

An Environmentally Friendly Catalyst for Aromatic Hydrocarbons Alkylations with 1-alkenes

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Abstract: - Nowadays, the alkylation of aromatic compounds using 1-alkenes is still conducted in industrial applications using Friedel-Crafts alkylations. The most commonly used catalysts are aluminum chloride (AlCl_3) and hydrofluoric acid (HF), both of which pose significant environmental concerns. An alternative approach involves the use of solid acid catalysts, specifically zeolites, which may offer a more environmentally acceptable option. In this study, the alkylation of toluene with 1-decene was performed in a batch reactor under autogenous pressure in the liquid phase at a temperature of 100 °C. Zeolite Y samples with varying sodium content (molar ratio of Si/Al approximately equal to 2.27), were employed as the parent catalysts. These zeolites underwent a dealumination process followed by the removal of residual sodium and the cationic form of aluminum via ion exchange with ammonium nitrate. Accessible physical and chemical methods were used for the characterisation of the prepared catalyst. The residues of sodium were found to influence the catalytic activity in the alkylation reaction. The formation of a secondary mesoporous structure enhanced the selectivity towards the production of 2-decyltoluene. Following the dealumination and ion exchange treatment, an increased ratio of Brønsted to Lewis acid sites was observed, resulting in the suppression of dimerization reactions in the alkylation products.

Key-Words: - Solid acid catalysts, Aromatics, Zeolites, Zeolite Y, Friedel-Crafts catalysts, Dealumination, 1-alkenes, Linear alkyltoluenes.

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1 Introduction

The alkylation of aromatics with various 1-alkenes or alcohols is extensively utilized in the chemical industry. The rate and mechanism of these reactions are influenced by several factors, including the structural characteristics of the alkylation agent, the polarity and solvation capacity of the solvent, and the nature of the catalyst employed. Traditionally, Friedel-Crafts alkylation reactions involving alkenes, chloroalkanes, or alcohols have been catalyzed by liquid-phase catalysts such as hydrofluoric acid and aluminum chloride, [1], [2]. The main issues of these catalysts are related to corrosion and stringent requirements for feedstock drying. The associated drawbacks of these conventional catalysts underscore the necessity for the development of alternative catalytic systems to facilitate a cleaner petrochemical process for detergent production, [3], [4], [5]. In this context, zeolite catalysts, such as HY zeolites, have emerged as the preferred choice for advancing this new alkylation process, [6], [7], [8].

The alkylation of aromatics with long-chain 1-alkenes using solid acid catalysts represents a promising approach for the synthesis of linear alkylaromatics. One of the examples of this type of reaction is the synthesis of linear alkyltoluenes (LATs). This process generally yields several positional isomers of the desired LAT product, with the 2-isomer being particularly advantageous due to its favorable environmental attributes. Specifically, the 2-isomer exhibits enhanced solubility, superior biodegradability, and effective detergent properties, [9].

Zeolites are microporous materials characterized by their high surface-to-volume ratio. One unique property of zeolites is that they have open channels, or pores, and cavities distributed throughout their lattice, [10]. They consist of three-dimensional tetrahedral units (TO_4) bonded by oxygen atoms. The T atoms are mostly aluminum and silicon. Through the combination of these units, zeolites form unique arrangements that result in the creation

of intra-crystalline channels and cavities. These channels have molecular-scale dimensions ranging from 0.3 to 2 nm, [11].

The faujasite (zeolite Y) has a primary structure composed of tetrahedral units with aluminum (AlO_4) and silicon (SiO_4) central atoms. Faujasite zeolites are particularly known for their large cages called "supercages," which have a diameter of 1.3 nm and a ball-shaped structure. These supercages are approachable through a window with 12 rings and a free aperture measuring 0.74 nm, making them larger than most organic molecules, [11].

The molar ratio of Si/Al in the TO_4 ($T = \text{Si}, \text{Al}$) framework influences the hydrophilic and hydrophobic properties of modified zeolites, which in turn affects their sorptive and catalytic capabilities. The principal methods for dealumination of faujasite-type zeolite on a commercial scale can be categorized into two main approaches: thermochemical treatment of NH_4Y using steam (steaming) [12], [13], and the treatment of NaY with SiCl_4 (substitution), [14]. In the steaming process, aluminum remains as extra-framework aluminum (EFAL) on the surface of the crystals, whereas the aluminum released from the framework during the SiCl_4 treatment dissolves in the washing process and can be largely extracted from the bulk of the zeolite.

