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Review

Zeolite-Containing Catalysts in Alkylation Processes

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Abstract

This article provides an overview of zeolite-containing catalysts used in the alkylation of benzene and toluene with olefins, isobutane with butenes and butane-butene fractions, gasoline and oil fractions with olefins, propane-propylene, and butane-butylene fractions of catalytic cracking. Zeolites have various types of structures, including BEA, MFI, MWW, FAU, etc., which differ in pore size and the number and location of the channels. High-silica zeolites have a large pore volume, high acidity, good hydrothermal stability, and molecular sieve properties that provide high selectivity in alkylation processes.

Keywords

Zeolite-containing catalysts; structures; types of zeolites; alkylation; gasoline and oil fractions; olefinic and paraffinic hydrocarbons

Recent advancements in the petrochemical industry include an increase in the depth of processing of raw materials, the use of new processes and technologies, and an increase in the selectivity of processes. Catalysts (especially zeolite-containing catalysts) strongly affect the processes associated with petrochemistry and oil refining.

Zeolite-containing catalysts are selective and have internal cavities with a developed surface and inlet windows of a specific size. They can adsorb molecules in both the gas and liquid phases and pass them based on the size of the inlet windows. Zeolites are aqueous aluminosilicates that also contain alkali and alkaline earth metals, which can be replaced by other metals, including noble metals.

Monovalent, divalent, and trivalent cations added to zeolites through ion exchange form the centers of donor-acceptor or redox interactions [1]. Proton-donor centers occur on the elements of the zeolite framework independent of cations. Bifunctional catalysts have acidic and hydrogenating functions (excluding the molecular sieve effect). The hydrogenating function [1] depends on the metal component of the catalyst, while the acidic function depends on the zeolite component. Based on the degree of substitution, zeolites are characterized by a certain silicate modulus (Si/Al ratio) and the content of various metals. Depending on the exchange of K^+, Na^+, and Ca^{2+} ions for ions of other metals, the pore size of zeolites can be altered.

In the industry, zeolite-containing catalysts are used for isomerization, alkylation, catalytic cracking, hydrocracking, hydrotreatment, and aromatization [2]. Additionally, they are used in the alkylation of paraffinic and aromatic hydrocarbons with olefins. These catalysts have sufficient activity to synthesize high-quality alkylates, and they have high selectivity and regeneration ability. Depending on the process being performed and the composition of the hydrocarbon feedstock, monofunctional or bifunctional catalysts with different levels of acidity are selected.

More than 2.5 million zeolite structures are theoretically possible [3]. The zeolite-containing catalysts that are widely used have 60% to 80% zeolite [4-7]. Zeolites of the ZSM-5, ZSM-11, MCM-22, and MCM-49 types with MFI and MWW frameworks are used as the active components [4]. The matrix might consist of Al_2O_3, SiO_2, amorphous aluminosilicate, or a mixture of these substances. Granules of a particular size are formed in various ways after mixing the components. These granules are then thermally treated, dried, and calcined.

Zeolites have various types of structures, including BEA, MFI, MWW, FAU, etc., which differ in pore size and the number and arrangement of channels [8-10]. Beta (BEA) and MFI (ZSM-5) zeolites have wide pores and high silica content. BEA has a three-dimensional system of intersecting channels with twelve-membered rings, while the MFI structure is formed from linear chains connected by four-, five-, and six-membered rings [10]. These zeolites are used for alkylation [8], isomerization, oligomerization [10], etc.

The MWW type zeolite (MCM-22), discovered in 1990 by Mobil, is a synthetic zeolite with high silica content, high pore volume, high acidity, good hydrothermal stability, and molecular sieve properties for high selectivity. Due to these properties, MCM-22 is widely used in alkylation, isomerization, hydroisomerization, and cracking [9]. The zeolite is formed by two types of pores; one type consists of zigzag channels, the size of which is limited by ten-membered silicon-oxygen rings and is 0.55 nm. The other type consists of 0.7 × 1.8 nm cavities, the entrance to which is limited by ten-membered rings.

