Catalysis Letters (2020) 150:738–752
https://doi.org/10.1007/s10562-019-02954-w

Ethylene Conversion into Propylene and Aromatics on HZSM-5: Insights on Reaction Routes and Water Influence

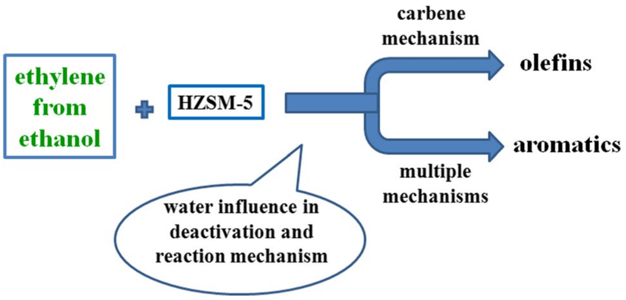
Débora S. Fernandes[1] · Cláudia O. Veloso[1] · Cristiane A. Henriques[1]

Received: 4 April 2019 / Accepted: 5 September 2019 / Published online: 25 September 2019

Abstract

Ethanol is an alternative for producing petrochemicals, especially propylene and aromatics (benzene, toluene, and xylenes). To understand ethanol processing routes into olefins and aromatics, it is interesting to use ethylene that is the major primary product of ethanol reaction into hydrocarbons and the intermediate for the formation of olefins and aromatics. In this work, the influence of the operating conditions (ethylene partial pressure, reaction temperature and contact time) in the ethylene conversion into propylene and aromatics, and in the product yield was investigated using HZSM-5 zeolite as catalyst. Lower contact time and ethylene partial pressure, and higher reaction temperature favored propylene yield. Olefin production was based on the formation of carbene species from ethylene that reacts with ethylene to produce propylene and on ethylene dimerization to form butenes. On the other hand, intermediate reaction temperatures and contact times, and higher ethylene partial pressure promote the formation of aromatics, where the dehydrocyclization reaction is favored over hydrogen transfer. The presence of water vapor in long-term reactions deactivated the catalyst. For propylene production, the decrease of ethylene conversion was due to zeolite framework dealumination, while for aromatic formation the reaction mechanism was changed.

Graphic Abstract



Keywords Ethylene · Propylene · Aromatics · Zeolites · Mechanism · Deactivation

1 Introduction

Raw materials from renewable sources reduce the oil dependence and preserve the environment. Ethanol is a promising alternative for producing petrochemical products, mainly propylene and aromatics such as benzene, toluene, and xylenes, through ethanol catalytic conversion under specific conditions [1–6].

According to the literature, ethylene is the main primary product from ethanol conversion into hydrocarbons at temperatures above 300 °C, and it is the intermediate for the

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-019-02954-w) contains supplementary material, which is available to authorized users.

✉ Cristiane A. Henriques
cah@uerj.br

[1] Instituto de Química, Programa de Pós-graduação em Engenharia Química, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, RJ 20550-900, Brazil

formation of other olefins and aromatics [5–10]. Thus, in order to understand the transformation routes of ethanol into hydrocarbons, an in-depth study of the formation of olefins and aromatics from ethylene is essential. In addition, the ethylene conversion into other petrochemical raw materials is strategic to meet a possible increase in the demand for propylene and aromatics from ethylene that is offered in excess.

Molecular sieves are widely used as catalysts for the transformation of ethylene into propylene and aromatics. The HZSM-5 zeolite shows high activity for this reaction [1, 4, 5, 11–13]. Acidity, chemical composition, and pore size are the main characteristics that provide good performance to HZSM-5 zeolite for the conversion of ethylene into propylene and aromatics. The variation of SiO_2/Al_2O_3 molar ratio and the impregnation of metals are often studied to increase selectivity for a given product. Another alternative to maximize the formation of desired products is the adjustment of reaction conditions such as ethylene partial pressure, reaction time, reaction temperature, and contact time [13–15].

The elucidation of the reaction mechanism is essential for achieving a good product yield. For the conversion of ethanol into hydrocarbons, it is well established that the first step is the ethanol dehydration into ethylene. The literature describes a few reaction mechanisms for the production of hydrocarbons from ethanol or ethylene such as the hydrocarbon pool [4, 12, 13, 16–19], the radical-assisted mechanism [20, 21], the carbene mechanism [15, 22–24] and the carbenium mechanism [25–28]. As can be seen, the mechanism for the conversion of ethanol or ethylene into hydrocarbons is not yet established.