During the hydrothermal treatment of the ammonium form of zeolite Y, temperatures ranging from 500 to 800 °C are utilized in a steam atmosphere. The high-temperature steam induces the dealumination of the zeolitic framework, hydrolyzing the framework aluminum, which is then partially substituted by silicon. The extracted aluminum remains as extra-framework aluminum within the zeolite structure. The types of extra-framework aluminum can vary based on the hydrothermal treatment conditions and the properties of the zeolite. This aluminum plays a significant role in influencing the catalytic properties of zeolite Y, [15].

Zeolites Y in their original as well as modified form are used in a wide range of chemical processes. These processes include biomass valorization [16], hydrocarbon cracking [17], VOC oxidation [18], oxidative dehydrogenation [19], and hydrocarbon adsorption [20].

In this work, new ecological catalysts for the alkylation of toluene were prepared. They were studied as a replacement for conventional technology using non-environmentally friendly catalysts. The novelty of the work lies in the observation of the relation of sodium residues in dealuminated zeolite Y in ammonium form on the

conversion, and selectivity for the desired product and product composition.

2 Experimental

2.1 Catalysts Preparation

Zeolite NaY (Si/Al = 2.69; Na_2O = 11.59 %) as a parent zeolite used for further treatment and testing was obtained from the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava

The parent catalyst was treated by decationization at the Department of Organic Technology, Catalysis, and Petroleum Chemistry. Three zeolite catalysts were prepared by decationization with different residues of sodium after treatment. 10 ml of NH_4NO_3 solution on 1 g of zeolite was used for all three zeolites. First zeolite Y (**Y-A**) with sodium molar content of 2.69 % was prepared by three-time repeated decationization with a solution of NH_4NO_3 (1.5 M) at room temperature. Second zeolite Y (**Y-B**) with a sodium content of 1.27 % was prepared by four-time repeated decationization with the same concentration of NH_4NO_3 solution (1.5 M) at the temperature of 90 °C. Third zeolite Y (**Y-C**) with a sodium content of 0.76 % was prepared by eight-time repeated decationization with NH_4NO_3 solution at the temperature of 90 °C. Zeolites after decationization were washed with distilled water several times. Washed zeolites were dried in an oven at a temperature of 80 °C and then hydrothermally treated in a deep bed at different temperatures of 560°C (**NH₄SY-4A, NH₄SY-4B, and NH₄SY-4C**) and 780 °C (**NH₄SY-2A, NH₄SY-2B, and NH₄SY-2C**). The last step of zeolite modification was removing residual sodium and extra framework aluminum by the solution of NH_4NO_3 (2 M) three times at the temperature of 90 °C.

For alkylation testing H-forms of zeolites were used. NH_4 -forms of zeolites Y were activated at 450°C (3 hours) to obtain H-form. Before reaction, the formed H-form was let to cool down in a desiccator.

2.2 Catalysts Characterization

The physical adsorption of nitrogen (−196 °C) was used for the measurement of textural properties. The used device was ASAP-2400 (Micrometrics). Measured zeolites were evacuated overnight (350°C) under the vacuum (2 Pa) before analysis. Conventional BET isotherm ($p/p_0 = 0.05\text{--}0.3$) method was used for specific surface area (S_{BET})

calculation. For the external surface area with the surface of mesopores (S_t) and the volume of micropores (V_{micro}) calculation, the t-plot using Harkins–Jura master isotherm was used. The volume of adsorbed nitrogen ($p/p_0 = 0.99$) was used for determination of total pore volume (V_p).