Zeolites A, X, Y, high-silicon MFI (ZSM-5), and MOR (mordenite) are used most frequently [11, 12]. Zeolites Y, ZSM-5, and mordenite have universal properties and are used in many processes [11, 12]. Zeolites with low silicon content have low acidity and high cation exchange capacity; hence, they are used in adsorption and ion exchange processes. Conversely, high-silica zeolites have high acidity and low cation-exchange capacity and are used as adsorbents for non-polar compounds.

1. Alkylation of Aromatic Compounds with Olefins

The MWW (MCM-22) zeolite is used in the alkylation of benzene with olefins [13, 14]. The alkylation of aromatic hydrocarbons occurs on the outer surface, on acid sites located in the half-cavities. The activity of the MWW zeolite was studied in the alkylation of benzene with ethylene and propylene, toluene with methanol, and phenol with tert-butanol [9, 13]. In the alkylation of benzene and toluene with unsaturated compounds, microporous zeolites (structural type FAU, BEA, MOR, and MFI) and micro-meso-macroporous zeolites H-Ymmm (FAU) and H-ZSM-5 (MFI) were also used [9, 13].

For alkylating benzene with the ethylene and ethane-ethylene fraction of pyrolysis [4], a Y zeolite that does not contain binders in the acidic H^+-form was used as a catalyst. The HY-BS catalyst was prepared based on the NaY-BS zeolite with a SiO_2/Al_2O_3 molar ratio of 5.5. The researchers preferred using the ethane-ethylene fraction of pyrolysis to polymerization-grade ethylene. Ethane occupied the strong acid sites of the zeolite and prevented the incorporation of ethylene molecules, which prevented side reactions. When both hydrogenated and non-hydrogenated ethane-ethylene pyrolysis fractions were used as an alkylating agent instead of polymerization-grade ethylene in the reaction of liquid-phase benzene alkylation on a catalyst modified with 0.3 N hydrochloric acid, the concentration of ethylbenzene in the alkylate and the selectivity of ethylbenzene formation were higher. This was probably because ethane, which occupied the strong acid sites of the zeolite, prevented the localization of ethylene on them and thus, prevented side reactions associated with the formation of harmful impurities.

During the alkylation of benzene with propylene [8] to synthesize cumene, zeolites such as BEA, MFI, and MWW exhibit catalytic activity. The BEA zeolite is the most active; however, its catalytic activity is stable only when propylene is highly diluted with benzene (at a benzene/propylene molar ratio of 6–8). The MWW zeolite is slightly less active; however, it retains its catalytic properties at a benzene/propylene molar ratio of 3–4. This significantly reduces energy consumption associated with benzene recycling and isolation of the target product.

Most zeolite-containing catalysts are quickly deactivated [8], which is associated with the formation of high-molecular hydrocarbons that block the porous structure and active centers on the surface.

The gas-phase and liquid-phase alkylation of benzene with ethylene using zeolite-containing catalysts was introduced into the industry by Mobil-Badger (ZSM-5), UOP and Lummus (wide-pore Y-type zeolite), Chevron, Polimeri Europe, and Mobil (BEA and MWW zeolites) [11]. Most zeolite-containing catalysts are quickly deactivated due to the formation of high-molecular hydrocarbons that block the porous structure and active centers on the surface. Therefore, the alkylation of benzene with ethylene is performed better by large-pore zeolites of the type Y, BEA, or mordenite, especially zeolite BEA, which occurs in the H+ form [12, 15]. The H-BEA catalyst could efficiently alkylate benzene with ethylene and showed a selectivity of 80% for ethylbenzene [15].

The catalytic activity of zeolite BEA for the alkylation of benzene with propylene is determined not by the concentration but by the nature of the distribution of acid sites over the volume of the zeolite crystal [16]. High localization of Bronsted centers in the zeolite crystal is preferable.