The ethylene to hydrocarbon reaction occurs over acid catalysts mainly zeolites with Brønsted acid sites [11, 13, 29, 30]. These acid sites are associated with the proton exchanged on aluminum sites [31, 32]. The ethylene activation in the presence of a Brønsted acid site still requires deeper knowledge [8]. Different possibilities can be found in the literature for example the formation of carbenium [25–28] and carbene [15, 22–24] species.

Deactivation is a process that reduces the catalytic performance of several materials and the identification of the factors that promote this process is very important. For the transformation of ethylene or ethanol into hydrocarbons in the presence of zeolites, deactivation can occur by coke deposition that blocks the acid sites [1, 7, 11, 13, 33]. When ethanol is the reagent, the modification of the zeolite framework caused by the presence of water produced during the process can also be added [1, 4, 7]. The contribution of these two types of deactivation processes in the transformation of ethanol into hydrocarbons is not systematically studied.

In this work, HZSM-5 zeolite was used as catalyst for the transformation of ethylene into hydrocarbons, mainly propylene and aromatics (benzene, toluene, and xylenes). The main aims of this study are to define the appropriated experimental conditions to selectively produce propylene and aromatics, to identify the reaction mechanism of these two processes, and to identify the causes of the deactivation of the HZSM-5 zeolite. In order to achieve these objectives, the influence of reaction conditions (ethylene partial pressure, reaction temperature, reaction time, and contact time) on the ethylene conversion and the product yield was evaluated so that the best experimental conditions for the production of propylene and aromatics were determined; the understanding of the reaction mechanism involving the formation of propylene and aromatics from the direct conversion of ethylene was also carried out; and the catalyst deactivation was studied by monitoring the reaction over a long reaction time and adding water to reactor feed.

2 Experimental

2.1 Catalyst

The NH_4ZSM-5 zeolite with nominal SiO_2/Al_2O_3 molar ratio equal to 30 and particle size between 0.5 and 1.5 µm was provided by CENPES/PETROBRAS. HZSM-5 sample was obtained through the thermal treatment of NH_4ZSM-5 under air flow (50 mL min^{-1}) at 500 °C for 4.5 h using a heating rate of 5 °C min^{-1}.

2.2 Chemical, Structural and Textural Characterization

The chemical composition of HZSM-5 zeolite was determined by X-ray fluorescence (XRF) in a Rigaku spectrometer (Supermini model) equipped with a Pd X-ray generator and controlled through ZSX software. Pellets of approximately 0.5 g of the sample and 1.5 g of boric acid were prepared for analysis.

The identification of crystalline phases was performed using X-Ray Powder Diffraction (XRPD) in a Rigaku Miniflex X-ray diffractometer using CuKα radiation, 30 kV, and 15 mA. IZA (International Zeolite Association) database was used to identify phases by comparing experimental diffractogram and IZA data files.

Textural properties were determined by N_2 adsorption/desorption at − 196 °C using Micromeritics ASAP 2020. Before nitrogen adsorption, samples were pretreated under vacuum for 12 h at 300 °C. Specific area was calculated by the Brunauer–Emmett–Teller (BET) method, microporous volume was determined by t-plot method and Harkins and Jura equation, and mesoporous volume was measured by Barrett–Joyner–Hallender (BJH) method.

2.3 Acidity Characterization

The density and strength distribution of acid sites were measured using Temperature-Programmed Desorption (TPD) of NH_3. The sample was treated in situ at 150 °C for 1 h and then at 500 °C for 1 h under a flow of 30 mL min^{-1} of He using a heating rate of 10 °C min^{-1}. After thermal treatment, NH_3 adsorption was carried out under a flow of NH_3/He (2.91%) mixture (30 mL min^{-1}) at 150 °C. The physisorbed molecules were removed under He (30 mL min^{-1}) at the same temperature. Another cycle of NH_3/He adsorption and desorption under He was carried out to quantify physically adsorbed ammonia. The desorption profiles of chemisorbed ammonia were obtained by heating the sample from 150 to 500 °C under He flow (30 mL min^{-1}) using a heating rate of 10 °C min^{-1}. The amount of ammonia chemically adsorbed at 150 °C was calculated from the difference between the total and physically adsorbed amount. So that acid site density can be determined.

