DOI: 10.6060/ivkkt.20236603.6759

УДК: 665.64.097.3

ТЕРМОКАТАЛИТИЧЕСКАЯ ДЕСТРУКЦИЯ ПОЛИСТИРОЛА В ПРИСУТСТВИИ ПОЛИТИТАНАТА КАЛИЯ

Н.А. Жердецкий, А.В. Гороховский

Никита Александрович Жердецкий (ORCID 0000-0001-7930-5365)*, Александр Владиленович Гороховский (ORCD 0000-0002-4210-3169)

Кафедра химии и химической технологии материалов, Саратовский государственный технический университет им. Ю.А. Гагарина, ул. Политехническая, 77, Саратов, Российская Федерация, 410054
E-mail: zherdetskey@yandex.ru*, algo54@mail.ru

Исследована возможность использования квазиаморфного полититаната калия (ПТК) в качестве нового типа катализатора деструкции полимерных материалов на примере полистирола (ПС). Термическую и термокаталитическую деструкцию полистирола проводили при 450 °С в реакторе оригинальной конструкции, предусматривающем крекинг полимеров в изотермических условиях и продувку инертным газом (азот), разделение и накопление жидких и газообразных продуктов. Установлено, что введение порошка ПТК в расплав полистирола в количестве 10 масс.% обеспечивает увеличение выхода полезных продуктов крекинга (газообразные и жидкие углеводороды) на 15,5 масс.%. При этом выход жидких углеводородов увеличивается на 13,6 масс.%, а газообразных углеводородов на 1,9 масс.%. Показано, что, в сопоставлении с термическим крекингом, введение в состав полимера 10% добавки ПТК увеличивает количество жидкого продукта (от 56,4 до 70,0 масс.%) и газообразного продукта (от 17,2 до 19,1 масс.%), а количество неразложившегося остатка снижается от 26,4 до 10,9 масс.%. Выявлено, что химический состав продуктов термической и термокаталитической деструкции полистирола значительно отличается. При этом в составе дистиллята продуктов термической деструкции преобладают ароматические углеводороды, около 80% которых составляют бензол и толуол. В продуктах термокаталитической деструкции в составе дистиллята содержится на 6,9% меньше соединений ароматического ряда и на 16,1 % увеличивается выход соединений ненасыщенного ряда (олефинов). Газообразный продукт термического крекинга обогащен этиленом и изобутиленом, и в его составе отсутствуют предельные углеводороды, а в газообразном продукте, полученном в результате термокаталитической деструкции, присутствует изобутан, при этом увеличивается выход этилена - на 5,4 масс.%, пропилена – на 10,5 масс.% и изобутилена – на 8,2 масс.%. Обсуждается механизм каталитического действия ПТК.

Ключевые слова: полититанаты калия, полистирол, термическая деструкция, каталитический крекинг

THERMOCATALYTIC DESTRUCTION OF POLYSTYRENE IN THE PRESENCE OF POTASSIUM POLYTITANATE

N.A. Zherdetsky, A.V. Gorokhovsky

Nikita A. Zherdetsky (ORCID 0000-0001-7930-5365)*, Alexander V. Gorokhovsky (ORCD 0000-0002-4210-3169)

Department of Materials Chemistry and Chemical Technology, Yuri Gagarin State Technical University, Politekhnicheskaya st., 77, Saratov, 410054, Russia
E-mail: zherdetskey@yandex.ru *, algo54@mail.ru

The thermocatalytic destruction of polystyrene under the action of quasi-amorphous potassium polytitanate (PPT), used as a new catalyst of the organic polymers destruction, has been studied. Thermal and thermocatalytic destruction of polystyrene was carried out at 450 °C in a reactor

of an original design, which provides cracking of polymers under isothermal conditions and purging with an inert gas (nitrogen), as well as separation and accumulation of liquid and gaseous products. It has been established that the introduction of PPT powder into the polystyrene melt in an amount of 10 wt.% provides an increase in the yield of useful cracking products (gaseous and liquid hydrocarbons) by 15.5 wt.%. The yield of liquid hydrocarbons increases by 13.6 wt.%, and gaseous hydrocarbons by 1.9 wt.%. It is shown that, in comparison with the thermal cracking, an introduction of the PPT powder (10 wt.%} in the molten polymer increases the amount of liquid product (from 56.4 to 70.0 wt.%) and gaseous product (from 17.2 to 19.1 wt.%), whereas, the amount of undecomposed residue is reduced from 26.4 to 10.9 wt.%. It is found that a chemical composition of the products of the thermal and thermo-catalytic destruction of polystyrene differ significantly. Although aromatic hydrocarbons predominate in the composition of the distillate of the thermal destruction (about 80% of which are benzene and toluene), liquid products of the thermo-catalytic destruction contain 6.9% less aromatic compounds as well as a yield of olefins increases by 16.1%. The gaseous product of the thermal cracking is enriched with ethylene and isobutylene, and does not contain alkanes, while iso-butane appeares in the gaseous product of the thermocatalytic destruction and a yield of ethylene increases by 5.4 wt.%, propylene - by 10.5 wt.% and isobutylene - by 8.2 wt.%. A mechanism of the catalytic action of PPT is discussed.

Key words: potassium polytitanates, polystyrene, thermal degradation, catalytic cracking, cracking

Для цитирования:

Жердецкий Н.А., Гороховский А.В. Термокаталитическая деструкция полистирола в присутствии полититаната калия. *Изв. вузов. Химия и хим. технология*. 2023. Т. 66. Вып. 3. С. 77–84. DOI: 10.6060/ivkkt.20236603.6759.