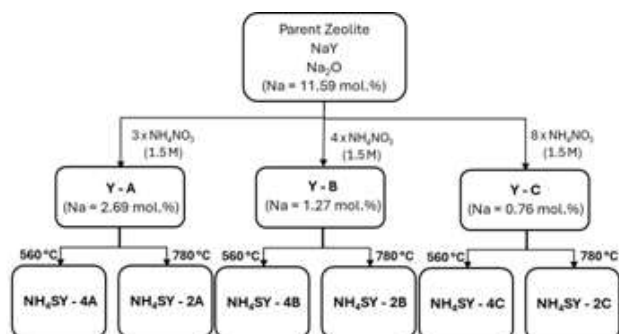


Fig. 1: Scheme of parent zeolite treatment

Temperature programmed desorption of ammonia (TPD-NH₃) method was used for the total acidity determination. Zeolites (300 mg) were treated in situ at 480 °C for 2 h (He flow) and then cooled down to 220 °C (He atmosphere) right before the adsorption. Ammonia was adsorbed at a temperature of 220 °C by using an NH₃/He mixture. The desorption of NH₃ was carried out at the temperature from 220 to 700 °C (He flow). During desorption, the effluent was led to the solution of H₂SO₄ (0.05 M). Titration of NaOH (0.05M) solution was used for the determination of desorbed ammonia.

Brønsted (BAS) and Lewis (LAS) acidic sites were measured by FTIR Genesis spectrometer (Mattson-Unicam). Infrared spectroscopy of pyridine adsorption was used for determination. Zeolites with a surface density of ca. 8 mg/cm² in the form of wafers were activated at 450 °C under a vacuum (10⁻⁴ Pa) for 3 h. The number of acid sites was determined based on the integrated area absorbances at 1550 (Brønsted) and 1450 cm⁻¹ (Lewis), respectively, in correlation with their extinction coefficients, [21]. KBr technique using FTIR spectra was used for the molar ratio Si/Al determination. the.

2.3 Catalytic Tests

All modified zeolites were tested in the alkylation process at a temperature of 100 °C in a stirred batch reactor (stainless-steel). Toluene p.a. (Mikrochem Pezinok, 99.0 %) and 1-decene (Spolana Neratovice, > 96 %) were used as feed of hydrocarbons. For catalytic testing 80 g of reaction mixture in a molar ratio of toluene to 1-decene 8.6:

1 was used for each experiment. An amount of 2.5 wt.% of calcined catalyst to the reaction mixture was used. After reaching the reaction temperature of 100°C (30 min) first sample of reaction products was taken. After that, every 30 minutes product samples were taken until reaching 240 minutes of reaction. Feed and reaction products were analyzed with a gas chromatograph Hewlett-Packard 5890 A (Series II) equipped with flame-ionisation detector. Alkyltoluenes and olefins structures from products were verified by GC-MS using MS25RFA Kratos, Manchester equipment.

The 1-decene conversion was calculated as the percentage of all products in sum with 1-alkenes to all products. Selectivity of 2-decyltoluene was calculated as a percentage of 2-decyltoluene in all prepared products.

3 Results and Discussion

3.1 Zeolite Characterization

For testing modified zeolites in the alkylation process, nine different samples of modified zeolites were prepared by changing conditions of zeolite treatment (Figure 1). As can be seen in Table 1, the changes in decationization conditions had a significant effect on catalyst properties. Especially it is possible to see the correlation between the molar ratio of Si/Al after the decationization process and sodium content. With the decreasing sodium content in treated zeolite, the molar ratio of Si/Al increased. The same trend is possible to see in relation to changes in hydrothermal treatment temperature. With increasing decationization temperature, the molar ratio of Si/Al is higher. Different methods were used for obtaining information about physical-chemical properties of tested zeolites pretreated by different conditions.

Table 1. Content of Na and the molar ratio of Si/Al in modified zeolites Y

Zeolite	Na ₂ O (wt.%)	Si/Al
Y-A	2.69	2.29
NH ₄ SY-4A	> 0.05	4.25
NH ₄ SY-2A	> 0.05	4.76
Y-B	1.27	2.26
NH ₄ SY-4B	> 0.05	4.94
NH ₄ SY-2B	> 0.05	6.65
Y-C	0.76	2.25
NH ₄ SY-4C	> 0.05	5.28
NH ₄ SY-2C	> 0.05	8.17

In Table 2 it is possible to see the physical-chemical properties of modified zeolites, specifically textural properties. Hydrothermal treatment as a last step of modifying zeolites at both temperatures caused a decrease in the specific surface area and volume of micropores in comparison with zeolites without hydrothermal stabilization.

