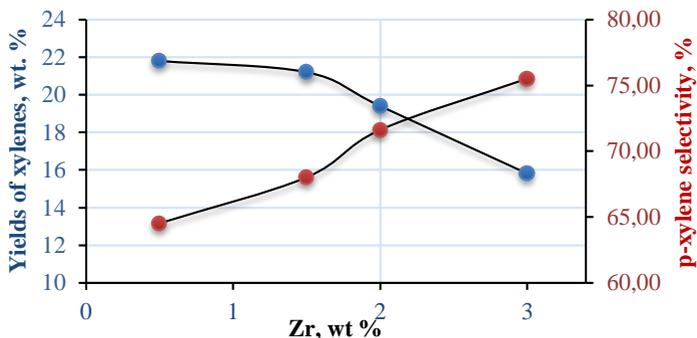


Figure 12: Effect of Zr nanopowder concentration on the yield of xylene fraction and p-xylene selectivity in bimetallic catalyst Zr 6% W-HZSM-5. (T=400°C, v=2.0h⁻¹)

Modifying the W-containing catalyst with 3.0 wt.% Zr reduces the concentration of strong acid centres to 198 $\mu\text{mol}\cdot\text{g}^{-1}$, also decreasing the specific surface area and pore volume of the catalyst. The loading of 3.0 wt.% Zr into the composition of 6% W- HZSM-5 reduces its specific surface area from 237.5 to 233.6 cm^2/g and pore volume from 0.183 to 0.168 cm^3/g .

Hence, modifying HZSM-5 with nanopowders redistributes its acidic sites by strength, establishes new active sites with modifiers, and reduces the pore volume of the catalyst. The nanopowder composition of Zr and W with HZSM-5 zeolite is an active catalyst for the production of p-xylene from methanol. HZSM-5 was modified with Zr and W nanopowders in the amount of 1.5-2.0 wt.% and 6.0 wt.% respectively to obtain a bimetallic catalyst showing higher para-selectivity (68.1-71.6%).

It is established, that increasing molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ in zeolite from 61 to 103 the yield of xylene fraction decreases from 15.9 wt.% to 13.8 wt.%. Similar to the case of W, the introduction of Mo nanopowder into the composition of pentasil has a promotive effect on its activity. The addition of up to 6.0 wt.% Mo nanopowder to the H-ultrasil composition increases the yield of the xylene fraction to 21.1 wt.%. The same effect is achieved upon modification of H- LiBH and HZSM type zeolites with Mo in an amount of 6.0 wt.%. On these catalysts, the p-xylene selectivity is up to 63.7-64.8%. Additional

modification of 6% Mo-HZSM catalyst with Cr nanopowder in an amount of 0.5-1.5 wt.% has little effect on the yield of xylene fraction, but contributes to a significant increase of para-selectivity (68.9%) (figure 13).

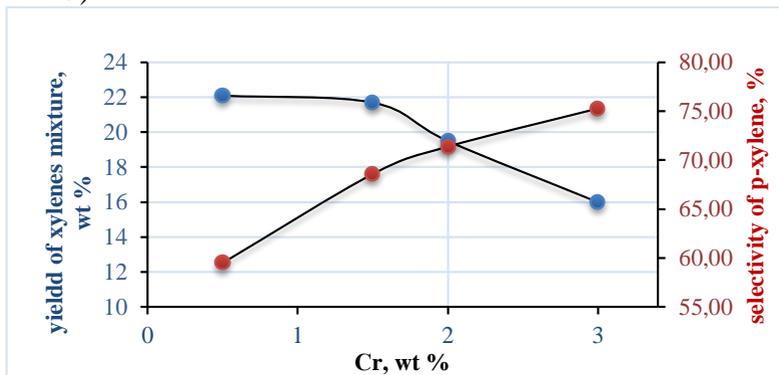


Figure 13. Effect of chromium nanopowder concentration in 6% Mo-HZSM on xylene fraction yield and p-xylene selectivity ($T=400^{\circ}\text{C}$, $v=2.0\text{h}^{-1}$).

