UDC -547.53:547525+665.652.4+661.183.6

ALKYLATION OF TOLUENE WITH ISOPROPANOL ON ZSM-5 TYPE ZEOLITE MODIFIED BY RARE-EARTH METALS

N.M. Abdullayeva

Baku State University
23, Z.Khalilov str., AZ 1148, Baku; e-mail:nigaramirova@yandex.ru

Received 11.12.2019

Abstract: *Influence of rare-earth elements (La, Ho, Yb, Pr) on acidic,textural and catalytic properties of ZSM-5 high-silica zeolite in the reaction of toluene alkylation with isopropanol was studied in the temperature range of 250-350 ° C in a flow unit of ideal displacement. It revealed that the nature of rare earth metal in zeolites ZSM-5 plays a crucial role in its para-selectivity and catalytic activity. Maximum selectivity with respect to cymols is achieved on a Yb modified zeolite and is 70.5%. The highest para-selectivity is displayed by La modified zeolite to make up 72.4%. It found that rise in selectivity for cymol is due to decrease in concentration of strong acid centers, rise in proportion of acid centers of moderate strength, as well as changes in the porous structure of the zeolite due to its chemical modification.*
Keywords: *ZSM-5, alkylation, toluene, cymols, acidic centers, modification.*
DOİ: 10.32737/2221-8688-2020-1-49-54

Introduction

Alkylaromatic hydrocarbons are widely used in petrochemical and organic syntheses. Isopropyltoluenes (cymols) obtained by alkylation of toluene with isopropanol in the presence of Friedel-Crafts acidic catalysts are used to produce iso- and terephthalic acids, cresols and other important products of organic synthesis [1,2]. Acid catalysts used in industry make it no possible to obtain a p-isomer enriched mixture of cymols. These catalysts have low stability, undergo no regeneration and pollute the environment. Conducting such a process at one stage on solid acid catalysts, corrosion-resistant and environmentally friendly is an important and urgent task. Therefore, much attention has recently been paid to the creation and introduction of zeolite catalysts for alkylation of aromatic hydrocarbons with olefins and alcohols [3-5]. Zeolite catalysts are replacing traditional homogeneous acid and heterogeneous oxide catalysts everywhere [6-8]. A very promising direction of zeolite alkylation was discovered due to the development of syntheses of high-silica zeolites such as ZSM-5 have a three-dimensional channel structure with two different channels and 10-membered oxygen rings with pores of size 0.53×0.56 nm [9].

The purpose of this report was to study the influence of rare-earth elements (REE) (La, Ho, Yb, Pr) on physicochemical and catalytic properties of ZSM-5 type zeolite in the alkylation of toluene with isopropanol.

Experimental part

For the study, a high-silica zeolite of the type of a ZSM-5 with a molar ratio SiO_2 / Al_2O_3 = 58 was used and then converted by ion exchange into the NH4-form according to the procedure described previously [10].

The H-form of the zeolite was obtained by thermal decomposition of the NH4-form at 500°C for 4 hours. Catalysts modified with 5.0 wt% REE were obtained by impregnating the H-forms of the zeolite with an aqueous solution of nitrates La, Ho, Yb, Pr at 80°C for 6 hours. Samples were dried in air for 16 hours, then 4 hours in an oven at 110°C, and finally calcined for 4 hours at 550°C.

The acidic properties of the modified zeolites were studied through ammonia thermal desorption. The porous structure of the samples was studied by means of low-temperature nitrogen adsorption at 77 K using the ASAP-2000 unit of Micromeritics.

Before the experiment, the catalysts were activated in air flow at a temperature of

550°C for 1 hour, then lowered a temperature to 400°C and hydrogen was supplied for 1 hour. Experiments were carried out on a flow-type installation in a quartz reactor with a stationary catalyst bed and a volume of 4 cm^3 at an atmospheric pressure in the presence of hydrogen in the temperature range 250-350°C, bulk flow rate of $2h^{-1}$ at a molar ratio of C_7H_8: i-C_3H_7OH: H_2 equal to 2: 1: 2. Analysis of the reaction products was performed by gas-liquid chromatography [10].