Zeolites such as Y, mordenite, and activated bentonite are also effective in the alkylation of benzene with higher α-olefins to obtain hydrocarbon raw materials for synthetic detergents [17].

A study [18] investigated the properties of Fe and Al-containing BEA zeolites during the alkylation of benzene with propylene. The presence of acid sites formed by the framework atoms of Fe and Al determines the high activity and stability of the modified zeolites.

The catalytic properties of microporous zeolites with different structures (FAU, BEA, MOR, and MFI), micro-meso-macroporous zeolite (H-Ymmm), and mesoporous aluminosilicate H-ZSM-5 were studied for the synthesis of quinolines, pyridines, and chloroalkylarenes [19-21]. The reaction was found to occur with a high conversion of aniline (90–99% on zeolites and 71% on ASM aluminosilicate). Very selective target products were formed with a high yield on the H-BEA and H-Ymmm catalysts. Based on the temperature-programmed desorption of ammonia, the total concentration of acid sites in the series of microporous zeolites decreases as follows: H-Y > H-MOR > H-BEA > H-MFA [20, 21].

The developed system of micropores in most zeolites imposes significant diffusion restrictions on the rate of reactions catalyzed by zeolites involving organic reagents with a high molecular weight. For using the active surface of the zeolite catalyst more efficiently, an additional system of larger pores of a specific size is created in it, known as the hierarchical system of micro-meso-macropores. Studies in the last 10–15 years have shown that hierarchical zeolites are considerably more active than traditional microporous catalysts in petrochemical reactions of alkylation, isomerization, and esterification, as well as, in the oxidation of organic substances [22].

2. Alkylation of Isobutane with Olefins and Olefin Fractions

At oil refineries, alkylation has the highest economic efficiency, since it allows the use of gaseous products during oil refining to synthesize strategically important petrochemical products and improve the quality of gasoline. The alkylate obtained during the alkylation of isobutane with olefins consists mainly of isoparaffin hydrocarbons. This alkylate is a component of eco-friendly motor fuels and increases their octane numbers.

Ethylene, propylene, butenes, propane-propylene, and butane-butylene catalytic cracking fractions are mainly used as the alkylating agent [23-32]. Among the individual aromatic hydrocarbons, benzene, toluene, p-xylene, pseudocumene, and mixtures of hydrocarbon-petroleum products, such as low-octane catalytic cracking gasoline, are considered for alkylation. Among the paraffinic hydrocarbons, the alkylation of isobutene is mostly focused on.

The alkylation of isobutane with butenes under traditional and supercritical conditions was conducted on Y zeolites in the H-form to obtain components of eco-friendly gasoline [23]. Performing alkylation under supercritical conditions [23] increases the duration of the operation of the catalyst due to the dissolution of the compaction products in supercritical fluids and their removal from the catalyst surface. Under supercritical conditions, 100% of butene is also converted. The composition of the products is determined [23] by the phase state of the reaction mixture, the reaction time, and the level of conversion of C_4 olefins. The selectivity of the formation of C_8 hydrocarbons during alkylation under supercritical conditions is 30–40%. Along with alkylation, parallel processes of oligomerization and cracking occur, which leads to the formation of hydrocarbons C_5–C_7 and C_9^+. When the reaction time is increased from 180 to 240 min, the oligomerization reaction predominates and C_8 products (selectivity of 85%) are formed, of which 90% are olefins.

Zeolite catalysts in the CaLnHX form were studied for the alkylation of isobutane with butylenes [24]. The optimal concentrations of metal oxides (Na-0.5, Ca-0.6, Ln-18.3% mass) at which the maximum conversion of butylenes is achieved is 97–100%.

During the alkylation of isobutane with olefins, olefin polymerization reactions are possible, resulting in the formation of heavier products and coke. The side reactions occur more often at higher temperatures; therefore, the reaction needs to be conducted at lower temperatures, while ensuring sufficient speed of the process [25]. High levels of circulating isobutane in the system prevent olefin polymerization and dealkylation.