An increase in the concentration of Cr nano-powder leads to a noticeable decrease in the yield of the xylene fraction (16.0 wt.%). Nature of the modifying nanopowder has an impact on the yield of the xylene fraction and the selectivity for p-xylene. Highest yield of xylenes is achieved on bimetallic catalysts containing Cr and V (21.7-22.3 wt.%). The highest p-xylene selectivity is attained on bimetallic catalysts containing Zn and V. The selectivity for p-xylene on these samples is 69.8-70.8%. The promoting effect of nanopowders (Cr, Zn, Ni, V) on the properties of pentasils is related to a redistribution of its acid sites in strength, the formation of new more moderate active acid sites, and a change in the porous structure of the catalyst. A change in the acidic characteristics of the modified zeolites has an effect on their catalytic properties in the conversion of methanol to aromatic hydrocarbons and the para-selectivity of the catalyst.

Effect of $\text{Ce}_{0.1}\text{Mg}_{0.90}\text{Al}_2\text{O}_4$ and $\text{Gd}_{0.1}\text{Mg}_{0.90}\text{Al}_2\text{O}_4$ nanopowders content on physico-chemical and catalytic properties of high silica zeolite type ZSM in the conversion of methanol into p-xylene.

The study of the physico-chemical and catalytic properties of H-pentasil composition with spinel nanopowders is of particular interest. X-ray diffraction analysis has revealed that the formation of the spinel phase takes place in the temperature range 800 - 1200°C. The size of the nanopowder depends on the calcination temperature. X-ray phase analyses were carried out for the heat-treated samples at 800, 1000 and 1200 °C for 2 hours. Diffractograms of samples of compositions MgAl_2O_4 , $\text{Ce}_{0,10}\text{Mg}_{0,90}\text{Al}_2\text{O}_4$, $\text{Ce}_{0,05}\text{Mg}_{0,95}\text{Al}_2\text{O}_4$ and CeO_2 are shown in figure 14. The catalytic compositions were prepared by mixing heat-treated nanopowders in an amount of 1.0-10.0 wt.% with 90-99% HZSM-5 zeolite. The effect of the nature of the catalyst on the selectivity of the formation of p-xylene from methanol is shown in figure 14. In the temperature range of 350-400 °C the degree of methanol conversion is 100 % both on H-form zeolite and on modified samples.

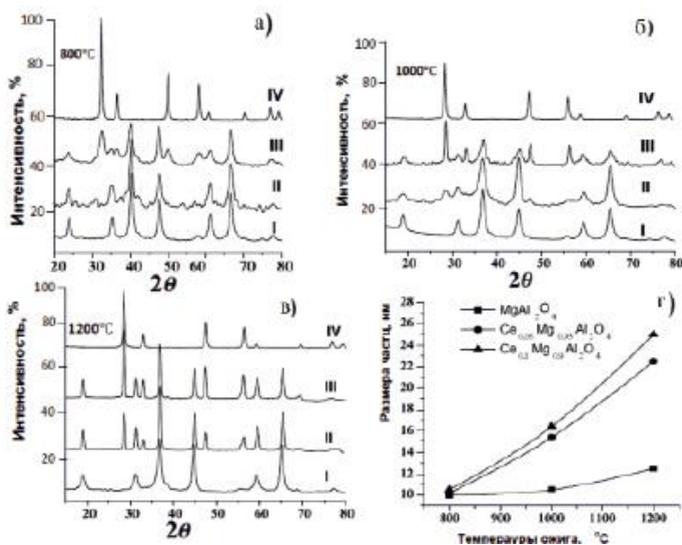
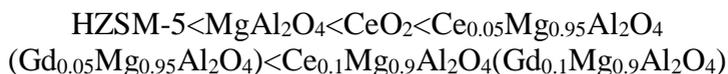


Figure 14. Diffractograms of compositions MgAl_2O_4 , $\text{Ce}_{0,10}\text{Mg}_{0,90}\text{Al}_2\text{O}_4$ and $\text{Ce}_{0,05}\text{Mg}_{0,95}\text{Al}_2\text{O}_4$

The main products of methanol conversion are $\text{C}_2\text{-C}_4$ olefinic (30-40 %), C_{5+} aliphatic (15-25 %) and $\text{C}_6\text{-C}_{10}$ aromatic hydrocarbons (25-40 %). The selectivity of p-xylene formation depends on the nature of the modifier. Modification of H-ZSM-5 with CeO_2 , Ce_xMg_1 .

