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DEPENDENCE OF THE CATALYTIC ACTIVITY OF ZEOLITE CATALYSTS ON THE TYPE OF MODIFICATION IN THE LOW-TEMPERATURE CRACKING OF POLYSTYRENE

The study focuses on the catalytic cracking of polystyrene in a hydrogen atmosphere in the presence of catalysts based on natural zeolite. The catalysts were synthesized through acid activation of zeolite, followed by its modification with nickel(II) oxide, cobalt(II) oxide, and titanium(IV) oxide. One of the most pressing issues is that, despite the rapid accumulation of plastic waste in the environment, particularly polystyrene, cost-effective and efficient industrial technologies for its conversion into valuable products remain largely unavailable. Modern plastic recycling methods often require high temperatures and significant energy inputs, which reduce their economic and environmental feasibility. Therefore, the development of technologies utilizing inexpensive natural materials for the production of plastic cracking catalysts remains relevant and highly demanded. Low-cost catalysts based on natural clinoptilolite from a Ukrainian deposit were obtained, with a significant increase in surface area following acid activation. However, this activation had no significant impact on the liquid-phase yield or styrene selectivity. Thus, natural clinoptilolite itself exhibited catalytic activity comparable to that of its acid-activated form. Further modification of the catalyst samples with metal oxides (NiO, CoO, TiO_2) significantly enhanced their catalytic activity, as confirmed by gas chromatography analysis. The results indicate a liquid-phase yield ranging from 40 % to 80 %, with high styrene selectivity exceeding 80 % in some cases. This effect is attributed to specific features of the proposed catalyst synthesis method. Acid activation facilitates the removal of natural impurities and increases the surface area for reactant-phase contact, which is crucial in heterogeneous catalysis. Additionally, metal oxide modification introduces additional catalytic centers. Due to the reduced cost of the synthesized catalysts, achieved by utilizing inexpensive natural Ukrainian zeolites, and the significant decrease in the cracking temperature, the proposed polystyrene recycling method appears promising and economically viable for industrial implementation. Furthermore, the high styrene selectivity enables substantial reductions in energy and material costs compared to traditional technologies. In contrast to existing polymer recycling technologies, the use of natural clinoptilolite as a catalyst support offers an efficient and environmentally friendly approach to plastic waste utilization.

Keywords: *polystyrene, catalytic cracking, catalytic pyrolysis, clinoptilolite, acid activation, metal oxides.*

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1. Introduction

Irresponsible plastic pollution has become one of the most significant global environmental threats. Studies indicate that the production of polymers for single-use plastics contributes to millions of tons of greenhouse gas emissions [1].

Each type of plastic possesses unique properties that make its application economically justified and difficult to replace in both consumer and industrial sectors. Specifically, polystyrene (PS), which is extensively used in the production of disposable tableware, packaging materials, insulation, and equipment components, accounts for approximately 10 % of total plastic waste [2]. Due to its resistance to biodegradation, polystyrene persists in the environment for decades, contaminating soil, water bodies, and the atmosphere.

It is known that bacterial strains such as *Rhodococcus ruber* and *Actinobacterium* can degrade only 0.04–0.57 % of PS waste within a few weeks [3]. Furthermore, when polystyrene is exposed to landfill conditions, it becomes brittle under the influence of air and sunlight, breaking down into microplastics (particles <5000 nm) and subsequently into nanoplastics (particles <100 nm). These particles infiltrate soils and water bodies, accumulating in sediments and posing significant risks to marine ecosystems [4]. In vivo and in vitro studies have demonstrated that plastic nanoparticles can enter the human body through the skin, respiratory tract, and digestive system, subsequently accumulating in living organisms and integrating into the food chain [5].

Conventional disposal methods such as incineration and landfilling are neither environmentally safe nor economically viable. Conversely, pyrolysis enables the thermal or catalytic decomposition of plastic waste at high temperatures (300–900 °C) in the absence of oxygen or in an inert gas or hydrogen atmosphere (for hydrogenation processes), converting large polymeric molecules into liquid, gaseous, and solid fractions. In this context, low-temperature catalytic cracking using modified catalysts offers a promising pathway for converting polystyrene into valuable chemical products, particularly aromatic hydrocarbons. Furthermore, chemical recycling of plastic waste into target chemical precursors represents a sustainable approach that is more tolerant to contaminated plastic waste [2, 6].

Catalytic cracking of polystyrene presents an opportunity for environmentally friendly plastic recycling while producing commercially valuable components for the chemical and petrochemical industries, reinforcing the relevance of this research. Consequently, the demand for polystyrene waste and scrap has been increasing, with exports of polystyrene waste and scrap rising by 20.8 % between 2021 and 2022. In 2022, polystyrene waste and scrap became a high-value commodity, with a total global trade volume of 236 million USD, accounting for 0.001 % of total global trade [7].

Various catalytic technologies have been successfully applied for plastic recycling, particularly using zeolite-based catalysts such as high-silica ZSM-5 and faujasite. These catalysts facilitate cracking at significantly lower temperatures. However, their high acidity and small pore size lead to the formation of lower hydrocarbons (C_1–C_4), limiting the production of more valuable C_{5+} compounds. Additionally, coke formation within micropores deactivates the catalyst, and in some cases, high temperatures are required, increasing energy consumption [8].