Table 2. Characteristics of physical-chemical properties of modified zeolites Y

Zeolite	S _{BET} (m ² /g)	S _t (m ² /g)	V _{micro} (cm ³ /g)	V _P (cm ³ /g)
Y-A	648	42	0.32	0.37
NH ₄ SY-4A	617	53	0.29	0.35
NH ₄ SY-2A	612	65	0.29	0.38
Y-B	690	30	0.35	0.38
NH ₄ SY-4B	642	67	0.30	0.39
NH ₄ SY-2B	611	77	0.28	0.41
Y-C	681	27	0.34	0.37
NH ₄ SY-4C	630	71	0.30	0.39
NH ₄ SY-2C	600	91	0.27	0.41

In the case of mesoporous volume and mesoporous surface, the opposite trend was observed, when hydrothermal treatment at both temperatures slightly increased these values. These results indicate, that after the dealumination, the secondary mesoporous structure was formed for all modified zeolites.

The acidic properties of modified samples from FTIR adsorbed pyridine and TPDA measurement are possible to see in Table 3. The impact of sodium content on the total acidity of modified zeolites was observed. The total acidity of zeolites hydrothermally treated at both temperatures shows lower total acidity with a lower molar ratio of Si/Al. The highest content of Lewis active sites was reached in NH₄SY-4A. The high presence of LAS is undesirable in context with the alkylation process, due to the formation of coke and that leads to catalyst deactivation. On top of that, the presence of LAS leads to the formation of undesirable by-products during the reaction, [22]. The higher molar ratio of Si/Al caused a decrease in the ratio of BAS/LAS. A higher BAS/LAS ratio positively influences the alkylation process.

The content of LAS and BAS and its molar ratio were determined by FTIR of desorbed pyridine. In Figure 2, the FTIR spectra of desorbed pyridine on modified catalysts by hydrothermal treatment at 560 °C in a deep bed are possible to see. The absorption band at 1540 cm⁻¹ belongs to Brønsted acid sites and the absorption band at 1450 cm⁻¹ represents the

Lewis basic sites. The absorption band at 1490 cm⁻¹ belongs to both acid types of acid sites, but this band is commonly not evaluated, [22].

Table 3. Acidic properties of modified zeolites Y from TPDA and FTIR

Zeolite	BAS (mmol/g)	LAS (mmol/g)	Ratio BAS/LAS	Acidity (mmol/g)
NH ₄ SY-4A	0.86	0.59	1.46	1.45
NH ₄ SY-2A	0.79	0.25	3.22	1.04
NH ₄ SY-4B	0.95	0.33	2.84	1.28
NH ₄ SY-2B	0.77	0.18	4.24	0.95
NH ₄ SY-4C	0.89	0.27	3.36	1.16
NH ₄ SY-2C	0.72	0.15	4.72	0.87

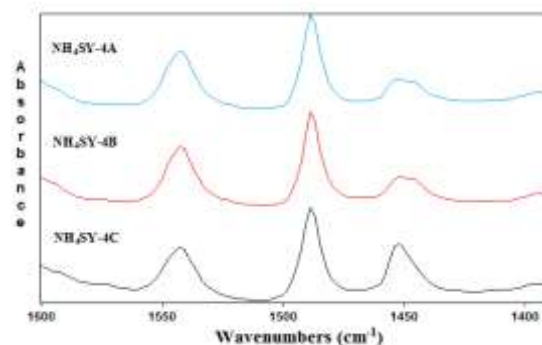


Fig. 2: FTIR spectra of desorbed pyridine on hydrothermally treated zeolite Y at 560 °C

3.2 Alkylation of Toluene over Modified Zeolites

Prepared modified zeolites before hydrothermal treatment (Y-A, Y-B, Y-C) and after hydrothermal treatment at 560 °C (NH₄SY-4A, NH₄SY-4B, and NH₄SY-4C) and 780 °C (NH₄SY-2A, NH₄SY-2B, and NH₄SY-2C) were used in alkylation process. Firstly, decationated zeolites without hydrothermal treatment were tested in the alkylation of toluene. The dependence of 1-decene conversion on TOS is shown in Figure 3.