For citation:

Zherdetsky N.A., Gorokhovsky A.V. Thermocatalytic destruction of polystyrene in the presence of potassium polytitanate. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2023. V. 66. N 3. P. 77–84. DOI: 10.6060/ivkkt.20236603.6759.

INTRODUCTION

Currently, there is an increase in the production of polymers all around the world. Each year more than 150 million tons of plastics are consumed in industry [1]. At the same time, the consumption of plastics for household needs has increased up to 1 t/year per person. That is why, the problem of recycling and reuse of polymer wastes intensifies every year taking into account that the industrial synthetic polymers are very stable materials and do not decompose in the environment for centuries.

Traditional methods of polymer utilization such as waste disposal, incineration and pyrolysis, have a lot of drawbacks (high energy costs, inability to obtain valuable products, etc.) and, consequently, low economic efficiency [2-4]. That is why, recycling of polymers is the most important direction of resource saving. Since non-renewable hydrocarbon raw materials are used for the production of polymers, chemical processing of polymer wastes is looking as a very promising direction because allows obtaining fuels and/or petrochemical products [5].

Catalytic cracking has shown high efficiency among the alternative methods of polymer waste recycling. Thermo-catalytic degradation is the reactions of cleavage of plastic waste in the range of 400-500 °C in a presence of heterogeneous catalysts and provides producing some useful liquid and gaseous hydrocarbon products [6, 7]. This process is characterized by short reaction time, high concentration of distillates containing short and medium chains, and has relatively low yield of solid products. The traditional heterogeneous catalysts of the thermal decomposition of hydrocarbons (aluminosilicates, aluminum oxides and various zeolites) are the materials with Lewis acid centers in their structure [8-12].

At the same time, although zeolite catalysts can effectively convert plastic waste into fuel products at lower temperatures, they produce more gaseous than liquid products [13-20]. Furthermore, these catalysts are very expensive and are characterized with excessive coke formation on their surface [12, 18-25].

Thus, R&D activity on development of new low cost and high effective catalysts supporting thermal degradation of different polymer wastes seems to be an urgent task. Taking into account that polystyrene makes up a significant percentage of the total amount of polymer wastes (5-7%), the above mentioned problem is especially important for the treatment of this kind of macromolecular compound.

It is known, that the protonated forms of different titanates are demonstrated to function as a highly active solid Lewis acid catalyst even near room temperature. The high catalytic activity can be attributed to the unique structure, which contains both Brønsted and Lewis acid sites [26, 27]. The hydrothermal treatment of TiO_2 with alkali solution and subsequent acidification significantly increases its BET surface area and the amount of acid sites on the surface of catalyst. At the same time, it was shown that the titanate catalysts used in the cracking processes were characterized with low rate of coke formation [28].

Layered quasi-amorphous potassium polytitanates (PPT), synthesized in the molten mixtures of the potassium hydroxide and nitrate [29] and characterized with highly distorted defective structure, could be considered as potential heterogeneous catalysts for the cracking of polymers due to a well-developed internal surface and a presence of Ti^{3+} (up to 20 at.% of the total titanium), which, altogether with multiple oxygen vacancies, forms free electron orbitals located below the lower border of the conduction zone (Lewis acidic centers) [30]. It is also important that PPT has a stable structure when heated up to temperatures of 600-700 °C, which exceed the temperature of the thermal cracking of polymers [6, 7]. Furthermore, the PPT synthesis [29] is much more simple and cheap process in comparison with the titanate nanutubes and exfoliated nanosheets manufacturing [26, 27].

In this regard, the aim of this research is related to the investigation of the catalytic effect of the PPT admixtures on the thermal decomposition of polystyrene used as a model polymer.

EXPERIMENTAL PART

Polystyrene granules from 0.3 mm to 0.5 mm in size were used as a raw material for the thermal and thermo-catalytic degradation.

The PPT powder, used as a catalyst, was produced in accordance with [29] by the thermal treatment of TiO_2 powder in the molten mixture of KOH and KNO_3 at 500 °C for 2 h. The used raw material mixture contained the components in a weight ratio of 30:30:40. The obtained potassium polytitanate was washed with distilled water to pH = 10.5; dried at 50 °C for 8 h and further dispersed in a ball milled to obtain a powder having average size of 2 µm.

Thermal and thermo-catalytic degradation of polystyrene was carried out using the laboratory setup shown in Figure.

Granulated polystyrene (25 g) or the mixtures of polystyrene granules (25 g) and PPT powder (2.5 g, 10 wt.%) was introduced into the stain steel reactor and heated up to the temperature of the thermal cracking (450 °C) in the atmosphere of the inert gas (N_2, 99.9% of purity), which was fed into the reactor with a controlled rate (50 ml/min) and the resulting products were discharged through the other tube on top of the reactor. The temperature used for the thermal and thermo-catalytic degradation of polystyrene was selected taking into account a practice of this process in a presence of other known catalysts.

Before each experiment, the rector was purged with nitrogen for 15 min to prevent oxidation processes. The heating rate of 10 °C per minute was carried out until the temperature reaches 450 °C. A temperature of the process was monitored by thermocouple (4) during the all cracking process (1 h).