Results and its discussion

Table 1 presents data on the activity and selectivity of HZSM-5 in the reaction of toluene alkylation with isopropanol. It is clear that as reaction temperature rises from 250^0 C to 350°C, the conversion of toluene increases from 8.8 to 27.1 mass%. The reaction products consist of benzene, cymols, propyltoluenes, C5 + aliphatic hydrocarbons and alkylaromatic hydrocarbons C_{8+}. Alkylation is accompanied by side reactions of transalkylation and isomerization of alkylation products, as well as dehydration of isopropanol, oligomerization of the resulting propylene followed by cracking and flavoring the resulting olefin fragments. As the reaction temperature increases to 330°C, the yield of by-products increases and the content of p-cymol in the mixture of cymols decreases from 43.8% to 33.7%, i.e., isomerization of p-cymol to m- and o-cymols occurs.

Table 1. Composition of toluene alkylation products with isopropanol on HZSM-5

t,°C	Conversion, wt.%		Selectivity for products in catalyzate,%					Isomeric composition of cymols,%		
	toluene	isopro-panol	ben-zene	cymols	propyl-toluenes	C_5+ aliph. hydro-carb.	ArH C_{8+}	m	p	o
250	8.8	94.2	0.3	52.5	33.3	12.4	1.5	50.8	43.8	5.4
300	19.5	99.1	2.5	56.4	30.2	8.8	5.1	53.2	40.3	6.5
330	27.1	99.7	3.1	55.8	29.0	6.2	5.9	58.2	33.7	8.1

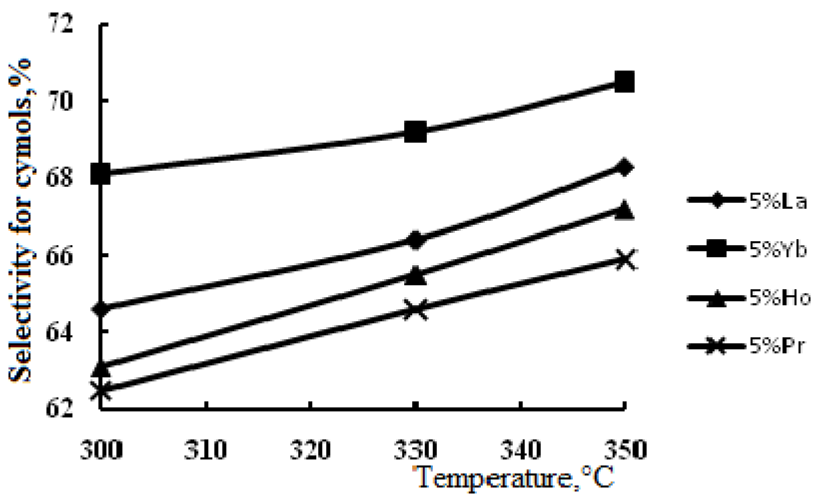

Fig. 1. Dependence of selectivity for cymols on the REE nature in the catalyst HZSM-5 at different temperatures.

Modification of REE zeolite significantly affects its activity and selectivity. Modification of HZSM-5 with metals amounting to 5.0 mass% significantly reduces the yield of by-products and raises the selectivity for p-cymol. It found that the modification of HZSM-5 by any of the REEs leads to rise both in the selectivity for cymols (Fig. 1) and the content of p-cymol in the catalyzate (Fig. 2).

The highest selectivity for cymols is observed on the Yb-modified catalyst, and at 350°C it makes up 70.5%. According to the selectivity of cymols formation depending on the modifying metal, the catalysts are arranged in a row as follows: Yb-HZSM-5> La-HZSM-5> Ho - HZSM-5> Pr - HZSM-5.

The difference in selectivities observed on Yb and La modified catalysts is 2.2%. As can be seen from Fig. 2, the highest content of p-cymol in a mixture of cymols is observed on a modified La catalyst, i.e. the highest p-selectivity is shown by the catalyst with 5% La / HZSM-5.