Notably, studies on the catalytic cracking of PS remain relatively scarce compared to research on the recycling of other polyolefins. This gap in knowledge underscores the need to develop efficient polystyrene cracking catalysts and strategies to mitigate its environmental impact. Recent studies have demonstrated the effectiveness of aluminosilicate catalysts. For instance, [9] reported the catalytic pyrolysis of various PS wastes using protonated and MgO-modified commercial ZSM-5 as acidic and basic catalysts, respectively.

In another study [10], pyrolysis of polystyrene waste (household waste, including food packaging residues and decorative materials) was investigated using bentonite and natural zeolite catalysts. The mass fraction of polystyrene in the reaction mixture varied from 0 % to 25 %. Both catalysts were pretreated by acid activation (HCl, 0.5 mol/l), and the pyrolysis process was conducted in a batch reactor at temperatures of 300, 350, 400, 450, 500, and 550 °C. The resulting liquid products were identified as benzene, toluene, ethylbenzene, styrene, and isopropylbenzene. Bentonite exhibited slightly better results, yielding a maximum styrene selectivity of 30.28 % at 400 °C, while natural zeolite achieved 28.88 % styrene selectivity. Overall, natural aluminosilicates are promising catalysts due to their availability, low cost, and beneficial catalytic properties [11].

The influence of reactor type on the qualitative and quantitative composition of polystyrene cracking products has also been investigated. Fluidized bed reactors offer improved catalyst-polymer mixing, enhancing heat distribution and increasing product yield. Conversely, vacuum reactors reduce by-product formation. The study utilized basic catalysts (e. g., metal oxides: ZnO, CaO, BaO), acidic catalysts (zeolites such as ZSM-5, HZSM), and mesoporous silicates like synthetic Al-MCM-41. Zeolitic catalysts exhibited high efficiency in producing valuable aromatic compounds such as styrene, toluene, and benzene [12].

Additionally, previous studies compared the efficiency of natural and synthetic zeolites (such as Y-type zeolite) in PS pyrolysis. Experiments conducted at 450 °C demonstrated that natural zeolite achieved a liquid yield of 54 % with styrene selectivity of 7.6 %, whereas synthetic zeolite provided a 50 % liquid yield but with higher styrene selectivity of 15.8 %. The superior selectivity of synthetic zeolite is attributed to its more uniform pore structure and higher acidity, which promote effective polystyrene cracking while reducing side reactions [13].

Research has also explored the catalytic pyrolysis of polystyrene foam waste using a specially designed reactor, yielding aromatic fuel components such as benzene, toluene, ethylbenzene, and styrene. The thermal pyrolysis process produced a liquid phase yield of 94.37 wt. % at 650 °C, while under multi-stage pyrolysis conditions at 550 °C, styrene content reached 46.30 wt. % [14].

Another study investigated the use of natural clinoptilolite as a catalyst for PS degradation at 400 °C, comparing its effectiveness with silica, HZSM-5, and thermal degradation. Natural clinoptilolite demonstrated high efficiency, comparable to HZSM-5, in producing liquid fractions with a carbon range of C_5–C_{12}, with styrene being the main cracking product [15].

A review of global scientific research highlights the evident potential of zeolites, including natural ones, as effective catalysts for the catalytic decomposition of polystyrene. Unlike synthetic zeolites, natural zeolites are a low-cost raw material that can be easily activated and modified while possessing excellent adsorption and ion-exchange properties, as well as the ability to function as molecular sieves [16–18]. Ukraine has a well-developed Sokyrnytsia zeolite deposit, one of the largest in the world. The value of these zeolites is determined by their clinoptilolite content, which ranges from 65 % to 75 %. Compared to Chinese zeolites, Ukrainian zeolites exhibit higher wear resistance, making them a promising material for catalytic applications [19–21].

The aim of this study is to synthesize and evaluate catalysts based on cost-effective natural zeolite from a Ukrainian deposit, modified with nickel, cobalt and titanium oxides, for the hydrogen-assisted low-temperature cracking of polystyrene. The conducted research demonstrates the feasibility of utilizing catalysts derived from low-cost natural materials to develop sustainable solutions for the increasing plastic waste problem.

2. Materials and Methods

In this study, catalysts based on Ukrainian natural zeolite (Zeo-0) sourced from the Sokyrnytsia deposit – characterized by a high clinoptilolite content (up to 85 %) and a particle size below 1 mm – were used.

The acid activation of natural zeolite (Zeo-0) was conducted following the procedure outlined in Fig. 1. The zeolite was treated with a 2M nitric acid (HNO_3) solution at 40 °C under continuous stirring for 4 hours. This treatment effectively removed impurities, as well as calcium and magnesium ions, which could potentially block the active sites on the zeolite surface. The acid-treated zeolite was subsequently washed with distilled water until the effluent pH stabilized within the range of 6–7. The final drying step was performed at 105 °C for 24 hours to ensure complete moisture removal, resulting in acid-activated zeolite (Zeo-1).