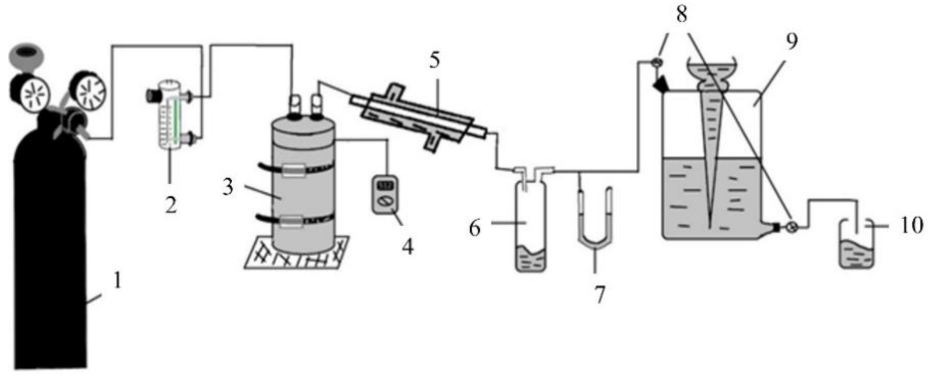


Fig. Schematic diagram of laboratory setup for thermal and thermocatalytic degradation of polymer materials. 1 - cylinder with inert gas; 2 - flow meter; 3 - reactor with raw materials; 4 - thermocouple; 5 - water cooler; 6 - trap-receiver; 7 - manometer; 8 - two-way cocks; 9 - gas meter; 10 - reservoir for displaced sodium chloride solution

Рис. Схема лабораторной установки термической и термокаталитической деструкции полимерных материалов. 1 – баллон с инертным газом; 2 – расходомер; 3 – реактор с сырьём; 4 – термопара; 5 – водяной холодильник; 6 – ловушка-приёмник; 7 – манометр; 8 – двухходовые краны; 9 – газометр; 10 – емкость для вытесненного газом раствора хлорида натрия

The products leaving the top of the reactor passed through the reverse water cooler (5). After the reflux condenser the vapor-liquid mixture was sent to the receiver (6), where the liquid products were accumulated. The gaseous products were collected in the gas-meter (9).

The chemical composition of the gaseous and liquid products of the thermal and thermo-catalytic cracking were investigated by gas-liquid chromatography (chromatograph "Crystal-5000") using the chromatographic columns filled with Porapak N sorbents.

RESULTS AND DISCUSSION

In accordance with the chromatographic data the thermal and thermo-catalytic cracking of polystyrene promoted obtaining: a liquid product in an amount of 56.4 and 70.0 wt. %; gaseous product in an amount of 17.2 and 19.1 wt. % and an undecomposed residue of 26.4 and 10.9 wt. %, respectively.

The complete compositions of the distillate products of the thermal and thermo-catalytic degradation of polystyrene, are reported in Table 1.

The obtained results allow us to note that the distillate product of the thermal destruction of polystyrene has a multicomponent composition with the predominance of aromatic hydrocarbons. About 80% of which are benzene and toluene. The data obtained correspond to the literature data [2, 26, 31, 32].

Table 1

Composition of the liquid products of the thermal and thermo-catalytic cracking of polystyrene

***Таблица 1.* Состав жидких продуктов термической и термокаталитической деструкции полистирола**

Group of products	Content, wt.%	
	Thermal destruction	Thermo-catalytic destruction
Alkenes	7.3	23.4
Cycloalkanes	7.0	0.4
Alkanes	3.0	1.4
Aromatics	79.4	72.5
Heterocyclic compounds	2.1	1.3
Ketones	1.1	1.1

Based on the data reported in Table 1, we can note that, in comparison with the thermal destruction, a presence of PPT in the thermo-catalytic process provided obtaining 6.9% less aromatic compounds and 16,1% more olefins.

These features of the catalytic cracking could be explained with the following proposed mechanism. At the first stage of both thermal and thermo-catalytic destruction, the polystyrene carbon chains break with the formation of high-molecular free radicals

$$[\text{-CH}(C_6H_5)\text{-CH}_2\text{-CH}(C_6H_5)\text{-}|\text{-CH}_2\text{-CH}(C_6H_5)\text{-CH}_2\text{-CH}(C_6H_5)\text{-}] = \text{-CH}(C_6H_5)\text{-CH}_2\text{-CH}(C_6H_5)^\bullet + {}^\bullet\text{CH}_2\text{-CH}(C_6H_5)\text{-CH}_2\text{-CH}(C_6H_5)\text{-}$$

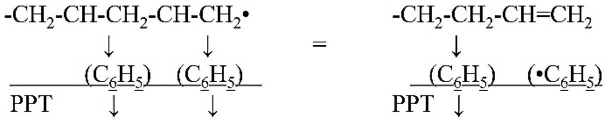
Taking into account breaking energy of the chemical bonds in the individual hydrocarbons for $E\{C\text{-}C_6H_5\}$ = 345-370 kJ/mol and $E\{H_2C\text{-}C(C_6H_5)\}$ = 300-310 kJ/mol [33], the following decomposition of the above mentioned high-molecular free radicals in the homogeneous conditions promotes obtaining, predominantly, styrene and another high-molecular free radical with more brief carbon chain

$$\text{-CH}_2\text{-CH}_2(C_6H_5)\text{-CH}_2\text{-CH}(C_6H_5)^\bullet = \text{-CH}_2\text{-CH}(C_6H_5)^\bullet + CH_2{=}CH(C_6H_5)$$

$$\text{-CH}(C_6H_5)\text{-CH}_2\text{-CH}(C_6H_5)\text{-CH}_2^\bullet = \text{-CH}(C_6H_5)\text{-CH}_2^\bullet + CH(C_6H_5){=}CH_2.$$

However, in a presence of the PPT particles, high-molecular free radicals, formed onto the surface of the catalyst as a result of the thermal decomposition of the adsorbed molecules of polystyrene, or appeared in the molten polymer and further adsorbed by this surface, could break down in other way considered below.