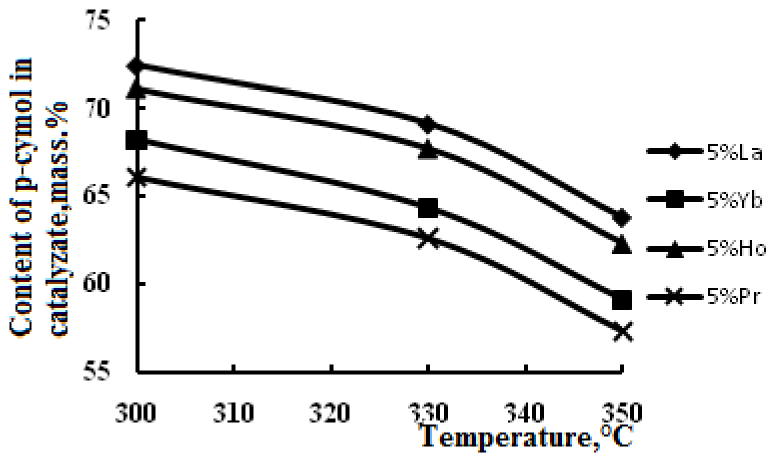

Fig. 2. Influence of the REE nature in the composition of HZSM-5 on the content of p-cymol in the catalyzate at different temperatures.

On this catalyst at 300°C, the selectivity for p-cymol is 72.4%. The rise in the reaction temperature from 300°C to 330°C significantly reduces the p-selectivity of modified catalysts. According to p-selectivity, depending on the modifying metal, the catalysts are arranged in the following row: La - HZSM-5> Ho – HZSM-5> Yb - HZSM-5> Pr - HZSM-5.

Effect of the modification and REE nature on the activity and para-selectivity of the zeolite catalyst may be due to changes in the acidic and textural properties of catalysts as a result of modification.

Table 2. Acid characteristics of modified catalysts

Catalyst	T_{max} forms,°C desorption of ammonia		Concentration of acid sites, (µkmol • g-1) ^{x}		C_1 /C_2
	T_I	T_{II}	C_1	C_2	
HZSM-5	198	421	625	548	1.14
5%La HZSM-5	183	284	182	103	1.77
5%Ho HZSM-5	185	296	197	119	1.65
5%Yb HZSM-5	189	314	349	231	1.51
5%Pr HZSM-5	190	326	358	242	1.48

T_I, T_{II} -peak temperatures for forms I and I I

C_1 and C_2 - concentrations of acid sites in forms (I) and (II).

As the Table 2 shows, two peaks are observed in the thermally desorbed spectrum for the initial HZSM-5 spectrum which indicates the presence of two forms of ammonia desorption from the zeolite catalyst: a low-temperature peak in the region of 120-230°C with a maximum peak temperature T_{max} = 198°C refers to the desorption of ammonia with weak Lewis acidic and high-temperature peak in the region of 300-500°C with T_{max} = 421°C related to ammonia desorption mainly from strong Bronsted acid centers which are hydrogen ions of bridging hydroxyl groups [11-12]. The introduction of modifiers into HZSM-5 leads to significant changes in its thermal desorption spectra. The largest decrease of strong acid sites concentration is observed when lanthanum HZSM-5 is modified: the concentration of strong acid sites decreases from 548 µmol /g to 103 µmol /g.

The concentration of strong acid sites on samples containing Yb and Pr is significantly higher than on samples containing La. When comparing the acidic and catalytic properties of modified catalysts, some assumptions can be made as follows: a decrease in the total number of acid sites leads to an increase in the p-selectivity for p-cymol, and the ratio of the proportion of medium to strong acid centers plays an important role The best results are provided by medium-strength acid centers of Bronsted and Lewis which were formed after modification of zeolite HZSM-5 with lanthanum and holmium. The catalyst 5% La HZSM-5 with its highest ratio of medium to strong acid sites (1.77) shows the highest selectivity for p-cymol.

The Table 3 presents textural properties of modified zeolites. It can be seen that the nature of the modifier significantly affects the porous structure of the zeolite. It is seen that as a result of the modification, the surface area, volume and radius of the pores decrease. Apparently, this is explained by the fact that during the preparation of the catalyst, part of the zeolite proton centers is exchanged for REE cations, as well as the deposition of REE oxides on the surface and in the channels of the zeolite, which leads to a change in the acid properties and geometry of the zeolite framework and, accordingly, the pore radius from R_{max} 10-110 to 8-83 Å, with which the activity and selectivity of zeolite systems are closely related.

