Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua
editorial e-mail: chem.dnu@gmail.com

UDC 547.678.7+502/504

PERSPECTIVES OF LOW-TEMPERATURE ATMOSPHERIC PRESSURE CATALYTIC DECOMPOSITION OF POLYSTYRENE

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Received 5 September 2024; accepted 15 May 2024; available online 10 July 2024

Abstract

Plastic pollution has become one of the global environmental threats to humans and the whole world. Plastics do not exist without the chemicals that emitted at every stage of their life cycle – from oil extraction to production, and disposal, especially when plastic waste is not disposed properly, but rather stored in the open air on unprotected soil near water sources. Chemical recycling of plastic waste, which is based on catalytic cracking, prevents the emission of toxic chemicals into the environment; produces liquid oils and additives for various fuels; and avoids significant energy costs using mechanical and thermal processing methods. Catalytic cracking of plastics in the presence of natural and synthetic zeolite catalysts allows to produce a wide range of aromatic hydrocarbons. The modified samples of CaY-based catalysts were used in the catalytic cracking of polystyrene, as a type of thermoplastic polymer. Depending on the selected type of zeolite catalyst (ZSM-5, Ni-ZSM-5, USY, NiHY), the practical yield the components of the liquid fraction was determined, as follows: styrene, styrene dimer, styrene trimer, ethylbenzene, methylstyrene, cumene, and others. The yield of styrene using ZSM-5 is 42 %, at Ni-ZSM-5 – 5.97 %, at USY – 1.26 %, at NiHY – 47.37 %. The yield of the liquid fraction at ZSM-5 is 67.2 %, at Ni-ZSM-5 – 38.5 %, at USY – 15 %, at NiHY – 70.3 %. According research results, it was found that the most selective and effective catalyst (among the above) for polystyrene cracking was a nickel-modified alumosilicate (NiHY). The yield of the liquid fraction using the NiHY catalyst is 70.3 %, and the yield of styrene is 47.37 %. In conclusion, the further development of catalysts is necessary to improve the selectivity and efficiency of low-temperature catalytic cracking reactions to obtain secondary raw materials for the synthesis of polystyrene.

Keywords: plastic waste; chemicals pollution; catalytic cracking; polystyrene; modified zeolite; Ni-modified catalysts.

ПЕРСПЕКТИВИ НИЗЬКОТЕМПЕРАТУРНОГО КАТАЛІТИЧНОГО КРЕКІНГУ ПОЛІСТИРОЛУ ЗА АТМОСФЕРНОГО ТИСКУ

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Анотація

Забруднення пластиком стало однією з глобальних екологічних загроз для людини і світу. Впродовж всього життєвого циклу пластмаси – від видобутку нафти до виробництва та утилізації, – вони виділяють хімічні речовини, особливо якщо пластикові відходи не утилізуються належним чином, а зберігаються просто неба на незахищеному ґрунті поблизу джерел води. Хімічна переробка пластикових відходів, яка базується на каталітичному крекінгу, запобігає викидам токсичних хімічних речовин у навколишнє середовище, дозволяє отримувати рідкі оливи та добавки до різних видів палива, а також уникати значних енергетичних затрат за використання механічних і термічних методів їх переробки. Каталітичний крекінг пластмас у присутності природних і синтетичних цеолітних каталізаторів дозволяє отримувати широкий спектр ароматичних вуглеводнів. Модифіковані зразки каталізаторів на основі CaY використано в каталітичному крекінгу термопластичного полімеру – полістиролу. Залежно від обраного типу цеолітного каталізатора (ZSM-5, Ni-ZSM-5, USY, NiHY) визначено практичні виходи компонентів рідкої фракції: стиролу, димеру стиролу, тримеру стиролу, етилбензолу, метилстиролу, кумолу та інших. Вихід стиролу у присутності ZSM-5 становив 42 %, Ni-ZSM-5 – 5.97 %, USY – 1.26 %, NiHY – 47.37 %. Вихід рідкої фракції у присутності ZSM-5 становив 67.2 %, Ni-ZSM-5 – 38.5 %, USY – 15 %, NiHY – 70.3 %. За результатами досліджень встановлено, що найбільш селективним та ефективним каталізатором крекінгу полістиролу (серед вищезазначених) є модифікований нікелем алюмосилікат (NiHY). Вихід рідкої фракції у присутності каталізатора NiHY становив 70.3 %, а вихід стиролу – 47.37 %. Отже, подальше вдосконалення каталізаторів необхідне для підвищення селективності та ефективності процесу низькотемпературного каталітичного крекінгу з метою отримання вторинної сировини для синтезу полістиролу.