The adsorption of polystyrene and high-molecular free radicals formed and based thereon takes place due to a presence of Lewis acidic centers located onto the PPT surface. The electron clouds of the benzene rings of polystyrene interact with these surface active centers (free orbitals of the PPT particles), as a result there is redistribution of the electron density in the structure of the adsorbed high-molecular free radicals, breaking energy of the $\{C\text{-}C_6H_5\}$ chemical bonds reduces and the subsequent thermal decomposition of free radicals can proceed as



$$\begin{array}{l} \text{-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2^\bullet \\ \qquad\quad \downarrow \qquad\quad \downarrow \\ \underline{\qquad\quad (C_6H_5)\ \ (C_6H_5)} \\ \text{PPT} \quad\ \downarrow \qquad\quad \downarrow \end{array} = \begin{array}{l} \text{-CH}_2\text{-CH}_2\text{-CH=CH}_2 \\ \qquad\quad \downarrow \\ \underline{\quad (C_6H_5) \quad ({}^\bullet C_6H_5)} \\ \text{PPT} \ \downarrow \end{array}$$

The benzyl radicals further interact with hydrocarbons and form benzene as in the interface (adsorbed) as in the melt (after desorption); whereas a molecule of the alkene, depending its molecular weight, can participate in the following stages of the chain decomposition process, forming lower-molecular-weight olefins and dienes, or, after desorption, evaporate as a product condensed in the distillate.

This mechanism explains a significant increase in the yield of unsaturated products, primarily olefins and dienes, in the catalytic decomposition of polystyrene and is also confirmed by chemical composition of the gaseous product presented in Table 2.

If the gaseous product obtained as a result of the thermal destruction of polystyrene is mainly enriched with ethylene and isobutane, and does not contain saturated hydrocarbons, similar to the data published earlier [3], such product generated by the thermo-catalytic degradation in a presence of PPT, is enriched in various olefins and depleted in butane. The yield of ethylene increased by 5.4 wt.%, propylene – by 10.5 wt.% and butene – by 8.2 wt.%. At the same time, an amount of isobutane and n-butane has decreased by 24,6 wt.%.

The influence of the PPT catalyst on the chemical composition of the thermal cracking of polystyrene is important due to increased producing the olefins which represent valuable raw materials for the organic and petrochemical synthesis.

Table 2

Compositions of the gaseous products of the thermal and thermo-catalytic cracking of polystyrene

***Таблица 2.* Составы газообразных продуктов термической и термокаталитической деструкции полистирола**

Substance	Content, wt.%	
	Thermal destruction	Thermocatalytic destruction
C_2H_4	35.9	41.3
C_2H_6	1.2	1.7
C_3H_6	5.4	15.9
C_4H_8	4.3	12.5
n-C_4H_{10}	2.4	1.9
i-C_4H_{10}	50.8	26.7

Thus, the proposed mechanism of catalytic activity of potassium polytitanate (PPT) in the thermal decomposition of polystyrene (PS) is associated with the adsorption of high molecular weight hydrocarbon radicals formed during its thermal decomposition in the melt, which facilitate the breaking of C-C_6H_5 chemical bonds in the alkyl carbon chains of the polymer and stimulates the formation of unsaturated hydrocarbons (first of all, liquid and gaseous olefins). As a result, the products obtained under the action of the PPT catalyst are characterized with significantly increased (up to 23 wt.%) yield of liquid alkenes, which could be considered as a useful secondary product.

On the other hand, a presence of the catalyst ensures complete degradation of polymer chains and reduces the amount of solid undecomposed carbonized residue. It is important that the investigated catalyst favored deepen degradation of polystyrene and promotes a little bit increased yield of the gaseous products, in contrast to natural and synthetic zeolites and oxides [3, 34, 35], which do not influence or reduce this parameter.

In any case, the potassium polytitante powder influences a mechanism of the thermal decomposition of polymers, could be considered as a promising catalyst of their cracking process and has to be investigated with more details for the thermal decomposition of different high-molecular hadrocarbons.

CONCLUSION

Potassium poititanate (PPT) exhibits high catalytic activity in the polystyrene thermal cracking process.

A yield of the liquid hydrocarbons formed under the thermal decomposition of polysterene at 450 °C in a presence of 10 wt. % the PPT powder increases by 13,6 wt.%, whereas a quantity of the solid residue of the cracking reduces in two times.

The thermo-catalytic cracking of polystyrene in a presence of the PPT powder is characterized with a significantly increased yield of olefins: by 16.1 and 5.4 % wt.% for liquid and gaseous products, respectively.

The change in the composition of polystyrene thermal cracking products in a presence of the PPT powder can be explained by the electron density redistribution in the adsorbed high-molecular-weight hydrocarbon radicals, which leads to a change in the ratio of the probability of their further decomposition in different directions.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

The authors declare the absence a conflict of interest warranting disclosure in this article.

ЛИТЕРАТУРА

1. **Ibrasheva R.K., Mataeva Z.T., Zhubanov K.A.** Oxidative Catalytic Cracking of Heavy Oil Residues. *Eurasian Chem. Tech. J.* 2001. V. 3. P. 97 – 106. DOI: 10.18321/ectj551.
2. **Nisar J., Ali G., Shah A., Iqbal M., Khan R.A., Sirajuddin A.F., Ullah R., Akhter M.S.** Fuel production from waste polystyrene via pyrolysis: kinetics and products distribution. *Waste Manag.* 2019. V. 88. P. 236–247. DOI: 10.1016/j.wasma n.2019.03.035.
3. **Honus S., Kumagai S., Molnár V., Fedorko G., Yoshioka T.** Pyrolysis gases produced from individual and mixed PE, PP, PS, PVC, and PET—Part II: fuel characteristics. *Fuel.* 2018. V. 221. P. 361–373. DOI: 10.1016/j.fuel.2018.02.075.
4. **Zakharyan E.M., Petrukhina N.N., Maksimov A.L.** Pathways of Chemical Recycling of Polyvinyl Chloride: Part 1.