The type of the acid sites was determined by adsorption of pyridine using diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). The spectra were acquired using an FTIR Spectrum 100 spectrometer (Perkin Elmer) equipped with a DTGS detector and a high-temperature chamber (Harrick) with CaF_2 windows. The sample was dried at 500 °C before being placed into the sample holder, where it was heated at 150 °C under vacuum for 1 h, and then at 500 °C using a heating rate of 5 °C min^{-1}. Then, the sample was exposed to a flow of pyridine/He (30 mL min^{-1}) for 1 min at 150 °C. This gas mixture was produced by passing He flow into pyridine at 0 °C (pyridine partial pressure = 5.4 g cm^{-2}).

2.4 Catalytic Evaluation

The catalytic tests were conducted at atmospheric pressure in a fixed-bed flow U-shaped Pyrex reactor. Ethylene and N_2 were feed through a mass flow controller. In order to evaluate the influence of operational conditions, reaction temperature (T = 300, 400, 450, and 500 °C), ethylene partial pressure ($p_{ethylene} = 0.12$, 0.20, and 0.35 atm) and contact time ($\tau = 0.15$, 0.20, 0.40, and 0.67 g_{cat} h $g_{ethylene}^{-1}$) were varied. The reactor effluent was analyzed online using a gas chromatograph (Varian 3900) equipped with a capillary column (25 m HP-Plot/Q) and a flame ionization detector. The products were identified as paraffins (C_1–C_4), propylene ($C_3^=$), butenes ($C_4^=$), fraction with five carbon atoms ($C_5 + C_5^=$), aromatics (BTX), and fraction with six or more carbon atoms (C_6^+).

Before the catalytic runs, the catalyst was heated at 150 °C for 1 h. Then, the temperature was raised to 500 °C and kept at this temperature for 1 h. The heating rate was 2 °C min^{-1}. All steps were conducted under N_2 flow (50 mL min^{-1}).

The optimum experimental conditions for propylene and aromatics formation were chosen to test the stability of the catalyst for long-term reactions (20 h) and also to study the influence of the presence of water in the catalyst activity. The N_2 stream passed through a saturator containing liquid water and maintained at a constant temperature by means of a thermostatic bath. The composition of this stream was 18 or 36 vol% of water.

Ethylene conversion and product yield were calculated considering chromatographic response factors, and the ratio between the number of carbon atoms present in a given product and in ethylene. The product yield was calculated taking into account the amount of ethylene consumed to generate a product and the molar amount of ethylene fed to the reactor. The conversion was calculated by the ratio between the total amount of ethylene consumed and the amount of ethylene fed into the reactor. The detailed procedure is presented in Supplementary Material.

3 Results and Discussion

3.1 HZSM-5 Characterization

Zeolite properties such as chemical composition, crystallinity, porosity, and acidity directly affect the catalytic performance of the zeolites. The chemical composition, textural properties, and acid site density and strength of HZSM-5 zeolite are presented in Table 1. The SiO_2/Al_2O_3 molar ratio provided by the supplier was confirmed. The specific area and pore volumes are in the expected range for this material (MFI structure, microporous volume ≈ 0.17 cm^3 g^{-1}), confirming that this material presents good crystallinity [34] that was also confirmed by the X-ray diffractogram of HZSM-5 sample (Fig. S1).

The density (Table 1) and the strength distribution of the acid sites were determined by ammonia desorption. The NH_3-TPD profile (Fig. S2) was decomposed into three peaks to establish acid site strength. The maximum temperature of each peak was 278, 327, and 482 °C indicating the presence of weak, intermediate and strong acid sites, respectively. Table 1 shows the maximum desorption temperatures of the three types of acid sites (weak, intermediate and strong), the total site density and the distribution of the number of weak, intermediate and strong sites. As can be seen, strong acid sites predominate in this HZSM-5 zeolite.