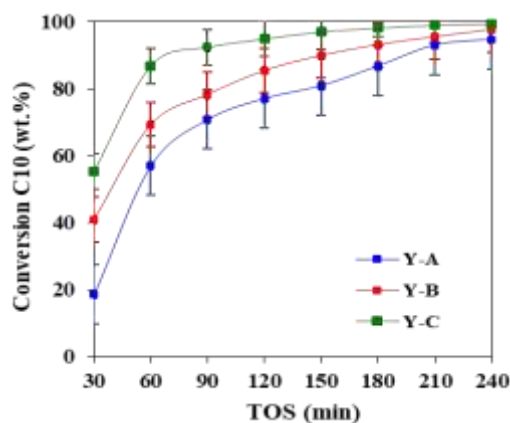


Fig. 3: Dependence of 1-decene conversion on TOS over modified zeolites Y

From the figure, it is possible to see, that different sodium content significantly influenced the course of the conversion of 1-decene. Even the first taken sample at 30 minutes of reaction, showed conversion over Y-C almost three times higher than Y-A. The course of the whole reaction copies this trend until almost the end of the reaction. These results indicate, that lower sodium content improves the catalytic activity in alkylation towards desired products. After the end of the reaction at 240th minutes of reaction, Y-C reached the highest conversion (Table 4) among all tested zeolites. From the view of selectivity to 2-decyltoluene (S_{2-DT}), the amount of sodium in tested zeolites did not show any differences.

Table 4. Results of alkylation with 1-decene at 240th minute of reaction

Zeolite	X _{C10} (wt.%)	S _{2-DT} (wt.%)	LAT (wt.%)	BAT (wt.%)	DIM (wt.%)	DAT (wt.%)
Y-A	94.7	29.6	91.3	8.3	0.2	0.2
Y-B	97.7	29.6	90.3	9.1	0.3	0.3
Y-C	99.4	29.6	89.7	8.1	0.8	1.4

The composition of products is formed by LAT (Linear alkyltoluenes), BAT (Branched alkyltoluenes), DIM (dimers of 1-decene), DAT (dialkyltoluenes). 2-decyltoluene as a part of LAT is in technology the most desired product (biodegradable) for detergent production. The composition of produced alkylaromates showed small differences, where in the case of using Y-C with the lowest sodium content, more undesirable products were made during the reaction.

Based on the reaction course of conversion during reaction time, the 60th minute was chosen to demonstrate other dependencies. This time was chosen based on the fact, that after this time the reaction course was stabilized and there were not that significant differences. Figure 4 demonstrates the dependence of 1-C₁₀ conversion on sodium content in prepared zeolites before hydrothermal treatment. The conversion of 1-decene is significantly influenced by sodium content. With higher sodium content, the conversion of 1-C₁₀ at the beginning of the reaction is lower. This observation could be explained by the blocking of active sites by sodium.

The impact of sodium content in the first steps of modification of parent zeolite was observed. To see, if the next step of modifications, hydrothermal treatment, can further influence catalyst activity and selectivity in alkylation, decationated zeolites

hydrothermally treated at 560°C and 780°C were tested in alkylation. During hydrothermal treatment at both temperatures in a deep bed, residual sodium is removed from the catalyst. Firstly, zeolites treated at 560°C were tested (Figure 5).

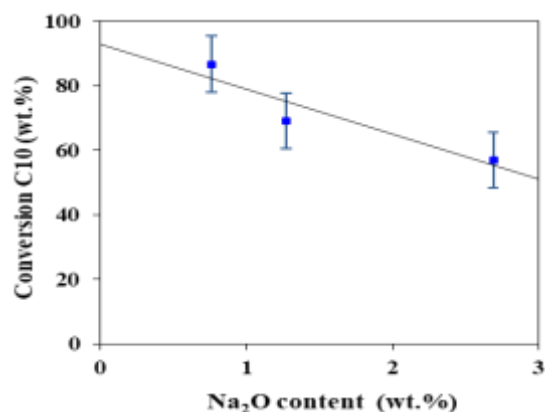


Fig. 4: The dependency of C₁₀ conversion on sodium content in the 60th minute of the reaction