REFERENCES

1. **Ibrasheva R.K., Mataeva Z.T., Zhubanov K.A.** Oxidative Catalytic Cracking of Heavy Oil Residues. *Eurasian Chem. Tech. J.* 2001. V. 3. P. 97 – 106. DOI: 10.18321/ectj551.
2. **Nisar J., Ali G., Shah A., Iqbal M., Khan R.A., Sirajuddin A.F., Ullah R., Akhter M.S.** Fuel production from waste polystyrene via pyrolysis: kinetics and products distribution. *Waste Manag.* 2019. V. 88. P. 236–247. DOI: 10.1016/j.wasma n.2019.03.035.
3. **Honus S., Kumagai S., Molnár V., Fedorko G., Yoshioka T.** Pyrolysis gases produced from individual and mixed PE, PP, PS, PVC, and PET—Part II: fuel characteristics. *Fuel.* 2018. V. 221. P. 361–373. DOI: 10.1016/j.fuel.2018.02.075.
4. **Zakharyan E.M., Petrukhina N.N., Maksimov A.L.** Pathways of Chemical Recycling of Polyvinyl Chloride: Part 1.

Russ. J. Appl. Chem. 2020. V. 93. P. 1271–1313. DOI: 10.1134/S1070427220090013.

5. **Miskolczi N., Nagy R.** Hydrocarbons obtained by waste plastic pyrolysis: comparative analysis of decomposition described by diferent kinetic models. *Fuel Process Technol.* 2012. V. 104. P. 96–104. DOI: 10.1016/j.fuproc.2012.04.031.
6. **Miandad R., Rehan M., Barakat M.A., Aburiazaiza A.S., Khan H., Ismail I.M.I., Dhavamani J., Gardy J., Hassanpour A., Nizami A.-S.** Catalytic pyrolysis of plastic waste: moving toward pyrolysis based biorefneries. *Front. Energy Res.* 2019. V. 7. DOI: 10.3389/fenrg.2019.00027.
7. **Gackowski M., Tarach K., Kuterasinski N., Podobiński J., Jarczewski S., Kustrowski P., Datka J.** Hierarchical zeolites Y obtained by desilication: porosity, acidity and catalytic properties. *Microporous Mesoporous Mater.* 2018. V. 263. P. 282–288. DOI: 10.1016/j.micromeso.2017.11.051.
8. **Busca G.** Acidity and basicity of zeolites: a fundamental approach. *Microporous Mesoporous Mater.* 2017. V. 254. P. 3–16. DOI: 10.1016/j.micromeso.2017.04.007.
9. **Anuar Sharuddin S.D., Abnisa F., Daud W.M.A.W., Aroua K.M.** A review on pyrolysis of plastic wastes. *Energy Convers. Manage.* 2016. V. 115. P. 308–326. DOI: 10.1016/j.enconman.2016.02.037.
10. **Lopez A., Marco I.D., Caballero B.M., Laresgoiti M.F., Adrados A., Aranzabal A.** Catalytic pyrolysis of plastic wastes with two different types of catalytic: ZSM-5 zeolite and Red Mud. *Appl. Catal. B Environ.* 2011. V. 104. P. 211-219. DOI: 10.1016/j.apcatb.2011.03.030.
11. **Marcilla A., Beltran M.I., Navarro R.** Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. *Appl. Catal. B. Environ.* 2009. V. 86. P. 78-86. DOI: 10.1016/j.apcatb.2008.07.026.
12. **Almustapha M.N., Andrésen J.M.** Recovery of valuable chemicals from high density polyethylene (HDPE) Polymer: a catalytic approach for plastic waste recycling. *Int. J. Environ. Sci. Dev.* 2012. V. 3. P. 263–267. DOI: 10.7763/ijesd.2012.v3.228.
13. **Artetxe M., Lopez G., Amutio M., Elordi G., Bilbao J., Olazar M.** Cracking of high density polyethylene pyrolysis waxes on HZSM-5 catalysts of different acidity. *Ind. Eng. Chem. Res.* 2013. V. 52. P. 10637-10645. DOI: 10.1021/ie4014869.
14. **Serrano D.P., Aguado J., Escola J.M., Rodrıguez J.M.** Nanocrystalline ZSM-5: a highly active catalyst for polyolefin feedstock recycling. *Stud. Surf. Sci. Catal.* 2002. V. 142. P. 77–84. DOI: 10.1016/S0167-2991(02)80014-3.
15. **Serrano D.P., Aguado J., Escola J.M., Rodrıguez J.M.** Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins. *J. Anal. Appl. Pyrolysis.* 2005. V. 74. P. 353–360. DOI: 10.1016/j.jaap.2004.11.037.
16. **Elordi G., Olazar M., Artetxe M., Castaño P., Bilbao J.** Effect of the acidity of the HZSM-5 zeolite catalyst on the cracking of high density polyethylene in a conical spouted bed reactor. *Appl. Catal. A: General.* 2012. V. 415. P. 89– 95. DOI: 10.1016/j.apcata.2011.12.011.
17. **Artetxe M., Lopez G., Amutio M., Elordi G., Bilbao J., Olazar M.** Light olefins from HDPE cracking in a two-step thermal and catalytic process. *Chem. Eng. J.* 2012. V. 208. P. 27–34. DOI: 10.1016/j.cej.2012.06.105.