The presence of Brønsted and Lewis acid sites was determined through pyridine adsorption using infrared bands in the range of 1400 to 1700 cm^{-1}. Fig. S3A shows the spectrum of pyridine adsorbed on HZSM-5 zeolite. The bands around 1642, 1634, and 1547 cm^{-1} indicates the presence of Brønsted acid sites, in which pyridine is adsorbed as pyridinium ion. Lewis acid sites, which are coordinated to pyridine,

Table 1 Physicochemical properties of HZSM-5 zeolite

Chemical composition			
SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	SAR[a]
93.8	5.7	–	28
Textural properties			
Specific area[b] ($m^2\ g^{-1}$)	Microporous volume[c] ($cm^3\ g^{-1}$)	Mesoporous volume[d] ($cm^3\ g^{-1}$)	
344	0.154	0.072	
Acid properties			
Site density (μmol NH_3g^{-1})	1628		
Site strength	Weak (278 °C)	Intermediate (327 °C)	Strong (482 °C)
	260 (16%)	570 (35%)	798 (49%)

[a] SiO_2/Al_2O_3 molar ratio

[b] BET method

[c] t-Plot method

[d] BJH method: 17–600 Å

can be identified by the bands at 1625 and 1444 cm^{-1}. Hydrogen-bonded pyridine can also be identified by bands at 1596 and 1444 cm^{-1}. The band at 1489 cm^{-1} is due to the adsorption at both types of sites and hydrogen-bonded pyridine.

The hydroxyl groups present on HZSM-5 zeolite were identified through infrared spectroscopy in the region of 3800–3400 cm^{-1} (Fig. S3B). The vibration band at about 3610 cm^{-1} can be attributed to bridged hydroxyl groups Si(OH)Al associated with Brønsted acid sites. In addition, there is a band around 3740 cm^{-1} that is assigned to silanol (Si–OH) groups. The band around 3650 cm^{-1}, usually associated with the presence of extraframework aluminum species (EFAL), was not observed indicating the absence of these species.

3.2 Catalytic Evaluation

The catalytic behavior of HZSM-5 zeolite in the transformation of ethylene into hydrocarbons was studied. Initially, the influence of the operating conditions (reaction time, contact time, reaction temperature and ethylene partial pressure) in ethylene conversion and product yield was evaluated. So that, the optimal conditions for the production of propylene and aromatics (BTX) were defined. According to the catalytic results, a reaction scheme was proposed. Then the stability of HZSM-5 zeolite in long-term experiments was investigated in the absence and presence of water.

3.2.1 Influence of Reaction Time

The influence of reaction time in ethylene conversion and product yield for the reaction of ethylene into hydrocarbons using HZSM-5 zeolite was evaluated varying ethylene partial pressure, contact time, and reaction temperature.

The typical behavior of ethylene conversion for different reaction time is shown in Fig. 1a for the partial pressure of 0.20 atm, the reaction temperature of 300 °C, and the contact time of 0.20 $g_{cat}\ h\ g^{-1}_{ethylene}$. A steep conversion decrease was observed after 5 min due to the formation of heavy polyolefinic compounds through ethylene oligomerization. As the reaction temperature is not high enough to either vaporize or promote cracking of these compounds, they are retained on catalyst surface blocking acid sites. At higher reaction temperatures (400, 450 and 500 °C), conversion remained constant over reaction time. An example of this behavior is shown for ethylene conversion in an experiment carried out using a partial pressure of 0.12 atm, a reaction

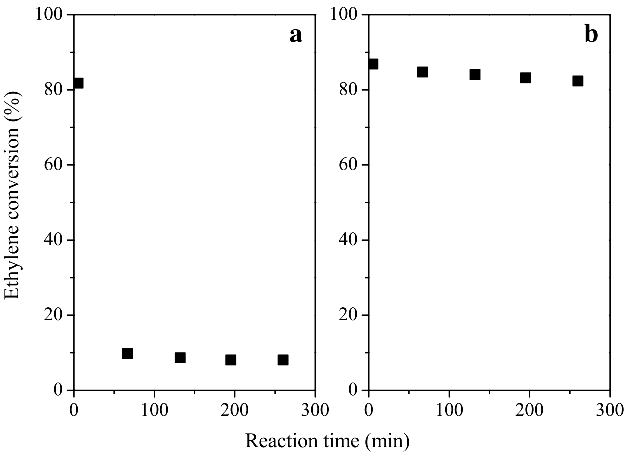


Fig. 1 Ethylene conversion with time on stream. **a** T = 300 °C; $p_{ethylene} = 0.20$ atm; $\tau = 0.20\ g_{cat}\ h\ g^{-1}_{ethylene}$. **b** T = 450 °C; $p_{ethylene} = 0.12$ atm; $\tau = 0.20\ g_{cat}\ h\ g^{-1}_{ethylene}$

temperature of 450 °C and a contact time of 0.20 g_{cat} h $g_{ethylene}^{-1}$ (Fig. 1b). Based on the results obtained at 300 °C, 5 min was chosen as reaction time to study the influence of different reaction conditions in ethylene conversion and product yield, since the effect of deactivation of the zeolites can be ignored until 5 min. This choice is also supported by all experimental conditions studied, because in only a few experimental conditions the reaction time influenced product yields.