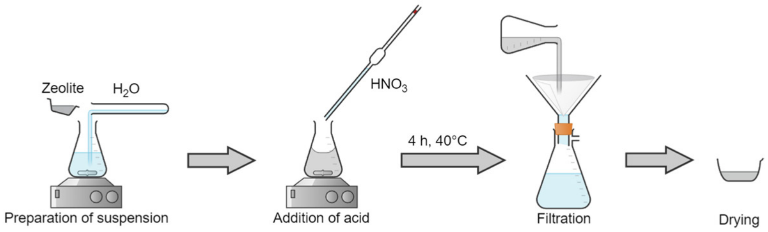

Fig. 1. Schematic representation of the acid activation process of natural zeolite

The synthesis of metal oxide-modified catalysts (CoO, NiO) was carried out using the procedure depicted in Fig. 2. The activated zeolite was dispersed in deionized water, followed by the addition of a metal nitrate precursor ($Co(NO_3)_2$, $Ni(NO_3)_2$). To adjust the pH to a neutral value (pH 7), ammonium hydroxide (NH_4OH) was added. The resulting suspension was subjected to hydrolysis at 80 °C under stirring for 3 hours until partial evaporation occurred. The final product was obtained by drying the material and calcination at 250–350 °C for 2 hours, yielding zeolite functionalized with the corresponding metal oxides.

The modification of zeolite with TiO_2 nanoparticles was performed following the procedure illustrated in Fig. 3. A precursor solution was prepared by dissolving 5.3 ml of titanium isopropoxide (TTIP) in 50 ml of isopropyl alcohol (IPA). In parallel, a 200 ml aqueous solution was prepared to facilitate hydrolysis and 9 g of zeolite was dispersed in this solution, then the pH was adjusted to 2 using HNO_3. The precursor solution was then introduced dropwise into the zeolite suspension under vigorous stirring using a magnetic stirrer. Hydrolysis was conducted at 80 °C for 3 hours, followed by drying at 100 °C and subsequent calcination at 500 °C for 2 hours.

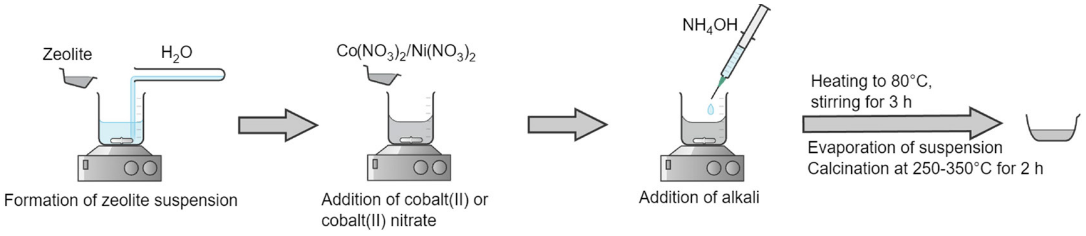

Fig. 2. Schematic representation of the zeolite modification process

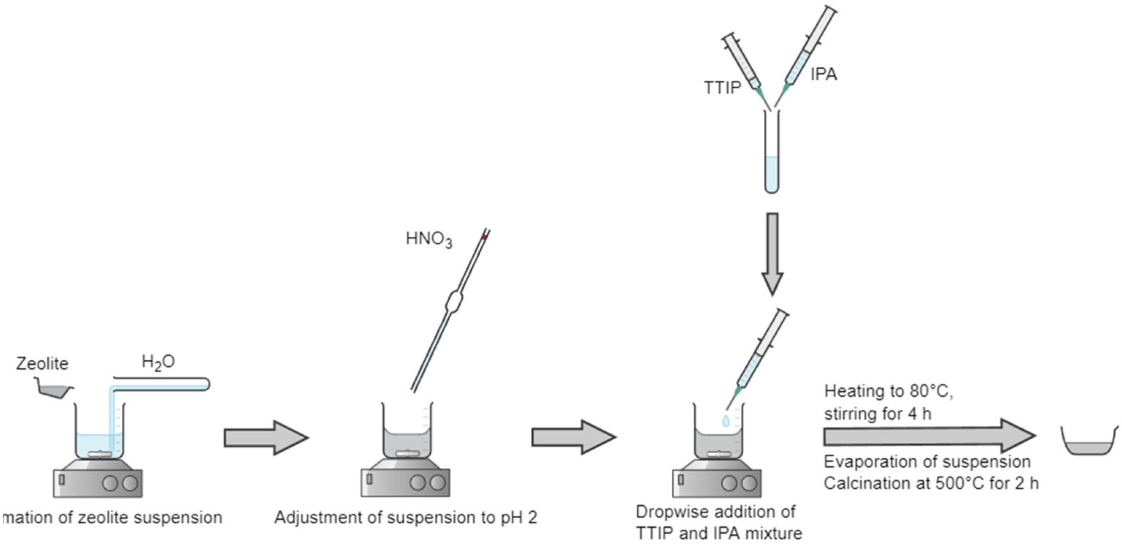

Fig. 3. Schematic representation of the zeolite modification process with TiO_2

The catalytic cracking of polystyrene was performed using the laboratory setup depicted in Fig. 4.

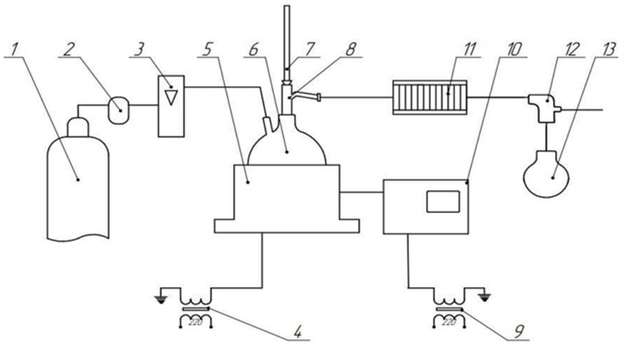

Fig. 4. Schematic diagram of the laboratory setup for catalytic polystyrene cracking: 1 – H2 gas cylinder; 2 – hydrogen regulator BVO-80DM; 3 – rotameter; 4, 9 – power supply units; 5 – heating mantle; 6 – two-neck round-bottom flask; 7 – thermometer; 8 – Wurtz adapter; 10 – temperature controller; 11 – reflux condenser; 12 – allonge; 13 – receiving flask