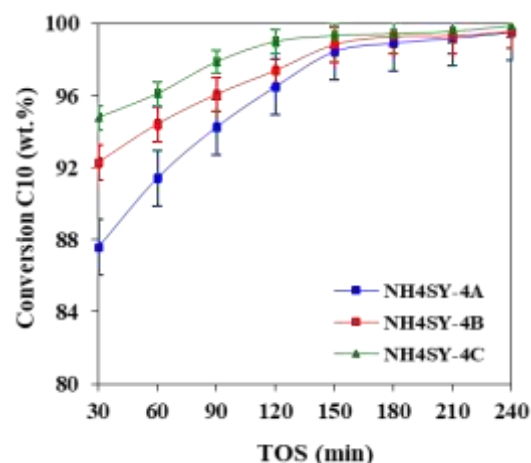


Fig. 5: Dependence of C₁₀ conversion on TOS over zeolites treated at 560 °C

The hydrothermal treatment at a lower temperature 560°C, improved catalyst activity in reaction. Even at first sight is possible to see at the beginning of the reaction (30 min), that is the conversion notably higher than in catalysts without hydrothermal treatment and sodium residue removal. While without hydrothermal treatment, the conversion at 30 minutes was between 20-55 % (Figure 3), after treatment at 560°C all tested zeolites reached conversion above 85 %. In the comparison of treated zeolites with different sodium content, the trend is the same, where the reaction course over zeolite with the lowest sodium content is significantly lower. The composition of products and final conversion of 1-C₁₀ is possible to see in Table 5.

Table 5. Results of alkylation with 1-decene at 240th minute of reaction over zeolites treated at 560 °C

Zeolite	X _{C10} (wt.%)	S _{2-DT} (wt.%)	LAT (wt.%)	BAT (wt.%)	DIM (wt.%)	DAT (wt.%)
NH4S Y-4A	99.5	31.8	86.4	10.6	0.1	2.9
NH4S Y-4B	99.6	31.6	84.5	12.0	0.0	3.5
NH4S Y-4C	99.9	31.5	83.3	12.5	0.0	4.2

From the composition of final products, the content of sodium influenced mostly the formation of LAT and BAT and the higher formation of DAT. This observation could be explained by a lower amount of Lewis acid sites, which could cause the formation of “liquid coke”, [23]. In comparison with zeolites without hydrothermal treatment, the formation of LAT is notably lower over zeolites treated at 560°C. Lower production of LAT and higher BAT production is related to the secondary mesoporous structure formation (S_t in Table 2).

The dependence of selectivity to 2-decyltoluene on 1-C₁₀ conversion over hydrothermally treated zeolites at 560°C is shown in Figure 6. With the increasing conversion of 1-decene, the selectivity to the desired product (2-DT) decreased, with the formation of by-products. But overall selectivity at the end of the reaction is higher in comparison with zeolites without hydrothermal treatment. This is caused by the formation of the secondary mesoporous structure after dealumination.

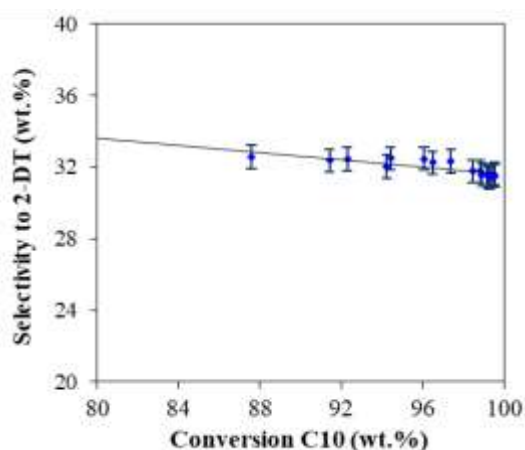


Fig. 6: The dependence of 2-DT selectivity on 1-C₁₀ conversion over zeolite Y treated at 560 °C.

Zeolites Y modified with the last step of hydrothermal treatment at 780°C were also tested in the alkylation process (Figure 7). In comparison

with lower treatment temperatures, there are some differences.