3.2.2 Influence of Operating Conditions on Conversion

The operating conditions, that is, ethylene partial pressure, contact time, and reaction temperature influenced ethylene conversion into products.

For partial pressure of 0.12 atm, an increase in contact time from 0.15 to 0.40 g_{cat} h $g_{ethylene}^{-1}$ resulted in an increase of conversion at all temperatures (Fig. 2a). However, when the reaction was conducted with 0.20 and 0.35 atm of ethylene (Figs. S4A and S4B), no clear trend was verified, since conversion values did not vary significantly with the increase in contact time, particularly for higher temperatures (400, 450, and 500 °C). For longer contact times, the residence time of the gas mixture in the catalytic bed is higher favoring a higher ethylene conversion into products. This effect was clear for lower partial pressures (0.12 atm). On the other side, for ethylene partial pressure of 0.35 atm, the high reactant concentration nearby the active sites makes the effect of increasing residence time, for contact time of 0.15 and 0.20 g_{cat} h $g_{ethylene}^{-1}$, imperceptible. Lin et al. [13] reported similar results for the transformation of ethylene into propylene and butenes using HZSM-5 zeolite (SAR = 30) at 300, 350, 400, 450, and 500 °C and contact time varying between 0.54 and 0.81 g_{cat} h $g_{ethylene}^{-1}$.

The correlation between reaction temperature and ethylene conversion was also evaluated for different ethylene partial pressures and contact times. No products were formed at 200 °C indicating that this temperature was not sufficient to promote ethylene transformation into hydrocarbons using HZSM-5 zeolite. At other temperatures (300, 400, 450, and 500 °C), a trend of increasing conversion with increasing temperature for most of ethylene partial pressures and contact times was noted (Figs. 2b, S5A and B).

The ethylene conversion increases when the reaction temperature increases from 300 to 400 °C. However, at temperatures above 400 °C, the conversion decreased. For all partial pressures and contact times, in most cases, the highest ethylene conversion was observed at 400 °C. This behavior can be explained considering that light olefins such as ethylene and propylene are produced through the cracking of the heavy compounds due to the temperature increase. Thus, the formation of ethylene at higher temperatures causes the decrease in conversion.