A mixture of shredded polystyrene and catalyst (4:1 ratio) was placed into the round-bottom flask *6* and purged with an H_2/N_2 gas mixture (50/50), where hydrogen acted as a hydrogenation reagent. The gas flow rate was controlled via the hydrogen regulator BVO-80DM *2* and monitored using the rotameter *3*. During the reaction, gaseous products passed through the reflux condenser *11*, where they condensed into a liquid phase that was subsequently directed through an allonge for vacuum distillation *12* into the receiving flask *13*.

Catalytic cracking of polystyrene was investigated using two operational modes: single-stage and two-stage configurations. In the single-stage scheme, the entire catalyst batch was loaded directly into the reactor, allowing for the evaluation of the efficiency of individual catalyst samples, including those modified with metal oxides. Additionally, to reduce the catalyst cost, mixtures of acid-activated zeolite with modified catalysts were examined. For these experiments, catalysts were combined in a 1:1 ratio, with a total mass of 3 g.

In the two-stage scheme, the functions of the catalysts were divided across two different zones: a less expensive, unmodified metal oxide-free catalyst was placed in the reaction zone to facilitate the decomposition of polystyrene into the gas phase, while a modified catalyst was positioned in the Wurtz adapter (Fig. 5). 3 g of catalyst was loaded into the reactor, with an additional 2 g placed in the Wurtz adapter. All experiments were conducted at temperatures ranging from 150–200 °C, with reaction times of 1–1.5 hours. This setup allowed polystyrene and its gaseous decomposition products to mix with hydrogen and undergo further conversion, enhancing selectivity toward styrene. Consequently, the resulting mixture of coke and zeolite remained free of metal oxides, making disposal more straightforward.

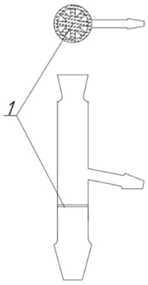

Fig. 5. Wurtz adapter with a dedicated catalyst compartment for the two-stage catalytic cracking of polystyrene: 1 – catalyst compartment partition

The characterization of the catalytic cracking products, particularly the liquid phase, was performed using nuclear magnetic resonance (NMR) spectroscopy and gas chromatography-mass spectrometry (GC-MS). NMR spectra were recorded using a Varian Unity Plus 400 spectrometer (400 MHz for protons), with tetramethylsilane as an internal standard. GC-MS analyses were carried out using an HP Agilent 5890/5972 chromatograph equipped with an electron ionization (EI) mass detector (70 eV).

Compounds were identified using GC-MS by comparing obtained spectra with reference mass spectral libraries and retention time data. The molecular masses of styrene, ethylbenzene, and methylstyrene were determined to be 104 g/mol, 106 g/mol, and 118 g/mol.

For NMR analysis, samples were dissolved in deuterated chloroform ($CDCl_3$), chosen for its high solubility and minimal spectral interference. Spectral data were processed using MestReNova software, facilitating phase correction, baseline adjustment, peak integration, and automated chemical shift identification [22]. The combination of GC-MS and NMR techniques enhanced compound identification accuracy by providing complementary structural and molecular mass information.

3. Results and Discussion

The natural and acid-activated zeolite samples were analyzed using X-ray diffraction (XRD) to assess their crystallinity and structural modifications (Fig. 6). The analysis confirms that both natural (Zeo-0) and acid-activated (Zeo-1) zeolites retain a well-defined crystalline structure with only minimal differences in peak intensities. This indicates that acid activation induces only minor structural and compositional changes, primarily affecting the surface chemistry rather than the overall framework integrity.

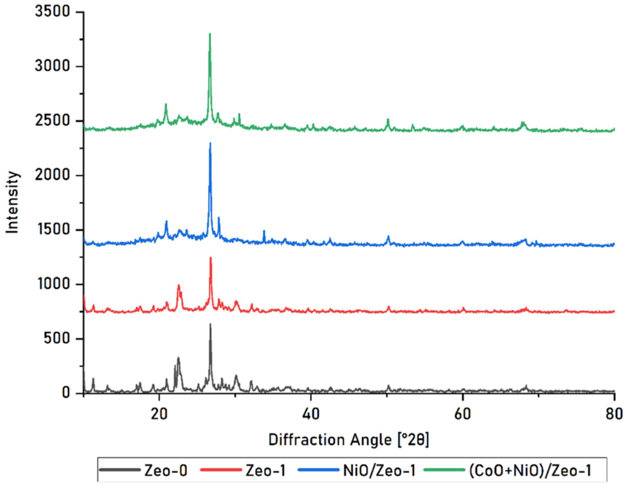

Fig. 6. X-ray diffraction (XRD) patterns of catalysts

For NiO/Zeo-1 and (CoO+NiO)/Zeo-1 samples, the XRD patterns do not display characteristic peaks of NiO or CoO phases. This absence is attributed to the low mass fraction of metal oxides (2 wt. %) and the relatively low calcination temperature range of 250–350 °C, which prevents the formation of well-defined crystalline domains. At these conditions, the metal oxides likely exist in an amorphous or highly dispersed state, making them undetectable by XRD.