Table 3. Textural characteristics of catalysts according to the BET method

Catalysts	S, м^2/г	V_{pore} (см^3/г)	R_{ef}, Å	R_{max}, Å
H-ZSM-5	266.3	0.24	10-110	65
5% La-ZSM-5	223.4	0.17	8-75	56
5% Yb-ZSM-5	231.4	0.19	8-77	58
5% Ho-ZSM-5	226.2	0.18	8-75	57
5% Pr-ZSM-5	236.7	0.20	8-83	61

Thus, the REE nature in HZSM-5 zeolites plays a decisive role in its paraselectivity and catalytic activity which is due to changes in the acidic and textural properties of zeolites as a result of their chemical modification. It found that the most active with respect to cymol is Yb-modified HZSM: the maximum selectivity for cymol is 70.5%. Maximum paraselectivity is observed on the modified lantan catalyst and is 72.4%.

References

1. Koshel G.N., Nesterova T.N., Rumyantseva Yu.B., Kurganova E.A., Ivanova A.A. Cymols. Obtaining cresols and their use. *Vestnik MITHT*, 2012, vol. 7, no. 6, pp. 56-59. (In Russian).
2. Neatu F., Culic G., Florea M., Parvulescu V.I. and Cavani F. Synthesis of Terephthalic Acid by p-Cymene Oxidation using Oxygen: Toward a More Sustainable Production of Bio-Polyethylene

Terephthalate. *ChemSusChem*. 2016, vol. 27, no. 9, pp. 3102-3112. https://doi.org/10.1002/cssc.201600718
3. Thakur R., Gupta R.K. and Barman S. A comparative study of catalytic performance of rare earth metal-modified beta zeolites for synthesis of cymene. *Chemical* Papers. 2017, vol. 71, pp. 137-148. https://link.springer.com/article/10.1007/s11696-016-0071-x
4. Upadhyayula S. Gas phase toluene isopropylation over high silica mordenite. *J. Chem. Sci*. 2010, vol. 122, no. 4, pp. 613-619. https://link.springer.com/article/10.1007/s12039-010-0096-6
5. Barman S., Maity S.K. and Pradhan N.C. Alkylation of toluene with isopropyl alcohol catalyzed by Ce-exchanged NaX zeolite. *Chem. Eng. J*. 2005, vol. 114, pp. 39-45. https://doi.org/10.1016/j.cej.2005.08.014.
6. Odedairo T., Al-Khattaf S. and Jermy R. Influence of Mesoporous Materials Containing ZSM-5 on Alkylation and Cracking Reactions. *J. Mol. Catal. A, Chemical*. 2011, vol._345, pp. 21-36. DOI:10.1016/j.molcata.2011.05.015
7. Chiang T-C., Chan J-C., Tan C-S. Alkylation of Toluene with Isopropyl Alcohol over Chemical Liquid Deposition Modified HZSM-5 under Atmospheric and Supercritical Operations. *Ind.* Eng. Chem. Res. 2003, vol. 42, no. 7, pp. 1334-1340. https://pubs.acs.org/doi/abs/10.1021/ie0206305
8. Janardhan H.L., Shanbhag G. and Halgeri A.B. Shape-selective catalysis by phosphate modified ZSM-5: Generation of new acid sites with pore narrowing. *Appl. Catal. A: Gen*. 2014, vol. 471, pp. 12-18. https://doi.org/10.1016/j.apcata.2013.11.029
9. Antony Raj K.J., Padma Malar E.J. and Vijayaraghavan V.R. Shape-selective reactions with AEL and AFI type molecular sieves alkylation of benzene, toluene and ethylbenzene with ethanol, 2-propanol, methanol and *t*-butanol. *J. Mol. Catal. A, Chemical*. 2006, vol. 243, pp. 99-105. https://doi.org/10.1016/j.molcata.2005.07.040
10. Amirova N.M., Mamedov S.E., Gakhramanov T.O. The effect of the concentration of magnesium oxide on the physicochemical and catalytic properties of high-silica zeolites of the ZSM type in the alkylation reaction of toluene with isopropanol. *Young scientist*. 2018, no. 10, (196), pp. 8-11. (In Russian).
11. Kazansky V.B., Borovkov V.Yu., Serykh A.I., van Santen R.A. and Anderson B.G. Nature of the sites of dissociative adsorption of dihydrogen and light paraffins in ZnHZSM-5 zeolite prepared by incipient wetness impregnation. *Catal. Lett.* 2000, vol. 66, pp. 39-47. https://link.springer.com/article/10.1023/A%3A1019031119325
12. Gong T., Zhang X., Bai T., Zhang Q., Tao L., Qi M., Duan C. and Zhang L. Coupling Conversion of Methanol and C_4 Hydrocarbon to Propylene on La-Modified HZSM-5 Zeolite Catalysts. *Ind. Eng. Chem. Res*. 2012, vol. 51, pp. 13589-13598. DOI: 10.1021/ie300515z