Alkylation on a zeolite-containing catalyst proceeds by a carbocation mechanism and includes the following stages:

- Initiation – the formation of carbenium ions;
- Alkylation – the interaction of the carbenium ions with olefin;
- Isomerization of the carbenium ions;
- Chain breakage – the transfer of hydride anion from isoparaffin to the carbenium ion;
- Polymerization – the interaction of the carbenium ions with olefins to form heavy products and coke;
- Dealkylation and cracking.

High temperatures facilitate the dealkylation and cracking reaction at high speeds. Through these reactions, a wide alkylate fraction is formed. To obtain an alkylate with a high octane number and yield, it is necessary to:

- Increase the rate of hydride transfer processes;
- Reduce the rate of polymerization of olefins, dealkylation, and cracking of products;
- Reduce the course of coking processes.

For this, during alkylation, the contact time between the olefin and the catalyst is shortened, a low temperature is maintained, and an excess of isoalkanes is used.

The process is based on alkylation with subsequent regeneration of the catalyst [26-29] and conducted in two reactors with a fixed catalyst bed.

The AlkyClean alkylation process of the ABB Lummus Global, Albemarle Catalysts, and Neste Oil companies is performed in the liquid phase at 50–90°C on the Albemarle zeolite catalyst [30-33]. The reactor block of the plant consists of three reactors, two of which are used for alkylation and soft regeneration, and the third one is used for hard regeneration. The samples modified with metals, such as Ni, Pt, and Pd, are used as alkylation catalysts.

When alkylating isobutane with butenes or butane-butene fraction on modified zeolite Y (Na_2O – 0.1; CaO – 0.98; Re_2O_3 -11.8; Al_2O_3+SiO_2 – up to 100% by weight with a SiO_2/Al_2O_3 – 22 ratio), the maximum amounts of trimethylpentane isomers were obtained [30].

In a study [31], the reactivity of C_3–C_5 olefins was investigated in the reaction of isobutane alkylation on zeolites of type Y modified with rare earth elements (0.36–13.5 wt%) with a molar ratio of $SiO_2/Al_2O_3 = 4.6$. The activity of such catalysts is imparted by acid sites formed when Na^+ cations are exchanged for H^+ and In^{+3} cations (for example). The experiments were conducted in an autoclave at 25–100°C under a pressure equal to the vapor pressure at the reaction temperature.

Based on the reactivity, olefins can be arranged in the following order: isobutene > butene > propylene > ethylene [31]. The secondary alkylation of various olefins increases in the sequence: propylene > isobutene > pentene-1. The greater the content of secondary products, the higher the rate of formation of cyclic hydrocarbons, and the faster the deactivation of the catalyst. The best activity of the catalyst is achieved at 60°C and an isobutane/butenes ratio of 7. The optimal conditions for alkylation include a temperature of 70°C, a molar ratio of the reagents of 5:1, and an operating time of the zeolite of 2 h.

Catalysts modified with Ca^{2+}, Ln^{3+}, Ce, and other cations are used for the alkylation of isobutane with butane-butene fraction [32, 33]. With an increase in the acidity of the catalyst, the main alkylation reaction dominates, and the proportion of side processes decreases. Adding lanthanum to NaX zeolite increases the alkylation of isobutane with butene to a greater extent than the addition of calcium.

The highest yield (70%) of the alkylate was obtained on Na-Ca-Ln-Y zeolite while remaining active for 70 h. The selectivity during alkylation depends on lanthanum under optimal conditions: temperature 90–110°C, hydrocarbon feed space velocity 1.0–1.2 h^{-1}, and an isobutane-to-butenes ratio of 100:1.