Fig. 7 presents the low-temperature nitrogen adsorption-desorption isotherms of the investigated catalysts. As observed, nearly all isotherms, except for TiO_2/Zeo-1, correspond to Type III according to the IUPAC classification [23], indicating physical adsorption on nonporous or macroporous adsorbents. According to the data in Table 1, natural clinoptilolite exhibits a low specific surface area (12.1 m^2/g), which increases more than threefold after acid activation due to the dissolution of natural impurities such as calcite. Therefore, activation does not change the pore structure type but rather increases the pore volume, leading to an increased specific surface area. Modification with cobalt, nickel, and cobalt-nickel oxides reduces the specific surface area from 40 to 33, 22, and 31 m^2/g, respectively, likely due to the blocking of smaller pores, thereby increasing the average pore size in the modified acid-activated zeolite samples (Table 1).

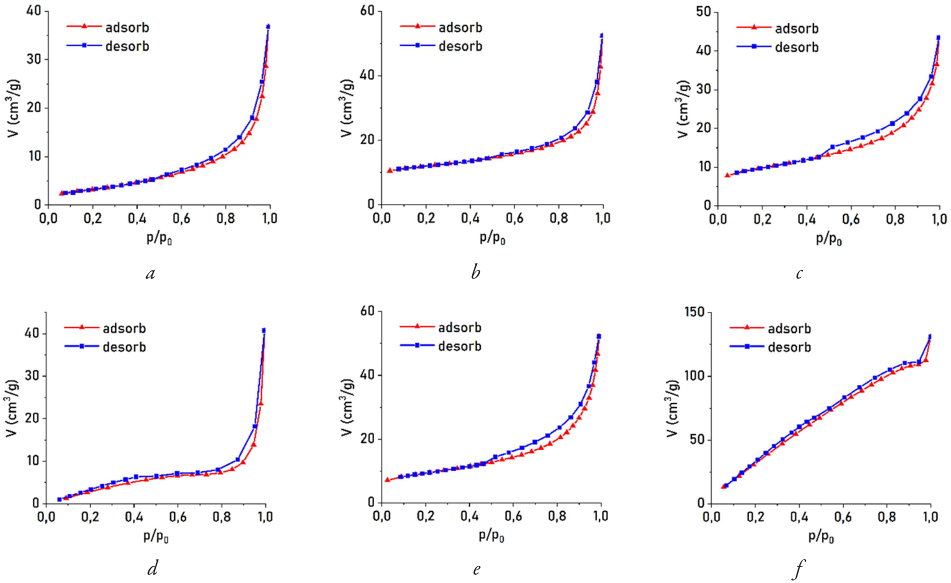

Fig. 7. Low-temperature nitrogen adsorption-desorption isotherms of the catalyst samples:
a – Zeo-0; *b* – Zeo-1; *c* – CoO/Zeo-1; *d* – NiO/Zeo-1; *e* – (CoO+NiO)/Zeo1; *f* – TiO_2/Zeo-1

A somewhat atypical (mixed-type) isotherm is observed for the TiO_2/Zeo-1 sample, which likely results from the superposition of different pore structures, specifically those of acid-activated zeolite and titanium (IV) oxide. The specific surface area of this sample increases more than fourfold (from 39 to 173.8 m^2/g), which, in our opinion, is due to the formation of a secondary porous structure of titanium(IV) oxide on the surface of acid-activated zeolite.

Table 1

Structural and adsorption characteristics of the catalysts

Sample	Isotherm type	Average pore diameter (nm)	BET Surface area (m^2/g)
Zeo-0	III	6.5	12.1
Zeo-1	III	4.1	39.0
CoO/Zeo-1	III	7.3	33.3
NiO/Zeo-1	III	9.9	22.0
(CoO+NiO)/Zeo-1	III	10.1	31.6
TiO_2/Zeo-1	Mixed	3.9	173.8

The results of catalytic polystyrene cracking in a single-stage configuration are presented in Fig. 8 and Table 2. As seen in Fig. 8, the highest styrene selectivity was achieved using NiO/Zeo-1 (68.2 %), while the highest liquid phase yield was obtained with TiO_2/Zeo-1, reaching 63 %, of which 58 % was styrene. In general, when using natural, acid-activated, and modified acid-activated catalysts, the styrene yield in the single-stage configuration ranged between 44.7 % and 68.2 %.

By-products such as methylstyrene and ethylbenzene can also be considered valuable products due to their use as additives in motor fuels.

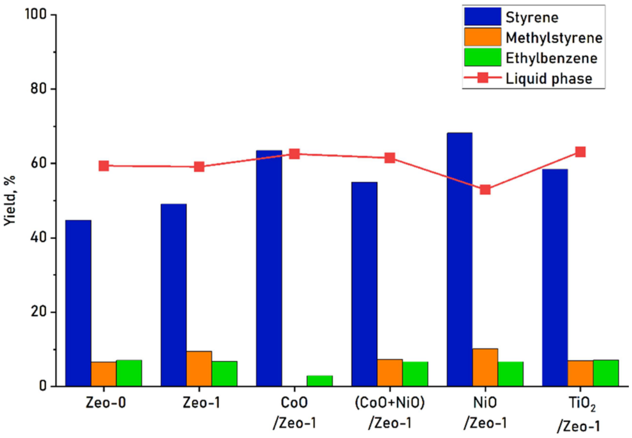

Fig. 8. Yield of liquid phase and main components (styrene, methylstyrene, ethylbenzene) in the single-stage configuration

Analysis of Table 2 shows that the conversion of polystyrene to styrene (styrene yield relative to initial plastic) varies between 26.6 % and 39.9 %. The highest styrene yield was obtained using the CoO/Zeo-1 catalyst. These results are promising, as they demonstrate that even with low-cost natural catalysts at low cracking temperatures, a minimum of 59 % liquid phase yield with 49 % selectivity and a maximum of 63.2 % yield with 68.2 % selectivity were achieved.