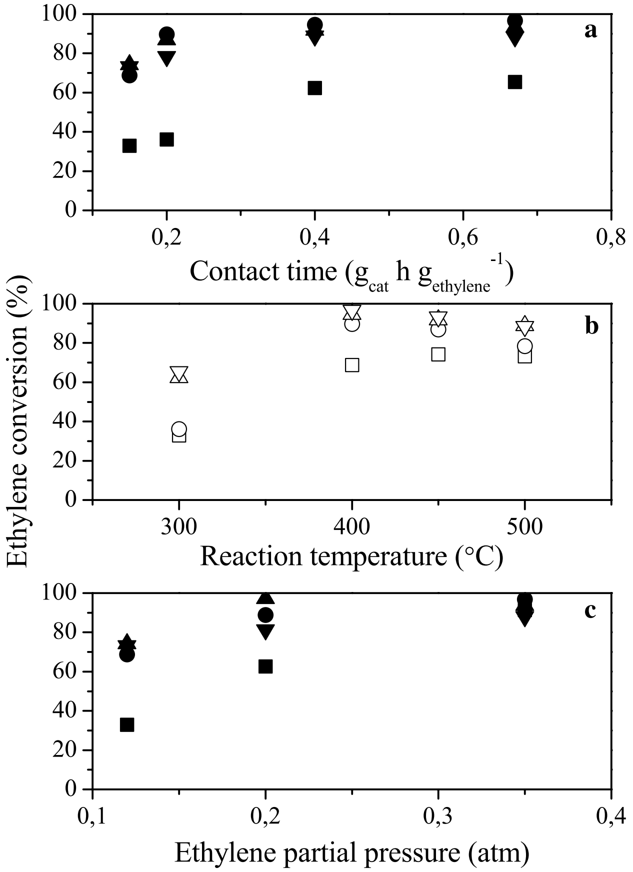


Fig. 2 Effect of contact time (**a**), reaction temperature (**b**) and ethylene partial pressure (**c**) on ethylene conversion at different reaction temperatures and contact times for ethylene reaction into hydrocarbons using HZSM-5 zeolite. Experimental conditions: **a** T = 300 (filled square), 400 (filled circle), 450 (filled triangle), 500 (filled inverted triangle) °C, $p_{ethylene}$ = 0.12 atm; **b** τ = 0.15 (open square), 0.20 (open circle), 0.40 (open triangle), 0.67 (open inverted triangle) g_{cat} h $g_{ethylene}^{-1}$, $p_{ethylene}$ = 0.12 atm; **c** T = 300 (filled square), 400 (filled circle), 450 (filled triangle), 500 (filled inverted triangle) °C, τ = 0.15 g_{cat} h $g_{ethylene}^{-1}$

At different reaction temperatures and constant contact time, the ethylene partial pressure variation also influenced conversion. The catalytic performance at all reaction temperatures indicated the increase in the conversion with ethylene partial pressure increase, mainly for the contact time of 0.15 g_{cat} h $g_{ethylene}^{-1}$ (Fig. 2c). The same behavior was verified at 300 °C using contact times of 0.20 and 0.40 g_{cat} h $g_{ethylene}^{-1}$ (Fig. S6A and B). It is important to highlight that the increase of contact time minimized the influence of ethylene partial pressure resulting in similar conversions. The increase of ethylene conversion caused by ethylene partial pressure increase is associated with a greater amount of reagent available at zeolite active sites. The literature reported similar trends when the catalytic conversion of ethylene into propylene and butenes using HZSM-5 was studied [13].

3.2.3 Influence of Operational Conditions on Product Yield

The correlation between operating conditions and product yield was also evaluated. The analysis was done using the results obtained after 5 min of reaction, where catalyst deactivation did not occur yet.

The variation of the product yield at different contact times (0.15, 0.20, 0.40, and 0.67 g_{cat} h $g^{-1}_{ethylene}$) for a given reaction temperature and the ethylene partial pressure of 0.12 atm was studied. Both reaction temperature and contact time strongly influenced product yield. In addition, significant changes occur at contact times between 0.15 and 0.40 g_{cat} h $g^{-1}_{ethylene}$. For higher values of this parameter, the product yield stabilized.

At 300 °C (Fig. 3), comparing to the other reaction temperatures, olefins predominated and contact time increase resulted in a decrease in propylene yield, as well as an increase in the yield to butenes, and hydrocarbons with five (C_5 and $C_5^=$) and six or more carbon atoms (C_6^+). Slightly changes were noticed for paraffins and aromatics yields at higher contact time.

For temperature higher than 300 °C (Figs. 4, S7, S8), aromatics and paraffins became the main products, an increase in their amount is observed as contact time increases. In addition, aromatics yield enhanced more strongly than paraffins yield. This effect is greater at higher reaction temperatures. On the other hand, a decrease in propylene and butenes yield is verified. The yield of hydrocarbons with five carbon atoms ($C_5 + C_5^=$) and hydrocarbons with six and more carbon atoms (C_6^+) have slightly decreased. It is important to note that, as reaction temperature increases, the behavior of these two groups of hydrocarbons becomes more similar.

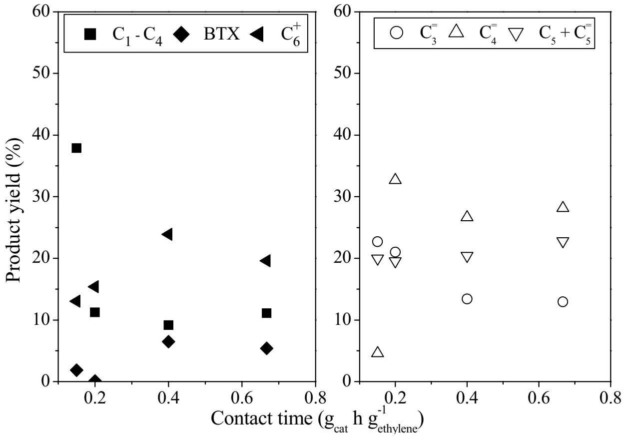


Fig. 3 Effect of contact time on product yield for ethylene reaction into hydrocarbons using HZSM-5 zeolite. Experimental conditions: T = 300 °C; $p_{ethylene} = 0.12$ atm. C_1–C_4 (filled square), $C_3^=$ (open circle), $C_4^=$ (open triangle), $C_5 + C_5^=$ (open inverted triangle), BTX (filled diamond), C_6^+ (filled left pointed triangle)