$x\text{Al}_2\text{O}_4$ ($\text{Gd}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$) and $\text{Ce}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ ($\text{Gd}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$) nanopowders in amounts of 1.0 wt.% results in changes in the catalytic properties of catalysts. The addition of 1.0 wt.% modifiers to H-ZSM-5 improves the p-xylene selectivity. Using 1.0 wt. % modifiers in H-ZSM-5 increases the p-xylene selectivity compared to H-ZSM-5 from 34 % to 63 %. The catalyst selectivity for p-xylene and the yield of aromatic hydrocarbons grows in the following order when HZSM-5 is modified with modifiers.



The sample modified with $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$ ($\text{Gd}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$) nanopowder exhibited the highest selectivity for p-xylene among the tested samples. With this in mind, the catalytic properties of HZSM-5 compositions with $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$ were further investigated. The effect of $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$ nanopowder concentration in HZSM zeolite on xylene fraction yield (1) and p-xylene selectivity (2) is shown in figure 15. It was revealed that increasing the content of the modifier to 10.0 wt.% leads to a decline in the yield of the xylene fraction (13.2%) and an increase in the selectivity of p-xylene. The optimum content of $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$ nanopowder, which provides favourable xylene yields (17.0 wt. %) and high p-xylene selectivity (75.0 %) in HZSM-5, has been found to be 5.0 wt. %. The same pattern is observed on a sample modified with 5.0 wt.% $\text{Gd}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$. The xylene fraction yield stands at 18.0 % and the p-xylene selectivity is 78.0 %.

Modification has a significant effect on the acidic and textural properties of the catalyst. The effect of increasing para-selectivity of HZSM catalysts modified with $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$ ($\text{Gd}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$), nanopowders is explained by the decrease in strength of strong Bronsted acid sites, formation of acid sites of moderate strength and by the change in porous structure of zeolite due to modification. Thus, HZSM-5 zeolites type modified with $\text{Ce}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$ ($\text{Gd}_{0.1}\text{Mg}_{0.9}\text{Al}_2\text{O}_4$) nanopowders in amount of 5.0% are active catalysts for the xylene synthesis from methanol and have high para-selectivity (75-78%).

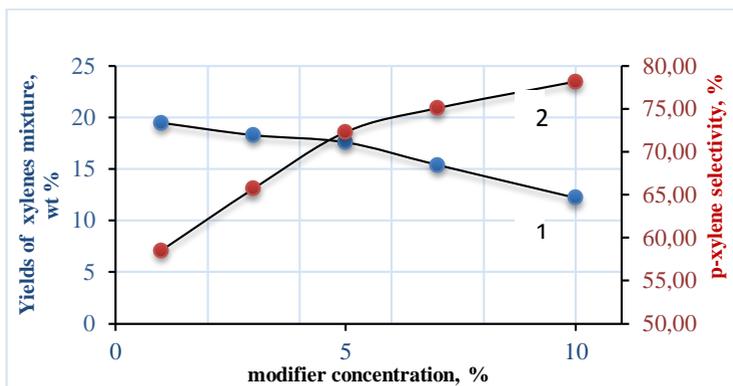


Figure 15. Effect of $Ce_{0.1}Mg_{0.9}Al_2O_4$ nanopowder concentration in HZSM-5 on xylene yield (1) and p-xylene selectivity (2) ($T=400^\circ C$, $v=2.0h^{-1}$)