Table 2

Results of catalytic polystyrene cracking using the single-stage configuration

Catalyst	Liquid phase yield (%)	Styrene Selectivity (%)	Styrene yield relative to feedstock (%)
Zeo-0	59.4	44.7	26.6
Zeo-1	59.1	49.1	29.0
CoO/Zeo-1	62.6	63.5	39.7
(CoO+NiO)/Zeo-1	61.5	55.0	33.8
NiO/Zeo-1	53.0	68.2	36.1
TiO_2/Zeo-1	63.2	58.5	36.9

The use of catalyst mixtures, such as the combination of Zeo-1 with NiO/Zeo-1, which proved to be the most effective, resulted in a liquid phase yield of 65 % with 62 % selectivity, as shown in Fig. 9. This suggests that this approach does not significantly enhance catalyst activity under single-stage conditions.

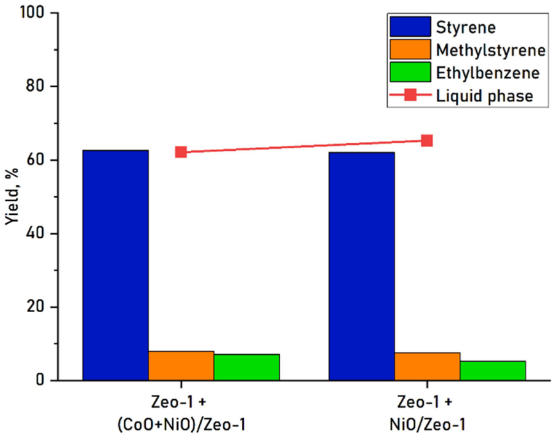

Fig. 9. Yield of liquid phase and main components (styrene, methylstyrene, ethylbenzene) in the single-stage configuration using catalyst mixtures

Data presented in Table 3 indicate a slight advantage in using catalyst mixtures, necessitating further studies to determine the optimal catalyst combination.

Table 3

Results of catalytic polystyrene cracking using the single-stage configuration and catalyst mixtures

Catalyst	Liquid phase yield (%)	Styrene selectivity (%)	Styrene yield relative to feedstock (%)
Zeo-1+(CoO+NiO)/Zeo-1	62.2	62.6	38.9
Zeo-1+NiO/Zeo-1	65.3	62.1	40.5

The results obtained from the two-stage catalytic cracking experiments are presented in Fig. 10 and Table 4. This approach improved styrene selectivity by combining catalysts with different functionalities. The best results were achieved with a combination of Zeo-0 in the first stage and CoO/Zeo-1 in the second stage, yielding a styrene selectivity of 81.9 % with an overall liquid phase yield of 50 %. Similarly, using Zeo-1 in the first stage and NiO/Zeo-1 in the second stage resulted in a styrene selectivity of 81.9 % at nearly 40 % liquid phase yield.

The data in Table 4 indicate that all catalysts exhibited high selectivity for styrene conversion. Specifically, using Zeo-0 in the first stage and CoO/Zeo-1 in the second stage not only achieved 81.9 % styrene selectivity but also the highest conversion of polystyrene to styrene (41.0 %).

Thus, the two-stage configuration proved to be more effective than the single-stage process, as it significantly increased styrene selectivity while maintaining high conversion rates. The ability to fine-tune catalyst combinations in each stage presents an opportunity for further optimization in polystyrene catalytic cracking.

The obtained research results indicate that the use of natural clinoptilolite as a raw material for the synthesis of catalysts in the process of low-temperature cracking of polystyrene allows to achieve a high yield of the liquid phase and selectivity for styrene. The conducted studies confirm the information from literary sources on the relevance of the use of natural aluminosilicate materials for the synthesis of polymer cracking catalysts, but the originality of the work is the use of natural raw materials of Ukrainian origin as the basis for the synthesis of catalysts.

The research results, namely the increase in the specific surface area after acid activation, are explained by the fact that it allows the process of zeolite decationization, which increases the surface area of the contact of the reagent phases, and modification with metal oxides ensures the formation of additional catalytic centers on the surface and thereby increases the efficiency of the cracking process, even with a low content of metal oxides in the samples (up to 2 %).

The practical significance of research is due to the use of natural clinoptilolite, which is an extremely cheap raw material. The use of a two-stage process scheme allows not only to increase the selectivity for styrene, but also to obtain an environmentally friendly solid carbonization residue that contains exclusively natural zeolite and does not contain heavy metals.

The limitations of the research are associated with the narrow temperature range of cracking, which may not fully reflect the behavior of catalysts under other conditions.

Research activities in the current conditions of martial law are significantly complicated by power outages when the equipment is not functioning, as well as by air raids, which force the immediate cessation of experimental processes and the search for shelter. These factors affect the pace of research and force the adaptation of the work schedule.