During the alkylation of isobutane with olefins, the effects of the number of aluminum atoms in the zeolite lattice, the SiO_2/Al_2O_3 ratio, and the unit cell size on the activity indices of zeolite catalysts were studied. The yield of hydrocarbons was found to depend on the number of aluminum atoms in the crystal lattice of the catalyst [34, 35]. In such cases, an increase in the number of silicon atoms associated with the number of aluminum atoms can increase the yield of C_8 target products.

Some studies [35, 36] found that with an increase in the acidity of the catalyst (FAU), the main alkylation reaction predominates, and the proportion of side processes decreases. Modification of the NaY zeolite (decationation and dealumination) leads to an increase in the yield of target products, i.e., C_8 isomers, and the suppression of oligomerization and reactions associated with coke formation.

A study [37] investigated the initial mechanism of C4 alkylation on H-[Al]-BEA and H-[B]-BEA catalysts with high and low acidity, respectively (Figure 1). The formation of tertiary butyl carbocation on H-BEA zeolite in the initial step of the C_4 alkylation reaction was studied by applying the calculations of density functional theory (DFT). The results showed that the hydrogen transfer route is the dominant pathway for the formation of tert-butylcarbocation with changes in the strength of the acid, which correlates well with the results of the experiment. In this process, the rate-determining steps of skeletal isomerization (Figure 2) and hydride transfer (Figure 3) are altered, and higher Gibbs free energy barriers are achieved by reducing the strength of the acid.

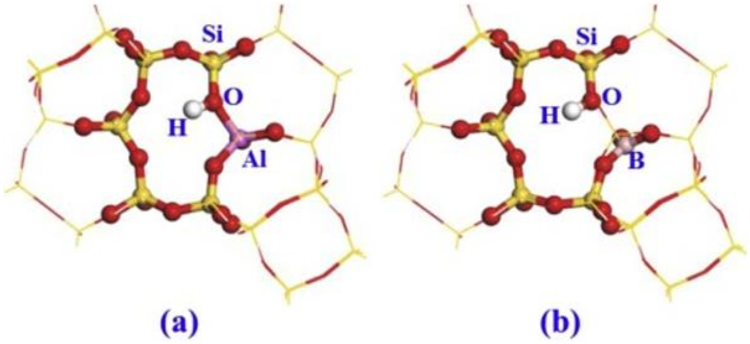

Figure 1 Optimized acid site geometries: (a) H-[Al]-BEA and (b) H-[B]-BEA [37].

Figure 2 Optimized species structures involved in the skeletal pathway [37].

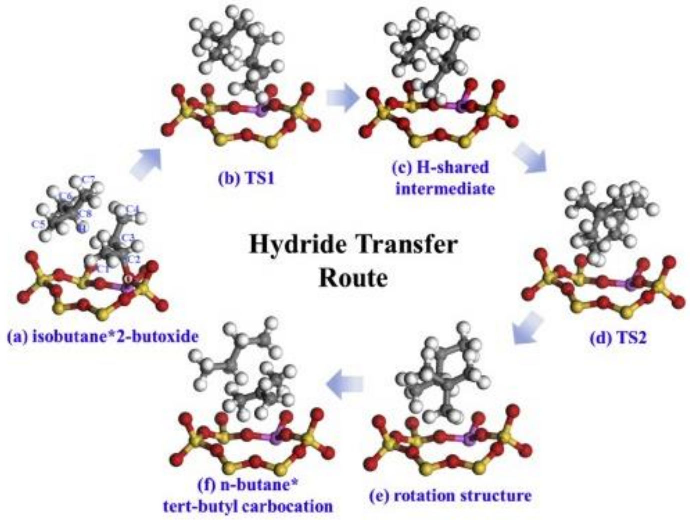

Figure 3 Optimized particle structures involved in the hydride transport pathway [37].

The efficiency of isobutane alkylation with olefins on zeolite-containing catalysts depends on the reactions of hydride ion transfer and oligomerization [38]. A high yield of alkylate and a longer activity of the zeolite might be achieved by increasing the transfer rate of the hydride ion and the ratio of isobutane to olefin.