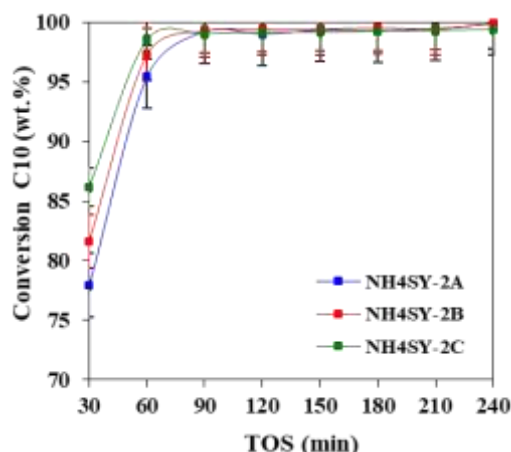


Fig. 7: Dependence of C₁₀ conversion on TOS over zeolites treated at 780 °C

While at the beginning of the reaction (30 min), conversion reached a lower value, at the 60th minute all tested catalysts reached conversion higher than 95%. After 90 minutes, conversion reached 99 % and further did not change. It can be stated, that the higher temperature of hydrothermal treatment improves the diffusion properties of zeolite Y. This allowed reactants to easily enter active sites, where product formation takes place. Product composition and selectivity to desired 2-DT over zeolite treated at 780°C are listed in Table 6.

Table 6. Results of alkylation with 1-decene at 240th minute of reaction over zeolite treated at 780 °C

Zeolite	X _{C10} (wt.%)	S _{2-DT} (wt.%)	LAT (wt.%)	BAT (wt.%)	DIM (wt.%)	DAT (wt.%)
NH4S Y-2A	99.5	34.7	87.7	9.1	0.0	3.2
NH4S Y-2B	99.6	34.9	87.8	8.9	0.0	3.3
NH4S Y-2C	99.9	34.8	87.9	8.7	0.0	3.4

Selectivity is notably higher in comparison with alkylation over zeolites treated by the last step of modification at 560°C. LAT production is slightly higher at the expense of the reduced formation of BAT. On the other hand, the formation of DIM as an undesirable by-product, was not observed in both modification temperatures. In the case of hydrothermal treatment at 780°C, the impact of sodium content on product composition was not observed. The increase of 1-decene conversion

caused a slight decrease in selectivity to 2-decyltoluene (Figure 8).

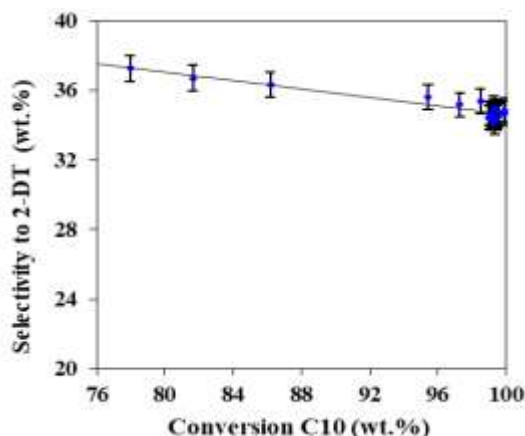


Fig. 8: The dependence of 2-DT selectivity on 1-C10 conversion over Zeolite Y treated at 780 °C

4 Conclusion

The main disadvantage of currently used technologies of alkylation process of aromatics is nonecological catalyst. Zeolites could be one of the possible replacements as an environmentally friendly catalyst. The results confirm the good activity of modified zeolites in toluene alkylation with 1-decene as a model reaction of aromatics alkylation. Steps of modification of parent zeolite Y showed a significant impact on catalyst activity in reaction. Zeolites Y after decationization without hydrothermal treatment confirmed their activity in the alkylation reaction. But in comparison with hydrothermally treated zeolites Y, the conversion of 1-decene and selectivity to 2-decyltoluene were notably lower. Another thing is the stability and regenerability of the prepared catalyst, where zeolites after hydrothermal treatment are more stable and could be regenerated and reused.

The achieved 1-decene conversion was the same as for commercial catalysts and the selectivity to 2-decyltoluene was higher by about 13%, while the amount of linear alkyltoluenes was retained. The amount of sodium left after decationization showed a notable effect on physical-chemical properties. Decationization followed by hydrothermal treatment at both temperatures (560 °C and 780°C) caused the formation of a secondary mesoporous structure, which enhanced the diffusion properties of zeolite Y in the alkylation process. Improvement of diffusion properties and accessibility of active sites in catalysts led to higher conversion of 1-decene and the selectivity to 2-decyl toluene. Prepared catalysts could be used as a potential replacement for

commercial alkylation catalysts such as HF or $AlCl_3$ in industry.

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Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this work the authors used chat GPT in order to grammar check. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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