Further research should be focused on finding other cheap and effective modifiers for natural zeolite and studying their rational content, which will further increase the activity of catalysts in the cracking process. Expanding the temperature range of the process, varying the ratio of catalyst to plastic, optimizing the operating modes of the two-stage scheme, and exploring the possibilities of scaling the technology are important areas for implementing the results obtained in real production, which will contribute to the creation of effective "green" technologies for recycling plastic waste.

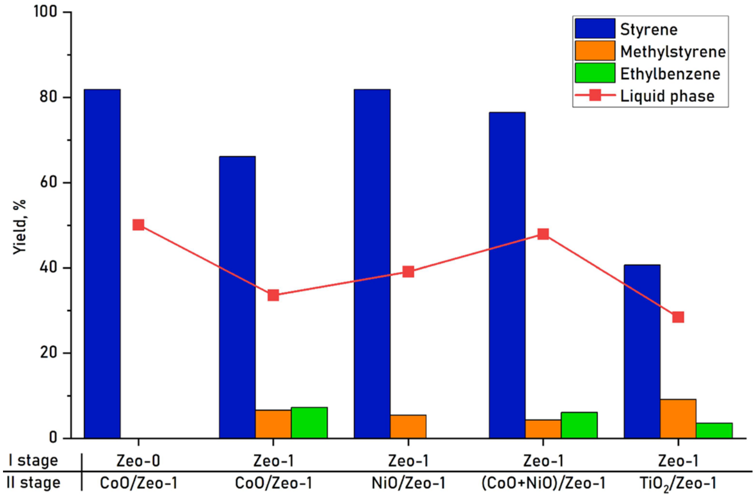

Fig. 10. Yield of liquid phase and main components (styrene, methylstyrene, ethylbenzene) in the two-stage configuration

Table 4

Results of catalytic polystyrene cracking using the two-stage configuration

Catalyst		Liquid phase yield (%)	Styrene Selectivity (%)	Styrene yield relative to feedstock (%)
I stage	II stage			
Zeo-0	CoO/Zeo-1	50.1	81.9	41.0
Zeo-1	CoO/Zeo-1	33.6	66.1	22.2
Zeo-1	NiO/Zeo-1	39.1	81.9	32.0
Zeo-1	(CoO+NiO)/Zeo-1	47.9	76.5	36.7
Zeo-1	ZrO_2/Zeo-1	38.6	67.2	26.0
Zeo-1	TiO2/Zeo-1	28.4	40.7	11.6

4. Conclusions

The studies presented in this work demonstrate the potential of utilizing low-cost natural raw materials, specifically Ukrainian-origin natural clinoptilolite, for the development of cracking catalysts aimed at implementing "green" solutions for the recycling of polystyrene-based plastic waste.

An acid-activated form of clinoptilolite was synthesized and subsequently modified with cobalt, nickel, cobalt-nickel, and titanium. The resulting catalysts were characterized using X-ray diffraction (XRD) analysis and low-temperature nitrogen adsorption-desorption techniques.

X-ray diffraction analysis revealed that after the activation of natural zeolite (Zeo0) into its acid-activated form (Zeo-1), the primary crystalline structure remained largely intact, with only minor variations in peak intensity, indicating minimal structural changes. Following modification with metal oxides (NiO, as well as a combination of NiO and CoO), no distinct diffraction peaks corresponding to these oxides were observed. This absence is attributed to the low mass fraction of these oxides or their amorphous nature. Adsorption-desorption isotherm analysis indicates that, with the exception of the TiO_2/Zeo-1 sample, nearly all catalysts exhibit Type III isotherms according to the IUPAC classification.

The synthesized catalysts, both those obtained through acid activation and those further modified with cobalt, nickel, and titanium oxides, demonstrated high catalytic activity and styrene selectivity, with liquid phase yields and selectivity ranging from 40 % to 80 %. Notably, the most promising catalysts were those derived from acid-activated zeolite further modified with cobalt salts, achieving styrene selectivity above 80 %. These results highlight the feasibility of developing low-cost catalysts based on natural clinoptilolite for the efficient catalytic recycling of plastics, particularly in low-temperature cracking processes.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this study, including financial, personal, authorship or other, which could affect the study and its results presented in this article.

Financing

The study was conducted without financial support.