The characteristics of the BEA-E zeolite catalyst were studied by the TGA-DTG, HRTEM, SEM, and XRD methods [39]. The main active sites for the C_4 alkylation reaction are located on the internal surface rather than on the external surface. The outer surface is more selective for the adsorption of C_4 olefins than isobutane, which increases the oligomerization reactions. The hydride transfer reaction does not occur on the outer surface.

The catalytic stability of zeolites is related to their adsorption selectivity [40]. The researchers showed that the adsorption affinity of zeolites for C_4 decreases as the Si/Al ratio increases. The adsorption affinity decreases with an increase in the Si/Al ratio in FAU-type zeolites, while for 1-butene the decrease is more prominent. The adsorption capacity of zeolites for isobutane and 1-butene depends on the interaction between the adsorbents and adsorbates at low pressures and the effective void volume of the adsorbents at high pressures, and MTW zeolites with large PLD/LCD ratios show high catalytic stability [40].

In a study [40], zeolites with different topologies and Si/Al ratios were investigated for isobutane alkylation. The adsorption affinity of zeolites for C4 was found to decrease with an increase in the Si/Al ratio. The catalytic stability of zeolites is related to their adsorption selectivity. BEA and MTW zeolites with large PLD/LCD ratios have high catalytic stability. The capacity of zeolites to adsorb isobutane and 1-butene depends on the interaction between the adsorbents and adsorbates at low pressures and the effective void volume of adsorbents at high pressures.

The high catalytic activity of the NaX zeolite in the alkylation of isobutane with butylenes was achieved by exchanging sodium cations for calcium cations and then for lanthanum cations under ultrasonic treatment [41].

Gasoline fractions with a high octane number were obtained from catalytic cracking gases on an industrial zeolite-containing Omnikat-210 P catalyst modified with Ni, Co, and Mo [42, 43]. Moreover, the effect of contact time, temperature, and volumetric feed rate on the yield of liquid reaction products was studied.

A study [44-46] investigated an effective catalytic system of 0.5%Co/HZSM-5/SO_4^{2-}(2%)-ZrO_2 for the joint processing of straight-run gasoline and propane-butane fraction. The system could convert 63% and 55% of C_4-and C_8+ components of the mixture, respectively, and yield 21 and 23 mass% of C_5-C_6 and C_7 paraffins, respectively. The primary activation of C_7+ alkanes and the formation of bimolecular intermediates occur with the participation of the active (oxidative) centers of the SO_4^2–ZrO_2 component, and the hydro-cleavage of the final products by the active (acidic) centers of N-zeolite (mass%). Based on the results, an assumption is made about the isomerization-disproportional transformation of C_{7+} components of straight-run gasoline with the participation of the M/H–zeolite/$SO_4^{2-}ZrO_2$ catalytic systems to form a bimolecular intermediate, its isomerization, and hydro-cleavage (mainly by β-bond).

Zeolite-containing catalysts are also widely used in the oligomerization of lower and higher α-olefins and olefin fractions [47-50]. Gasoline, diesel fractions, and aromatic hydrocarbons are formed in the process.

3. Alkylation of Oil Fractions with Olefins

Recently, studies have investigated ways to improve the viscosity-temperature properties of oils in the alkylation of oil fractions with olefinic hydrocarbons on zeolite-containing catalysts. The saturation of oil fractions with isoparaffinic hydrocarbons improves their rheological properties, reduces volatility, and increases thermal-oxidative stability and several performance indicators. Alkylation increases isoparaffin hydrocarbons by converting normal paraffins into isoparaffins and also increases the amount of alkylaromatic hydrocarbons with long alkyl chains by converting of monoaromatic or alkylaromatic hydrocarbons with short chains.