Ключові слова: пластикові відходи; хімічне забруднення; каталітичний крекінг; полістирол; модифікований цеоліт; Ni-модифіковані каталізатори.

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Introduction

The accumulation of plastic waste in the environment, that has been growing rapidly in recent years, is a matter of global concern. Globally, 46 % of plastic waste is disposed on landfills, while 22 % is not covered by the waste management system and becomes garbage over the time. Unlike other materials, plastic does not biodegrade and could take up to 1000 years to destruct according to various expert estimates [1].

The excellent mechanical properties of plastics, their low cost of production and well-proven technologies make plastic products indispensable in different areas of our lives. Given the growing use of polymer products, on the one hand, and the inability to biodegrade the main assortment of plastics and inadequate methods of handling, on the other hand, raises the problem of plastic pollution to the level of the most urgent challenges of today [2]. The importance of improving the legal requirements for the proper polymeric waste management system and using chemical energy obtained from this waste – justifies the search for better methods and technologies for their processing [3].

One of the most relevant and, at the same time, insufficiently studied method is catalytic processing of the plastic waste. Unlike mechanical and thermal recycling, chemical recycling minimizes energy costs, reduces massive toxic emissions, and offers the possibility of recycling plastic waste into valuable commercial products instead of producing low-quality plastic products [4; 5].

Polystyrene (PS) is a thermoplastic material that is resistant to biodegradation in the environment [6; 7], making PS persistent in the nature for a long time. Meanwhile, the percentage of PS in the total volume of plastic waste is 20 %, causing a significant negative impact on environmental safety. According to the research, the presence of PS in cultivated soils containing a wide range of microbes, fungi and invertebrates has not resulted in even 1 % of its biodegradation, even after 90 days. The hydrophobic properties of thermoplastics make them resistant to hydrolysis, while their high molecular weight and low water solubility prevent microorganisms to transport these materials into cells for metabolism. However, there are a number of researches [8; 9] focused on the development of certain potential microorganism strains that can be successfully used in PS degradation (bacteria, fungi, algae and insects) due to various microbial degradation mechanisms (colonization, bio fragmentation, assimilation and mineralization).

The process of biofilm formation and partial biodegradation of PS by the actinomycete Rhodococcus ruber were studied in the work [10]. The monitoring of the C208 biofilm formation kinetics during its cultivation on polystyrene flakes showed that most bacterial cells have a good adhesion to the PS surface during several hours. Moreover, the addition of mineral oil caused the prolongation of biofilm formation up to 8 weeks and slightly reduced the weight of polystyrene (0.8 %), demonstrating the perspectives for further researches in PS processing area.

Taking into account the fact that PS is extremely inert to effective degradation in mild natural conditions, the use of catalytic methods of its processing, in particular, oxidative decomposition, is increasingly drawing the attention of scientists. In the study [11], a group of scientists continued to research the activation of oxygen (O_2) in the aerobic oxidation reaction of plastic and proposed a simple method for the selective oxidative degradation of PS to formic acid (1.72 %), benzoic acid (2.40 %), and benzophenone (3.2 %). This method of PS degradation under oxygen (1 bar) as an oxidizing agent and violet-blue light irradiation (405 nm) allows to carry out selective degradation of PS waste using singlet oxygen, temperature and atmospheric pressure, as well as using widely available catalysts (inorganic/organic photoacids, in particular trifluoroacetic acid – 5 mol.%, HOTf). This research area may open up new approaches to oxidative recycling of plastics without the usage of photosensitizers, which had previously been considered impossible for aerobic degradation of PS or other polymers. The similar approach using the catalytic oxidation of PS to aromatic oxygenates over visible light irradiation in the presence of heterogeneous graphitic carbon nitride catalysts was shown in work [12]. Benzoic acid, acetophenone, and benzaldehyde are the main liquid products at polystyrene conversion rates above 90 % and temperatures up to 150 °C.