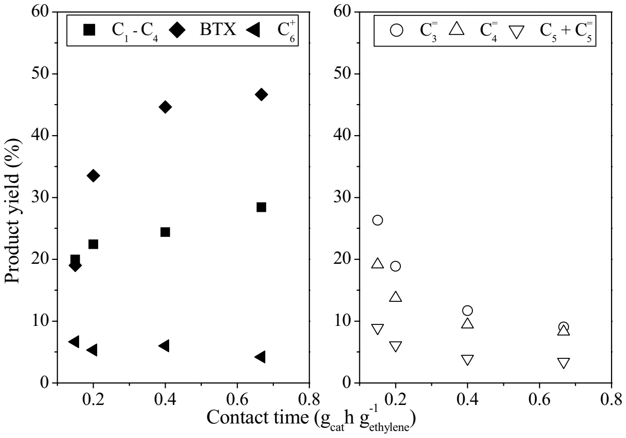


Fig. 4 Effect of contact time on product yield for ethylene reaction into hydrocarbons using HZSM-5 zeolite. Experimental conditions: T = 450 °C; $p_{ethylene} = 0.12$ atm. C_1–C_4 (filled square), $C_3^=$ (open circle), $C_4^=$ (open triangle), $C_5 + C_5^=$ (open inverted triangle), BTX (filled diamond), C_6^+ (filled left pointed triangle)

The effect of contact time for reaction temperatures above 300 °C was similar to that reported by Lin et al. [13] in the catalytic conversion of ethylene into propylene and butenes using HZSM-5 zeolite as catalyst. These authors concluded that propylene and butene were primary reaction products, while aromatics and paraffins (propane and butane) appeared as secondary compounds. It was observed that the increase in aromatics yield occurred at the same time as propylene yield decreased, indicating that aromatics would be mainly formed from propylene.

Higher contact times resulted in higher ethylene conversion and lower propylene yield in the conversion of ethylene into propylene using a dealuminated SSZ-13 zeolite [14]. At the same time, an increase in paraffins yield was observed, which, according to the authors, indicated that hydrogen transfer reaction, which forms paraffins and aromatics, occurred more easily if propylene, which was considered the main reaction product, had a longer contact time on the active acid sites of the catalyst. Differently from our work, in which the formation of aromatics and paraffins occurred simultaneously, Dai et al. [14] did not observe aromatic production, probably due to the small pores of SSZ-13 zeolite, so that aromatic compounds remained trapped within zeolite porous structure.

According to Van der Borght et al. [18] and Batchu et al. [12], the mechanism of ethanol or ethylene conversion into hydrocarbons is composed of four steps [12], which were established using the transient pulse-response technique. When ethanol is the reactant its dehydration to ethylene occurred through monomolecular or bimolecular way with diethyl ether as an intermediate product [18]. The dimerization of ethylene to butene is the first step (step I) via alkylation of adsorbed ethylene by ethylene in the gas phase [18].

It was possible to have an insight into the acid catalytic cracking routes of short-lived aliphatic surface intermediates (step II) using pulse experiments of higher olefins. Surface intermediates were detected and their influence in the product formation was studied [12] indicating the presence of dienes. The cyclization of these dienes is a bridge between aliphatic and aromatic surface species (step III). The aromatic surface species can be formed from cyclodienes (step IV) and then propene is released due to side-chain alkylation and paring mechanisms. As this information was evaluated at the early beginning of the reaction, it cannot be compared to the present work. However, the hydrocarbon pool approach mentioned above is considered by several authors [13, 16, 17, 19].

The pattern noted for the influence of contact time in product yield at different temperatures was consistent with the mechanism proposed by Takahashi et al. [15] according to which the formation of carbene species from ethylene occurs first. Then, these highly active species react with ethylene producing propylene. According to the literature [35], ethylene can interact with the hydroxyl group of HZSM-5 zeolites leading to a stable π-complex that weakens the O–H and C=C bonds. Probably, the carbene species can be formed due to the weakening of the C=C bond on ZSM-5 and it can act as a transient intermediate in propylene production.