NADİR TORPAQ METALLARI İLƏ MODİFİKASİYA OLUNMUŞ ZSM-5 NÖVLÜ SEOLİTİN İŞTİRAKINDA TOLUOLUN İZOPROPANOLLA ALKİLLƏŞMƏSİ

N.M. Abdullayeva

Bakı Dövlət Universiteti
AZ 1148, Bakı, Z. Xəlilov küç.,23; e-mail: nigaramirova@yandex.ru

Axın tipli qurğuda 250-350^{O}C temperatur intervalında toluolun izopropanolla alkilləşməsi reaksiyasında nadir torpaq elementlərinin (La,Ho,Yb,Pr) təbiətinin yüksək silisiumlu ZSM-5 növlü seolitin turşu, tekstur və katalitik xassələrinə təsiri öyrənilmişdir. Müəyyən olmuşdur ki, *ZSM-5 seolitdə nadir torpaq elementlərinin təbiəti onun para-seçiciliyinə və katalitik aktivliyinə mühüm dərəcədə təsir edir. Cimollara görə maksimal seçicilik Yb ilə modifikasiya olunmuş seolitdə baş verir və 70.5% təşkil edir. Para-seçiciliyə görə daha yüksək seçicilik La ilə modifikasiya olunmuş seolit göstərir(72.4%). Müəyyən olunmuşdur ki, kimyəvi modifikasiya nəticəsində p-cimola görə seçiciliyin artması güvvətli turşu mərkəzlərinin azalması, orta turşu mərkəzlərinin payının artması və seolitin məsaməli quruluşunun dəyişməsi ilə əlaqəlidir.*

Açar sözlər: *ZSM-5, alkilləşmə, toluol, izopropanol, cimol, turşu mərkəzləri, modifikasiya.*

АЛКИЛИРОВАНИЕ ТОЛУОЛА ИЗОПРОПАНОЛОМ НА ЦЕОЛИТЕ ТИПА ZSM-5, МОДИФИЦИРОВАННОГО РЕДКОЗЕМЕЛЬНЫМИ МЕТАЛЛАМИ

Н.М. Абдуллаева

Бакинский государственный университет
AZ 1148, Баку, ул. З.Халилова, 23; e-mail: nigaramirova@yandex.ru

В интервале температур 250-350° С в проточной установке идеального вытеснения изучено влияние природы редкоземельных элементов (La, Ho, Yb, Pr) на кислотные, текстурные и каталитические свойства высококремнеземного цеолита типа ZSM-5 в реакции алкилирования толуола изопропанолом. Установлено, что природа редкоземельного металла в цеолитах ZSM-5 играет определяющую роль в его пара-селективности и каталитической активности. Максимальная селективность по отношению к цимолам достигается на цеолите, модифицированном Yb и составляет 70.5%. Наибольшую пара-селективность проявляет цеолит, модифицированный La и составляет 72.4%. Установлено, что возрастание селективности по цимолу связано с уменьшением концентрации сильных кислотных центров, увеличением доли кислотных центров средней силы, а также изменением пористой структуры цеолита в результате его химического модифицирования.

Ключевые слова: *ZSM-5, алкилирование, толуол, изопропанол, цимолы, кислотные центры, модифицирование.*