Catalytic cracking is one of the most promising methods of chemical processing of plastic waste into liquid fuels that can be commercialized [13; 14]. The study of catalytic cracking of polystyrene (PS) in the presence of a catalyst, which is a fly ash catalyst impregnated by potassium nitrate, allowed to obtain a liquid product with a yield of 88.4%. Moreover, the optimal temperature regime was much milder than for the conventional thermal cracking. The process temperature was 425 °C for a duration of 60 minutes. Gas Chromatography/Mass Spectrometry (GC/MS) analysis showed that the products of polystyrene cracking are hydrocarbons of the C_3-C_{24} range (a mixture of gasoline and kerosene fractions with a predominant content of hydrocarbons of the C_3-C_{24} olefinic range). The study [15] described the catalytic degradation of PS based on solid acid-base catalysts, in the synthesis of which acids and bases were partially combined to improve their selectivity for liquid products. It was found that the solid base catalyst (KFe/γ-Al_2O_3) was more effective for the selective depolymerization process of PS with 83.2 % styrene selectivity and ~83 % liquid yield. The catalyst showed prolonged activity and stability; the catalyst was not required to be regenerated for several cycles, indicating its perspective application in plastic depolymerization processes.

In this work [16], the catalytic decomposition of polystyrene was studied with the following zeolite catalysts HZSM-5, Hβ, HY, and USY (Si/Al molar ratio in the range of 5.3–11.5). The ultra-stable Y zeolites (USY) with a large pore size (5.6 nm), high surface area (734 m^2/g) and an abundant number of strong acid sites (1.21 mmol/g) showed the highest selectivity for benzene (31.1 % yield) and ethylbenzene (34 % yield).

The authors studied [17] the catalytic pyrolysis of different types of plastics (PS, PE, PP, and PET) and their mixtures in different ratios in the presence of modified natural zeolite (NZ) catalysts. The NZ was modified by thermal activation (TA-NZ) at 550 °C and acid activation (AA-NZ) with HNO3, to enhance its catalytic properties. The catalytic pyrolysis of PS produced a higher liquid oil (70 and 60 %) than PP (40 and 54 %) and PE (40 and 42%), using TA-NZ and AA-NZ catalysts, respectively. The gas chromatography-mass spectrometry (GC-MS) analysis of oil showed a mixture of aromatics, aliphatic and other hydrocarbon compounds. Importantly, the catalytic pyrolysis of PS was characterized by a lower process temperature than similar pyrolysis of other plastics. Furthermore, it was observed that the acidity of the zeolite influenced the number of char formed (dispersed carbon) during PS pyrolysis and the increase in the amount of free carbon in the pyrolysis products in the presence of AA-NZ. Thus, this work shows the prospect of using catalytic pyrolysis in the presence of zeolites to produce additives for transportation fuels.

Interesting results were obtained [18] in the process of catalytic pyrolysis of PS using natural zeolite (it was extracted from the Harrat Ash-Shamah area located in the northwest of KSA) and synthetic zeolite (ZEOLYST™ CBV 780 CY (1.6) Zeolite SDUSY Extrudate). The work also includes a thermal pyrolysis of polystyrene and a comparison of the products of such pyrolysis with the products of catalytic pyrolysis in the presence of zeolites. The GC-MS results showed that around 99 % aromatic hydrocarbons were found in the liquid oils produced by both thermal and catalytic pyrolysis. In thermal pyrolysis oil, the major compounds were styrene (48.3 %), ethylbenzene (21.2 %), toluene (25.6 %) and benzo (b) triphenylene (1.6 %). In catalytic pyrolysis with natural zeolite, the major compounds were styrene (60.8 %), methylstyrene (10.7 %), azulene (4.8 %), 1H-indane (2.5 %) and ethylbenzene (1.3 %). While in catalytic pyrolysis with synthetic zeolite, the major compounds were alpha-methylstyrene (38.4 %), styrene (15.8 %), benzene (16.3 %), ethylbenzene (9.9 %), and isopropylbenzene (8.1 %). It should be noted that the higher heating value (HHV) in MJ/kg of the feedstock and the resulting liquid products and coal was studied in this work. Determined that the average HHV of plastic raw materials based on polystyrene, liquid products of thermal and catalytic pyrolysis using natural and synthetic zeolites is 39.3, 41.6, 41.7, and 40.6 MJ/kg, respectively. This demonstrates that the produced liquid oils can be suitable for energy generation and heating purposes after further processing.