Russ. J. Appl. Chem. 2020. V. 93. P. 1271–1313. DOI: 10.1134/S1070427220090013.

5. **Miskolczi N., Nagy R.** Hydrocarbons obtained by waste plastic pyrolysis: comparative analysis of decomposition described by diferent kinetic models. *Fuel Process Technol.* 2012. V. 104. P. 96–104. DOI: 10.1016/j.fuproc.2012.04.031.
6. **Miandad R., Rehan M., Barakat M.A., Aburiazaiza A.S., Khan H., Ismail I.M.I., Dhavamani J., Gardy J., Hassanpour A., Nizami A.-S.** Catalytic pyrolysis of plastic waste: moving toward pyrolysis based biorefneries. *Front. Energy Res.* 2019. V. 7. DOI: 10.3389/fenrg.2019.00027.
7. **Gackowski M., Tarach K., Kuterasinski N., Podobiński J., Jarczewski S., Kustrowski P., Datka J.** Hierarchical zeolites Y obtained by desilication: porosity, acidity and catalytic properties. *Microporous Mesoporous Mater.* 2018. V. 263. P. 282–288. DOI: 10.1016/j.micromeso.2017.11.051.
8. **Busca G.** Acidity and basicity of zeolites: a fundamental approach. *Microporous Mesoporous Mater.* 2017. V. 254. P. 3–16. DOI: 10.1016/j.micromeso.2017.04.007.
9. **Anuar Sharuddin S.D., Abnisa F., Daud W.M.A.W., Aroua K.M.** A review on pyrolysis of plastic wastes. *Energy Convers. Manage.* 2016. V. 115. P. 308–326. DOI: 10.1016/j.enconman.2016.02.037.
10. **Lopez A., Marco I.D., Caballero B.M., Laresgoiti M.F., Adrados A., Aranzabal A.** Catalytic pyrolysis of plastic wastes with two different types of catalytic: ZSM-5 zeolite and Red Mud. *Appl. Catal. B Environ.* 2011. V. 104. P. 211-219. DOI: 10.1016/j.apcatb.2011.03.030.
11. **Marcilla A., Beltran M.I., Navarro R.** Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. *Appl. Catal. B. Environ.* 2009. V. 86. P. 78-86. DOI: 10.1016/j.apcatb.2008.07.026.
12. **Almustapha M.N., Andrésen J.M.** Recovery of valuable chemicals from high density polyethylene (HDPE) Polymer: a catalytic approach for plastic waste recycling. *Int. J. Environ. Sci. Dev.* 2012. V. 3. P. 263–267. DOI: 10.7763/ijesd.2012.v3.228.
13. **Artetxe M., Lopez G., Amutio M., Elordi G., Bilbao J., Olazar M.** Cracking of high density polyethylene pyrolysis waxes on HZSM-5 catalysts of different acidity. *Ind. Eng. Chem. Res.* 2013. V. 52. P. 10637-10645. DOI: 10.1021/ie4014869.
14. **Serrano D.P., Aguado J., Escola J.M., Rodrıguez J.M.** Nanocrystalline ZSM-5: a highly active catalyst for polyolefin feedstock recycling. *Stud. Surf. Sci. Catal.* 2002. V. 142. P. 77–84. DOI: 10.1016/S0167-2991(02)80014-3.
15. **Serrano D.P., Aguado J., Escola J.M., Rodrıguez J.M.** Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins. *J. Anal. Appl. Pyrolysis.* 2005. V. 74. P. 353–360. DOI: 10.1016/j.jaap.2004.11.037.
16. **Elordi G., Olazar M., Artetxe M., Castaño P., Bilbao J.** Effect of the acidity of the HZSM-5 zeolite catalyst on the cracking of high density polyethylene in a conical spouted bed reactor. *Appl. Catal. A: General.* 2012. V. 415. P. 89– 95. DOI: 10.1016/j.apcata.2011.12.011.
17. **Artetxe M., Lopez G., Amutio M., Elordi G., Bilbao J., Olazar M.** Light olefins from HDPE cracking in a two-step thermal and catalytic process. *Chem. Eng. J.* 2012. V. 208. P. 27–34. DOI: 10.1016/j.cej.2012.06.105.