CONCLUSIONS

1. ZSM-5 type of high silica zeolites in H- and cationic forms containing multicharge cations (Sr, Ba, Sc, Zn, Gd) are active catalysts for conversion of methanol into aromatic hydrocarbons at $350-400^\circ C$. The properties of the cations can be adjusted by changing the nature, charge and size of the Me^{n+} ion in the zeolite. The modified zeolites are arranged in order of aromatic hydrocarbon yield:

$Gd-ZSM-5 > Sc-ZSM-5 > Zn-ZSM-5 > Sr-ZSM-5 > Ba-ZSM-5$

Zeolites with heavier cations (Sr, Ba) having low activity exhibit a higher selectivity for p-xylene (60.5-64.3%). The most active catalyst, Gd-ZSM-5, shows a p-xylene selectivity of 55.7%.

2. It has been revealed that not only the Bronsted (B) but also the Lewis (L) acid sites are responsible for the synthesis of aromatic hydrocarbons from methanol. Substitution of Na^+ cations with multi-charge Me^{n+} cations significantly decreases the concentration of strong Bronsted acid sites on the zeolite surface and forms new Lewis acid sites, which leads to an increase of aromatic hydrocarbons yield and p-xylene selectivity.

3. The nature of the metal and its concentration loaded into zeolite ZSM-5 by impregnation method plays a decisive role in the formation of aromatic hydrocarbons and the distribution of p-xylene in the

xylene mixture. The catalysts rank in order of selectivity for the formation of aromatic hydrocarbons and p-xylene:

Zr-HZSM-5>La-HZSM-5>Cr-HZSM-5>Ga-HZSM-5>HZSM-5

The highest p-xylene selectivity is achieved with a catalyst containing 5% Zr-HZSM-5 and is 73%.

4. The structure and textural properties of the catalysts have been investigated by electron microscopy, X-ray phase analysis and low-temperature nitrogen adsorption. It has been proven that zeolite modification does not lead to structural changes in the morphological structure of the zeolite. A significant change in the specific surface and porous structure of the zeolite is achieved through solid-phase modification and impregnation. Change of catalytic activity of zeolite catalyst for aromatic hydrocarbons and selectivity for p-xylene is due to direct interaction of modifiers with strong acid sites on zeolite surface, localization of modifier nanoparticles on external surface and inside zeolite pores.

5. Mono- and bimetallic catalysts have been obtained by solid-phase modification of HZSM-5 zeolite using nanopowders (Mo, W, V, Cr, Ni, Zn) and their properties in conversion of methanol into aromatic hydrocarbons have for the first time been studied. Bimetallic catalysts exhibit higher activity for aromatic hydrocarbons and for p-xylene than catalysts obtained by ion exchange and impregnation. The bimetallic systems Zr- W/HZSM-5 and V-Mo/HZSM-5 have the highest selectivity for the xylene fraction yield (20.0-21.0%).

6. The regularities of deactivation of HZSM-5 zeolite with silicate modules 61 and 200 during methanol conversion at 450°C were studied. It was revealed that methanol conversion and product selectivity strongly correlate with the zeolite silicate modulus. As the silicate modulus increases, the stability of the catalyst clearly increases. The HZSM-5 (M=61) completely loses activity when the running time is increased to 22h, and for HZSM-5 (M=200) the product selectivity changes insignificantly. It was established that loss of activity of zeolite HZSM-5 (M=61) is connected with sharp decrease of its specific surface (from 288 to 27 m²/g), total volume of pores (from 0.24 cm³/g to 0.03 cm³/g), blocking of strong acid centres and zeolite pores by coke deposit leading to disappearance of strong

acid centres.

7. New bimetallic zeolite catalysts and methods of their synthesis and modification have been proposed based on regularities of synthesis and catalytic action of metal-zeolite catalysts with adjustable properties. Bimetallic catalysts obtained by solid-phase modification with Mo, W, Zr, V and $Gd_{0.1}Mg_{0.90}Al_2O_4$ nanopowders have high work stability (100h) and provide high selectivity of p-xylene formation (75-78%) from methanol.

The main results of the thesis are published in the following publications.

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