Availability of data

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

References

1. Yanushevska, O., Dontsova, T., Krymets, G., Kyrii, S., Krasuliak, O., Dorozhko, K.; Fesenko, O., Yatsenko, L. (Eds.) (2023). Prospects for the Catalytic Conversion of Plastic Waste. Nanooptics and Photonics. *Nanochemistry and Nanobiotechnology, and Their Applications.* Cham: Springer International Publishing, 73–82. https://doi.org/10.1007/978-3-031-18104-7_5
2. Gonzalez-Aguilar, A. M., Pérez-García, V., Riesco-Ávila, J. M. (2023). A Thermo-Catalytic Pyrolysis of Polystyrene Waste Review: A Systematic, Statistical, and Bibliometric Approach. *Polymers, 15 (6),* 1582. https://doi.org/10.3390/polym15061582
3. Kik, K., Bukowska, B., Sicińska, P. (2020). Polystyrene nanoparticles: Sources, occurrence in the environment, distribution in tissues, accumulation and toxicity to various organisms. *Environmental Pollution, 262,* 114297. https://doi.org/10.1016/j.envpol.2020.114297
4. Kyrii, S., Dontsova, T., Karaschuk, O., Yanushevska, O.; Fesenko, O., Yatsenko, L. (Eds.) (2023). State of the Art of Microplastic and Nanoplastic Pollution: Origin and Removal Methods. *Nanomaterials and Nanocomposites, Nanostructure Surfaces, and Their Applications.* Cham: Springer International Publishing, 229–241. https://doi.org/10.1007/978-3-031-18096-5_12
5. Tokiwa, Y., Calabia, B. P., Ugwu, C. U., Aiba, S. (2009). Biodegradability of Plastics. *International Journal of Molecular Sciences, 10 (9),* 3722–3742. https://doi.org/10.3390/ijms10093722
6. Rehan, M., Miandad, R., Barakat, M. A., Ismail, I. M. I., Almeelbi, T., Gardy, J. et al. (2017). Effect of zeolite catalysts on pyrolysis liquid oil. *International Biodeterioration & Biodegradation, 119,* 162–175. https://doi.org/10.1016/j.ibiod.2016.11.015
7. *Polystyrene waste or scrap (HS: 391520) Product Trade, Exporters and Importers.* The Observatory of Economic Complexity. Available at: https://oec.world/en/profile/hs/polystyrene-waste-or-scrap
8. Zhang, X., Xu, S., Tang, J., Fu, L., Karimi-Maleh, H. (2022). Sustainably Recycling and Upcycling of Single-Use Plastic Wastes through Heterogeneous Catalysis. *Catalysts, 12 (8),* 818. https://doi.org/10.3390/catal12080818
9. Inayat, A., Fasolini, A., Basile, F., Fridrichova, D., Lestinsky, P. (2022). Chemical recycling of waste polystyrene by thermo-catalytic pyrolysis: A description for different feedstocks, catalysts and operation modes. *Polymer Degradation and Stability, 201,* 109981. https://doi.org/10.1016/j.polymdegradstab.2022.109981
10. Dewangga, P. B., Rochmadi, Purnomo, C. W. (2020). Styrene Recovery from the Pyrolysis of Polystyrene Waste Using Bentonite and Natural Zeolite Catalyst. *Key Engineering Materials, 849,* 84–89. https://doi.org/10.4028/www.scientific.net/kem.849.84
11. Yanushevska, O. I., Dontsova, T. A., Aleksyk, A. I., Vlasenko, N. V., Didenko, O. Z., Nypadymka, A. S. (2020). Surface and Structural Properties of Clay Materials Based on Natural Saponite. *Clays and Clay Minerals, 68 (5),* 465–475. https://doi.org/10.1007/s42860-020-00088-4
12. Maafa, I. (2021). Pyrolysis of Polystyrene Waste: A Review. *Polymers, 13 (2),* 225. https://doi.org/10.3390/polym13020225

13. Miandad, R., Barakat, M. A., Rehan, M., Aburiazaiza, A. S., Ismail, I. M. I., Nizami, A. S. (2017). Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts. *Waste Management, 69,* 66–78. https://doi.org/10.1016/j.wasman.2017.08.032

14. Verma, A., Sharma, S., Pramanik, H. (2021). Pyrolysis of waste expanded polystyrene and reduction of styrene via in-situ multiphase pyrolysis of product oil for the production of fuel range hydrocarbons. *Waste Management, 120,* 330–339. https://doi.org/10.1016/j.wasman.2020.11.035

15. Lee, S. Y., Yoon, J. H., Kim, J. R., Park, D. W. (2001). Catalytic degradation of polystyrene over natural clinoptilolite zeolite. *Polymer Degradation and Stability, 74 (2),* 297–305. https://doi.org/10.1016/s0141-3910(01)00162-8

16. Montalvo, S., Guerrero, L., Borja, R., Sánchez, E., Milán, Z., Cortés, I., Angeles de la la Rubia, M. (2012). Application of natural zeolites in anaerobic digestion processes: A review. *Applied Clay Science, 58,* 125–133. https://doi.org/10.1016/j.clay.2012.01.013

17. Pal, P.; Pal, P. (Ed.) (2017). *Nanotechnology in Water Treatment. Industrial Water Treatment Process Technology.* Butterworth-Heinemann, 513–536. https://doi.org/10.1016/b978-0-12-810391-3.00007-2

18. Tran, Y. T., Lee, J., Kumar, P., Kim, K.-H., Lee, S. S. (2019). Natural zeolite and its application in concrete composite production. *Composites Part B: Engineering, 165,* 354–364. https://doi.org/10.1016/j.compositesb.2018.12.084

19. *Sokyrnytskyi tseolitovyi zavod TZOV.* Available at: https://zeolite.ub.ua/

20. Ivanenko, O. I., Nosachova, Yu. V., Krysenko, T. V. (2020). Comprehensive use of natural clinoptylolite in environmental protection technologies. *Proceedings of the NTUU "Igor Sikorsky KPI". Series: Chemical Engineering, Ecology and Resource Saving, 4,* 66–82. https://doi.org/10.20535/2617-9741.4.2020.219786

21. Pavlovskyi, D. O., Krymets, H. V., Yanushevska, O. I., Levandovskyi, I. A., Dontsova, T. O. (2024). Perspectives of low-temperature atmospheric pressure catalytic decomposition of polystyrene. *Journal of Chemistry and Technologies, 32 (2),* 276–283. https://doi.org/10.15421/jchemtech.v32i2.286999

22. Field, L. D., Sternhell, S., Kalman, J. R. (2013). *Organic Structures from Spectra.* Wiley, 510.

23. Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K. S. W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry, 87 (9-10),* 1051–1069. https://doi.org/10.1515/pac-2014-1117

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