18. **Ibanez M., Artetxe M., Lopez G., Elordi G., Bilbao J., Olazar M., Castano P.** Identification of the coke deposited on an HZSM-5 zeolite catalyst during the sequenced pyrolysis–cracking of HDPE. *Appl. Catal B: Environ.* 2014. V. 148. P. 436–445. DOI: 10.1016/j.apcatb.2013.11.023.
19. **Nwankwor P.E., Onuigbo I.O., Chukwuneke C.E., Yahaya M.F., Agboola B.O., Jahng W.J.** Synthesis of gasoline range fuels by the catalytic cracking of waste plastics using titanium dioxide and zeolite. *Int. J. Energy Environ. Eng.* 2020. 12. P. 77-86. DOI: 10.1007/s40095-020-00359-9.
20. **Фурда Л.В., Смальченко Д.Е., Титов Е.Н., Лебедева О.Е.** Термокаталитическая деструкция полипропилена в присутствии алюмосиликатов. *Изв. вузов. Химия и хим. технология.* 2020. Т. 63. Вып. 6. С. 85-89. DOI: 10.6060/ivkkt.20206306.6202.
21. **Colantonio S., Cafiero L., De Angelis D., Ippolito N.M., Tuffi R., Cipriotі S.V.** Thermal and catalytic pyrolysis of a synthetic mixture representative of packaging plastics residue. *Front. Chem. Sci. Eng.* 2020. V. 14. P. 288–303. DOI: 10.1007/s11705-019-1875-3.
22. **Palomar-Torres A., Torres-Jiménez E., Kegl B., Bombek G., Volmajer-Valh J., Lešnik L.** Catalytic pyrolysis of plastic wastes for liquid oils' production using ZAP USY zeolite as a catalyst. *Int. J. Environ. Sci. Technol.* 2022. P. 1-14. DOI: 10.1007/s13762-022-04023-z.
23. **Агулло Х., Кумар Н., Беренгуер Д., Кубичка Д., Марцилла А., Гомез А., Салми Т., Мурзин Д.Ю.** Каталитический пиролиз полиэтилена низкой плотности на цеолитах H-β, H-Y, H-морденит и H-ферьерит. Влияние кислотности и структуры. *Кинетика и катализ.* 2007. Т. 48. № 4. С. 570–575. DOI: 10.1134/S002315840704009X.
24. **Elordi G., Olazar M., Lopez G., Castaño P., Bilbao J.** Role of pore structure in the deactivation of zeolites (HZSM-5, H-β and HY) by coke in the pyrolysis of polyethylene in a conical spouted bed reactor. *Appl. Catal. B: Environ.* 2011. V. 102. P. 224–231. DOI: 10.1016/j.apcatb.2010.12.002.
25. **Heikkinen J.M. Hordijk J.C., Jong de W.** Thermogravimetry as a tool to classify waste components to be used for energy generation. *J. Anal. Appl. Pyrolysis.* 2004. V. 71. P. 883-900. DOI: 10.1016/j.jaap.2003.12.001.
26. **Kitano M., Nakajima K., Kondo J.N., Hayashi S., Hara M.** Protonated titanate nanotubes as solid acid catalyst. *J. Am. Chem. Soc.* 2010. V. 132. P. 6622-6623. DOI: 10.1021/ja100435w.
27. **Dias A.S., Lima S., Carriazo D., Rives V, Pillinger M., Val A.A.** Exfoliated titanate, niobate and titanoniobate nanosheets as solid acid catalysts for the liquid-phase dehydration of D-xylose into furfural. *J. Catal.* 2006. V. 244. P. 230–237. DOI: 10.1016/j.jcat.2006.09.010.
28. **Kim T., Song K.H., Yoon H., Chung J.S.** Steam reforming of n-dodecane over $K_2Ti_2O_5$-added Ni-alumina and Ni-zirconia (YSZ) catalysts. *Int. J. Hydrogen Energy.* 2016. V. 41. P. 17922-17932. DOI: 10.1016/j.ijhydene.2016.08.009.
29. **Sanchez-Monjaras T., Gorokhovsky A.V., Escalante-Garcia J.I.** Molten salt synthesis and characterization of polytitanate ceramic precursors with varied TiO_2/K_2O molar ratio. *J. Am. Ceram. Soc.* 2008. V. 91. P. 3058-3065. DOI: 10.1111/j.1551-2916.2008.02574.x.

18. **Ibanez M., Artetxe M., Lopez G., Elordi G., Bilbao J., Olazar M., Castano P.** Identification of the coke deposited on an HZSM-5 zeolite catalyst during the sequenced pyrolysis–cracking of HDPE. *Appl. Catal B: Environ.* 2014. V. 148. P. 436–445. DOI: 10.1016/j.apcatb.2013.11.023.
19. **Nwankwor P.E., Onuigbo I.O., Chukwuneke C.E., Yahaya M.F., Agboola B.O., Jahng W.J.** Synthesis of gasoline range fuels by the catalytic cracking of waste plastics using titanium dioxide and zeolite. *Int. J. Energy Environ. Eng.* 2020. 12. P. 77-86. DOI: 10.1007/s40095-020-00359-9.
20. **Furda L.V., Smalchenko D.E., Titov E.N., Lebedeva O.E.** Thermocatalytic degradation of polypropylene in presence of aluminum silicates. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2020. V. 63. N 6. P. 85-89. DOI: 10.6060/ivkkt.20206306.6202.
21. **Colantonio S., Cafiero L., De Angelis D., Ippolito N.M., Tuffi R., Cipriotі S.V.** Thermal and catalytic pyrolysis of a synthetic mixture representative of packaging plastics residue. *Front. Chem. Sci. Eng.* 2020. V. 14. P. 288–303. DOI: 10.1007/s11705-019-1875-3.
22. **Palomar-Torres A., Torres-Jiménez E., Kegl B., Bombek G., Volmajer-Valh J., Lešnik L.** Catalytic pyrolysis of plastic wastes for liquid oils' production using ZAP USY zeolite as a catalyst. *Int. J. Environ. Sci. Technol.* 2022. P. 1-14. DOI: 10.1007/s13762-022-04023-z.
23. **Agullo H., Kumar N., Berenguer D., Kubicka D., Marcilla A., Gomez A., Salmi T., Murzin D.Y.** Catalytic pyrolysis of low density polyethylene on H-β, H-Y, H-mordenite and H-ferrierite zeolites. Influence of acidity and structure. *Kinetika Katal.* 2007. V. 48. N 4. P. 570-575 (in Russian). DOI: 10.1134/S002315840704009X.
24. **Elordi G., Olazar M., Lopez G., Castaño P., Bilbao J.** Role of pore structure in the deactivation of zeolites (HZSM-5, H-β and HY) by coke in the pyrolysis of polyethylene in a conical spouted bed reactor. *Appl. Catal. B: Environ.* 2011. V. 102. P. 224–231. DOI: 10.1016/j.apcatb.2010.12.002.
25. **Heikkinen J.M. Hordijk J.C., Jong de W.** Thermogravimetry as a tool to classify waste components to be used for energy generation. *J. Anal. Appl. Pyrolysis.* 2004. V. 71. P. 883-900. DOI: 10.1016/j.jaap.2003.12.001.
26. **Kitano M., Nakajima K., Kondo J.N., Hayashi S., Hara M.** Protonated titanate nanotubes as solid acid catalyst. *J. Am. Chem. Soc.* 2010. V. 132. P. 6622-6623. DOI: 10.1021/ja100435w.
27. **Dias A.S., Lima S., Carriazo D., Rives V, Pillinger M., Val A.A.** Exfoliated titanate, niobate and titanoniobate nanosheets as solid acid catalysts for the liquid-phase dehydration of D-xylose into furfural. *J. Catal.* 2006. V. 244. P. 230–237. DOI: 10.1016/j.jcat.2006.09.010.
28. **Kim T., Song K.H., Yoon H., Chung J.S.** Steam reforming of n-dodecane over $K_2Ti_2O_5$-added Ni-alumina and Ni-zirconia (YSZ) catalysts. *Int. J. Hydrogen Energy.* 2016. V. 41. P. 17922-17932. DOI: 10.1016/j.ijhydene.2016.08.009.
29. **Sanchez-Monjaras T., Gorokhovsky A.V., Escalante-Garcia J.I.** Molten salt synthesis and characterization of polytitanate ceramic precursors with varied TiO_2/K_2O molar ratio. *J. Am. Ceram. Soc.* 2008. V. 91. P. 3058-3065. DOI: 10.1111/j.1551-2916.2008.02574.x.