The authors [19] studied the thermocatalytic degradation (500 °C) of polyethylene of high and low density, (HDPE, LDPE), polypropylene (PP) and polystyrene (PS) on the H-Y zeolite was performed. Liquid product yields ranged from ~42 and ~44 % wt% for polyethylenes and PP, while the production of PS showed ~71 wt%.

The analysis of scientific researches presented above, demonstrates the prospects of using the natural and synthetic zeolites in the processes of thermocatalytic decomposition of plastics, in particular polystyrene, into liquid oils that can be used as additives to petroleum fuels or undergo further treatment to improve their properties.

The aim of this work is to determine the composition of the products of the PS catalytic cracking reaction using different catalysts based on synthetic aluminosilicate materials at low temperature and atmospheric pressure.

Experimental part

Catalytic cracking was chosen as the method of polystyrene processing. Polystyrene is a type of thermoplastic polymer consisting of granules that are extruded or molded into the designated size. In this work, samples of polystyrene waste with a size of 2×2 cm were used. The structural formula of polystyrene is shown in Fig. 1.

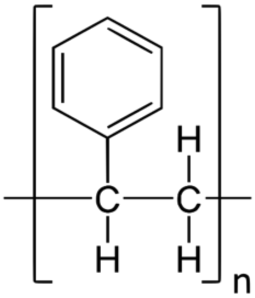

Fig. 1. Structural formula of polystyrene

ZSM-5 zeolite with a high silicon content in the crystal lattice was used as a catalyst for cracking. The catalyst is characterized by high thermal stability and resistance to acids. Characteristics of ZSM-5 zeolite are given in Table 1.

Table 1

Characteristics of the ZSM-5 catalyst

Parameter	Value
Relative crystallinity, %	>85
Pore diameter, nm	2.21
Pore volume, cм^3/g	0.2
SiO_2/Al_2O_3 mole ratio	25/1
Total surface area, m^2/g	560
Na_2O, %	<0.1

Natural calcium alumosilicate (CaY) was also used as a catalyst for cracking. The formula of the aluminosilicate is $Me^+[Si_xAl_yO_z]\cdot mH_2O$, where Me^+ – cation, $[Si_xAl_yO_z]$ is zeolite main framework, and mH_2O – water molecule in sorbed phase. The characteristics of CaY are given in Table 2.

Table 2

Characteristics of the CaY catalyst

Parameter	Value
Total surface area, m^2/g	500
Pore diameter, nm	12.47
SiO_2/Al_2O_3 mole ratio	7-8/1
Na_2O, %	1.6
CaO, %	13.5

Before modification of ZSM-5 and CaY, the two zeolites were pre-activated to convert into the H-form. In this case, stirring in suspensions of 5 wt % aqueous solution of HCl was conducted for 2 hours. The resulting activated forms were recovered by filtration and repeatedly washed with distilled water (1 dm^3) until the wash water was obtained pH=7. The catalyst was then dried and calcined at 600 °C.

Ni-modified materials (1 wt.% Ni) were prepared on the base of their H-forms. The H-CaY and H-ZSM-5 zeolites were impressed in a solution of $NiCl_2\cdot6H_2O$, which consist of 0.404 g $NiCl_2\cdot6H_2O$ and 30 mL of distilled water. The resulting solid was recovered by filtration and repeatedly washed with distilled water to remove the $NiCl_2$ residuals. The solid was dried for 5–6 h. The obtained samples of the catalyst based on CaY and ZSM-5 were labeled NiHY and Ni-ZSM-5 respectively.

Figure 2 shows a polymer catalytic cracking system that operates on the principle of simple distillation at atmospheric pressure. This type of distillation is based on heating a liquid to a boil and condensing its vapors in a refrigerator. The distillate is enriched with the more volatile (low-boiling) component and separated after condensation, while the less volatile (high-boiling) component is left in the un-distilled liquid.