Alkylation of the turbine oil fraction with decene-1 and hexene-1 on the catalysts Zeokar-2 and Zeokar-600 increased the viscosity index by 8–12 units. The oil fraction was isolated from the resulting alkylate [51]. Additionally, the pour point of this fraction remained unaltered, i.e. (-40°C), at the level of the original turbine oil. The alkylation of turbine oil distillate with liquefied catalytic cracking gases was conducted on the catalysts Zeokar-600 and Omnikat-210P [52, 53]. Conducting the process on the catalyst Zeokar-600 at 50°C, 0.6 MPa, and an oil-to-gas ratio of 1:1 increases the viscosity index of the turbine oil distillate from 32 to 80–81. Alkylation on the Omnikat-210P catalyst increases the viscosity index to a lesser extent (from 32 to 66). A study [53-56] found that the kinematic viscosities and viscosity indices of distillate oil fractions increase during alkylation. This is due to an increase in the length and number of alkyl substituents of aromatic hydrocarbons through the addition of propylene and butylene units of olefinic hydrocarbons from catalytic cracking gases.

Performing alkylation of industrial oil distillate (I-8A) with catalytic cracking gases (propane-propylene and butane-butylene fractions) on a Zeokar-600 catalyst increases the viscosity index of the distillate from 79 to 146 [57].

Alkylation is accompanied by side reactions, including cracking, oligomerization, aromatization, disproportionation, isomerization, dehydrocyclization, etc., which lead to the formation of hydrocarbons with different types of structures [58]. Combining certain hydrocarbons changes the properties of the oil, including viscosity, the viscosity index, and the pour point. Therefore, it is important to select a catalyst and reaction conditions that can drive the reaction in the required direction with the formation of hydrocarbons and produce oils with the desired properties. Since olefinic, paraffinic, naphthenic, and aromatic hydrocarbons are present in petroleum oils, and because all of them can be converted, studying the conversion of all hydrocarbon groups during alkylation on zeolite-containing catalysts is important.

The alkylation of oil fractions proceeds almost simultaneously with the oligomerization of olefin hydrocarbons and the addition of olefin fragments to the aromatic hydrocarbons of the oil [55, 56]. Both these reactions have a positive effect on the properties of the oil. These reactions are facilitated by zeolites, which have many Brensted acid sites. Alkylation temperature also affects catalyst activity, process selectivity, and viscosity-temperature properties of oils.

Depending on the zeolite catalyst used, alkylation, polymerization, isomerization, and cracking reactions can occur to a greater or lesser extent [55, 56, 58]. The Brönsted (protic) acid sites in zeolites are active in the oligomerization reaction, while aprotic sites promote side reactions of aromatization and coke deposition. The oligomerizing activity of the hydrogen forms of zeolites increases with an increase in the aluminum content or the concentration of proton centers. The ratio of silicon to aluminum in the zeolite lattice, the degree of decationation or the properties of the introduced cations, and the molecular sieve effect inherent in zeolites are important for the development of zeolite catalysts.

4.Conclusions

Previous studies have found that zeolites of the pentasil type (with a narrow pore size) promote the formation of less branched hydrocarbons and in smaller amounts than highly porous zeolites. Additionally, zeolites are quickly deactivated, and above 200°C, they promote the formation of aromatic, polycyclic hydrocarbons and resins. However, the formation of resins is undesirable because they deactivate the catalyst.

Alkylation of individual hydrocarbons occurs to a greater extent than alkylation of a mixture of hydrocarbons, such as gasoline and oil fractions.

The alkylation of hydrocarbon mixtures, such as gasoline and oil fractions, is considerably more complicated than that of individual hydrocarbons, especially when olefin fractions are the alkylating agent. This process is understudied, and further investigation and selection of active zeolite-containing catalysts are required.

Author Contributions

Galina Huseynova general project management, data verification, summarizing results, responses to reviewers' comments, correspondence with the editorial board. Gulbeniz Muxtarova literary assistance. Nushaba Aliyeva literary assistance. Gular Gasimova literary assistance, English translator. Sanubar Rashidova literary assistance.

Competing Interests

The authors have declared that no competing interests exist.

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