30. **Зимняков Д.А., Гороховский А.В., Третьяченко Е.В., Кочубей В.И., Ювченко С.А., Сина Дж.С.** К спектральным оценкам параметров зонной структуры наночастиц полититаната калия, модифицированного в растворах солей переходных металлов. *Письма в ЖТФ.* 2014. Т. 40. № 10. С. 80-87. DOI: 10.1134/S1063785014050265.
31. **Жердецкий Н.А., Шляхтин Н.Ю., Ромаденкина С.Б., Аниськова Т.В.** Влияние параметров процесса крекинга термопластичных полимеров на выход продуктов. *Бутлеров. сообщ.* 2018. Т. 56. № 10. С. 123-126.
32. **Park K.-B., Jeong Y.-S., Guzelciftci B., Kim J.-S.** Two-stage pyrolysis of polystyrene: Pyrolysis oil as a source of fuels or benzene, toluene, ethylbenzene, and xylenes. *Appl. Energy.* 2020. V. 259. P. 356. DOI: 10.1016/j.apenergy.2019.114240.
33. **Магарил Р.З.** Механизм и кинетика гомогенных термических превращений углеводородов. М.: Химия. 1970. С. 17.
34. **Sharuddin S.C.A., Abnisa F., Daud, W.M.A.W. Aroua, M.K.** A review on pyrolysis of plastic waste. *Energy Convers. Manage.* 2016. V. 115. P. 308-326. DOI: 10.1016/j.enconman.2016.02.037.
35. **Ukei H., Hirose T., Horikawa S.** Catalytic degradation of polystyrene into styrene and a design of recyclable polystyrene with dispersed catalysts. *Catal. Today.* 2000. V. 62. P. 67-75. DOI: 10.1016/S0920-5861(00)00409-0.

30. **Zimnyakov D.A., Gorokhovsky A.V., Tret'yachenko E.V., Kochubei V. I., Yuvchenko S.A., Sina J.S.** Spectral estimation of the energy-band-structure parameters of nanoparticles of potassium polytitanate modified in transition metal salt solutions. *Tech. Phys. Lett.* 2014. V. 40. N 5. P. 445-448. DOI: 10.1134/S1063785014050265.
31. **Zherdetsky N.A. Shlyahtin N.U., Romadenkina S.B., Aniskona T.V.** Influence of thermoplastic polymer cracking process parameters on product yield. *Butlerov Soobshch.* 2018. V. 56. N 10. P. 123-126 (in Russian).
32. **Park K.-B., Jeong Y.-S., Guzelciftci B., Kim J.-S.** Two-stage pyrolysis of polystyrene: Pyrolysis oil as a source of fuels or benzene, toluene, ethylbenzene, and xylenes. *Appl. Energy.* 2020. V. 259. P. 356. DOI: 10.1016/j.apenergy.2019.114240.
33. **Magaril R.Z.** Mechanism and kinetics of homogeneous thermal transformations of hydrocarbons. M.: Khimiya. 1970. P. 17.
34. **Sharuddin S.C.A., Abnisa F., Daud, W.M.A.W. Aroua, M.K.** A review on pyrolysis of plastic waste. *Energy Convers. Manage.* 2016. V. 115. P. 308-326. DOI: 10.1016/j.enconman.2016.02.037.
35. **Ukei H., Hirose T., Horikawa S.** Catalytic degradation of polystyrene into styrene and a design of recyclable polystyrene with dispersed catalysts. *Catal. Today.* 2000. V. 62. P. 67-75. DOI: 10.1016/S0920-5861(00)00409-0.

Поступила в редакцию 08.11.2022
Принята к опубликованию 12.12.2022

Received 08.11.2022
Accepted 12.12.2022