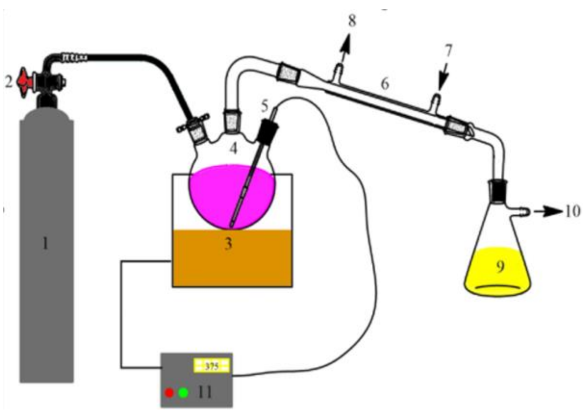

Fig. 2. Catalytic cracking system
1 – inert gas cylinder; 2 – gas supply controller; 3 – heating jacket; 4 – three-necked flask; 5 – thermocouple; 6 – Liebig condenser; 7 – water inlet to the water cooling system; 8 – water outlet from the water cooling system; 9 – receiver flask; 10 – non-condensable gas products; 11 – controller

The combined polymer sample with the catalyst (in a certain ratio) is loaded into a three-necked flask 4. Cylinder 1 with inert gas is connected to the three-necked flask. Regulator 2 is used to control the gas supply. A gas with a lower boiling point, which is produced during the reaction mixture is heated, condenses in a Liebig condenser 6, which is connected to a condenser flask 7 to collect the condensate. The flask 4 is connected to a thermocouple 5 that sends a signal to the controller 8. The controller is connected to the heating jacket 3 to control the temperature of the reaction mixture

Identification and analysis of the liquid fraction composition was carried out using (GC/MS). GC/MS analyses were conducted on an Agilent 1200. Methanol (CH_3OH) was chosen as the stationary phase. The surface chemistry of the obtained samples and cracking products were identified and studied by infrared spectroscopy. The infrared spectra were recorded using a Fourier transform infrared spectrometer IRAffinity-1S (Shimadzu, Japan) in the spectral range 4000–400 cm^{-1} (number of scans – 32, resolution – 4 cm^{-1}). The supplier's software was used to spectra processing.

Results and their discussion

The catalytic cracking of PS in the presence of ZSM-5 and USY zeolite-based catalysts and ZSM-5 and HY Ni-modified catalysts were analyzed. The results of the catalytic cracking are given in Table 3. The cracking products were analyzed by IR spectroscopy (Fig. 3–5) and GC/MS.

Table 3 shows that the use of the ZSM-5 catalyst in catalytic cracking results to the formation of the following products in the liquid phase: styrene, ethylbenzene, and methylstyrene. Nickel modification of the catalyst reduces the yield of styrene, where dimers and trimers are formed in addition to styrene. A similar result was obtained using the USY catalyst, but with a much lower yield of the liquid phase and, accordingly, styrene and its dimers and trimers. The use of nickel-activated and nickel-modified CaY catalyst allows to obtain the maximum yield of styrene, but with the presence of other by-products (ethylbenzene, methylstyrene, cumene).

The analysis of the obtained liquid phase components demonstrates the following. The styrene produced in the catalytic cracking process is a perspective secondary raw material for polystyrene production. For instance, work [20] demonstrates that at atmospheric pressure without a catalyst, polystyrene decomposition requires a temperature of 500–550 °C. Methylstyrene formed along with styrene does not require its separation, as it is used in the production of polystyrene to increase its heat resistance [21]. Ethyl benzene is an important precursor in petrochemical synthesis, contained in petroleum, and can also be a key product of catalytic cracking of polystyrene, for the production of which selective and efficient catalysts must be developed. Similarly, cumene is a raw material for the production of acetone and phenol, as well as an additive to increase the petrol octane number. Therefore, we can also consider its production from polystyrene, for which selective catalysts must be obtained. Styrene dimers and trimers have no practical use and are undesirable products.

Table 3

Conditions and results of catalytic cracking of polystyrene

Catalyst	T_{max}, °C	PS/kat	Yield of liquid fraction		Styrene yield, %	Other reaction products	
			m, g	%		Product	%
ZSM-5	165	5	16.8	67.2	42	ethylbenzene methylstyrene other	11.3 21.89 24.81
USY	205	5	7.5	15	1.26	styrene dimer styrene trimmer other	10.43 5.92 82.39
NiHY	175	5	35.15	70.3	47.37	ethylbenzene methylstyrene cumene other	17.54 25.37 6.84 2.88
Ni-ZSM-5	165	5	19.25	38.5	5.97	styrene dimer styrene trimmer other	32.57 37.28 24.18

The analysis of the obtained liquid phase composition indicates that the most effective catalyst is NiHY, which demonstrated high liquid phase yield (70.3 %) and selectivity for styrene (47.37 %), and the selected conditions (low temperature ~ 165–205 °C and atmospheric pressure) can be optimal for the production of styrene from polystyrene, thereby developing a circular economy. The used catalysts including the NiHY, require further modification to obtain a pure styrene with the possible presence of methylstyrene in the catalytic cracking process over these conditions.

The infrared spectrum of the cracking liquid fraction with the Ni-ZSM-5 catalyst shown an intense absorption band of methyl (CH_3-) and ethyl (C_2H_5-) groups in the spectral range 990–540 cm^{-1} (Fig. 3). The fluctuation of the absorption band at 500–400 cm^{-1} corresponds to the presence of monosubstituted benzene. The intense absorption band in the spectral range 1700–1450 cm^{-1} corresponding to the vinyl group (CH_2=CH-) and aromatic hydrocarbons is observed. As shown Fig. 3, olefins and alkanes are present in the sample (the spectral range 3080–2930 cm^{-1})

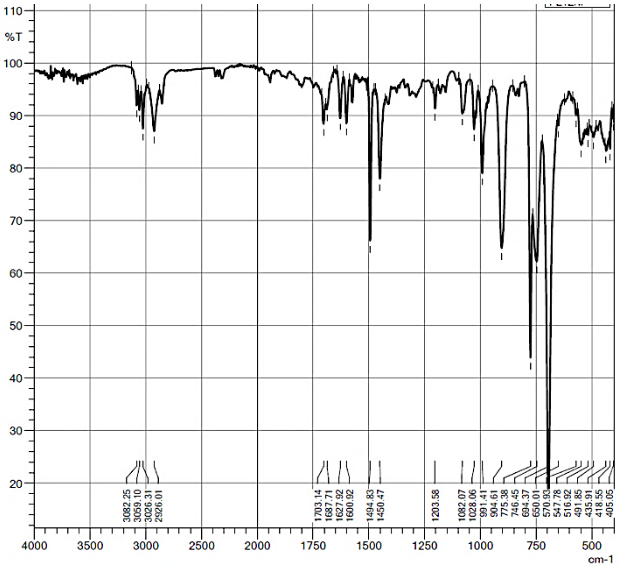

Fig. 3. IR-spectra of the cracking liquid fraction with Ni-ZSM-5 catalyst obtained at temperature of 165 °C

Figure 4 shows the infrared spectrum of the cracking liquid fraction with the NiHY catalyst. As shown Figure 5, the fluctuation of the absorption band almost coincides with the infrared spectrum of the cracking liquid fraction with Ni-ZSM-5 catalyst (Fig. 3).

The results of infrared spectroscopy of NiHY and Ni-ZSM-5 catalyst samples are shown in Figure 5. The model sample was native silica. The Figure 5 shows that the fluctuation of the absorption band for Ni-ZSM-5 almost coincides with the fluctuation of the band of the model sample. Intense vibrations are observed in the spectral range 1300–900 cm^{-1}. NiHY is characterized by an intense absorption band in the spectral range of 900–500 cm^{-1} and 3600–3200 cm^{-1}.

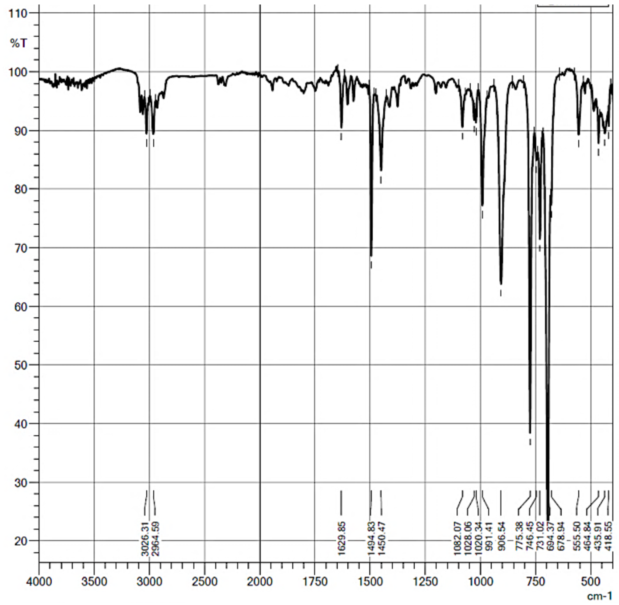

Fig. 4. IR-spectra of the cracking liquid fraction with NiHY catalyst obtained at temperature of 175 °C

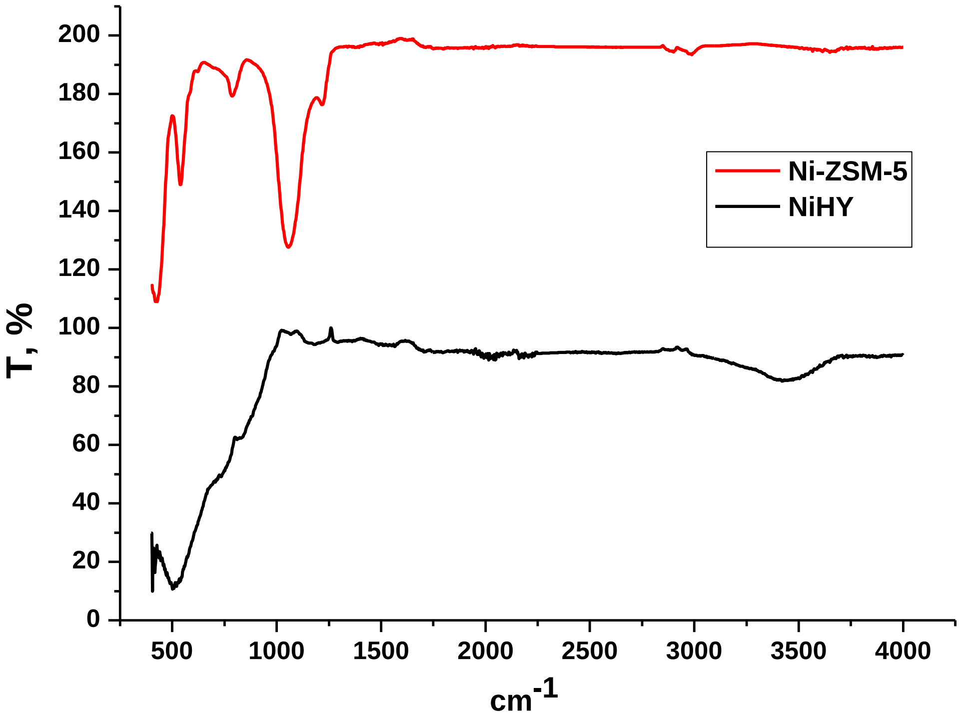

Fig. 5. IR-spectra of NiHY and Ni-ZSM-5 catalysts samples

Conclusions

The low-temperature atmospheric pleasure catalytic cracking of polystyrene was successfully carried out using different catalysts based on synthetic aluminosilicate materials. The work demonstrates that under these conditions and with aluminosilicate catalysts, styrene can be a key product, which has perspectives for use as a secondary raw material in polystyrene production processes. Thus, further search for effective catalysts can contribute to the implementation of the circular economy principles and ensure the proper disposal of plastic waste throughout its life cycle.

Infrared spectroscopy and gas chromatography with mass detection identified a wide range of hydrocarbons in polystyrene cracking products: styrene, ethylbenzene, methylstyrene, cumene using NiHY and ZSM-5 catalysts, and styrene, styrene dimer, styrene trimer when using USY and Ni-ZSM-5 catalysts. The yield of styrene at ZSM-5 is 42 %, at Ni-ZSM-5 – 5.97 %, at USY – 1.26 %, at NiHY – 47.37 %. The yield of the liquid fraction at ZSM-5 is 67.2 %, at NiZSM-5 – 38.5 %, at USY – 15 %, at NiHY – 70.3 %.

The most selective and efficient catalyst for polystyrene cracking was a Ni-modified aluminosilicate (NiHY). Using NiHY catalyst, the yield of the liquid fraction is 70.3 %, and the yield of styrene is 47.37 %. Despite the high selectivity and yield of the liquid phase, the NiHY catalyst requires further improvement for obtaining secondary raw materials for polystyrene production. Improving the composition of catalysts and changing the parameters of catalytic cracking are the further steps.

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