At the same time, ethylene dimerization occurs. At 300 °C, a gradual increase in butenes yield with contact time was observed. It can be assumed that dimerization occurs at a lower rate than propylene formation by carbene intermediates. At higher temperatures, dimerization rate would increase, which in turn explains that propylene and butene yields tend to exhibit similar behaviors at temperatures higher than or equal to 400 °C. The relation between butenes and C_6^+ compounds also supported the reaction scheme proposal, by which the formation of compounds with six or more carbon atoms occurs through the reaction between ethylene and butene. Propylene consumption concomitant with C_5^+ range increase, observed at 300 °C, as contact time increases, indicate the formation of these compounds from propylene under these conditions.

Some authors [14, 36, 37] suggest that propylene formation occurs by the cracking of C_6^+ compounds formed from the reaction between butenes and ethylene. The literature points to C_6^+ yield decrease, while propylene yield increase as a strong indicator of the occurrence of this mechanism. However, such behavior was not verified in the range of experimental conditions employed in the present study.

While olefin formation was predominant at 300 °C, aromatic compounds became the main products at higher temperatures and their formation can be explained by the occurrence of both hydrogen transfer and dehydrocyclization reactions. In the former, olefins and cyclic compounds (naphthenics formed from C_6^+ polyolefins cyclization) produced paraffins and aromatics in a molar ratio approximately equal to 3/1, while in the second, olefins (C_3 and C_4) are consumed to form several aromatics with 6, 7 and 8 carbon atoms, that is, benzene, toluene and xylenes, without paraffins formation [38]. The possibility of paraffin formation via hydrogen transfer between carbenium ions (adsorbed olefins on Brønsted acid sites) and paraffins already formed cannot be eliminated.

The fact that olefin amount decreased with increasing contact time, while aromatic yield increased at a rate greater than the increase in paraffin yield suggests that aromatic formation by dehydrocyclization is favored compared to hydrogen transfer. According to Takahashi et al. [15], aromatics can be formed by dehydrocyclization, benzene formed from propylene, toluene produced by the reaction of propylene and butene, and xylenes derived exclusively from butenes.

In addition to producing aromatics, the dehydrocyclization reaction releases hydrogen in the reaction medium. So, it cannot be ruled out that a fraction of paraffins is produced by olefin hydrogenation. However, this hypothesis cannot be proven in the present work, since H_2 could not be measured in effluent stream.

Moreover, it was observed that the difference between aromatic and paraffin yields increased with temperature and contact time increase, which supported the hypothesis that aromatic compounds formation occurs through different mechanisms, which are influenced by temperature.

The effect of reaction temperature on product yield for different contact times and ethylene partial pressure of 0.12 atm was studied. For the shortest contact time ($\tau = 0.15\ g_{cat}\ h\ g_{ethylene}^{-1}$) shown in Fig. 5, it was observed that

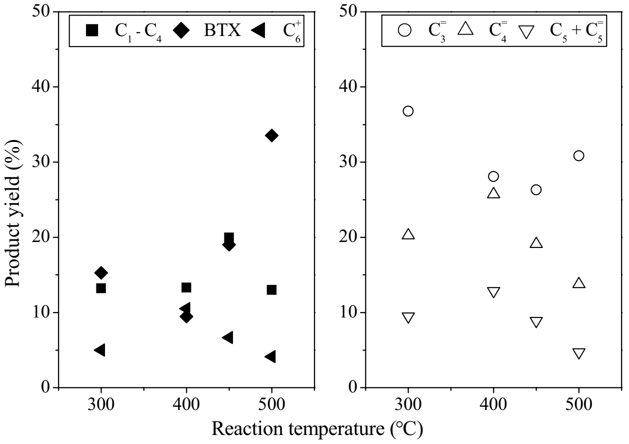


Fig. 5 Effect of reaction temperature on product yield for ethylene reaction into hydrocarbons using HZSM-5 zeolite. Experimental conditions: $\tau = 0.15\ g_{cat}\ h\ g_{ethylene}^{-1}$; $p_{ethylene} = 0.12$ atm. C_1–C_4 (filled square), $C_3^=$ (open circle), $C_4^=$ (open triangle), $C_5 + C_5^=$ (open inverted triangle), BTX (filled diamond), C_6^+ (filled left pointed triangle)

propylene yield decreases as reaction temperature increases, reaches a minimum at 450 °C and then increases again. On the other hand, the C_5 fraction decreased as the temperature increases, and butenes and C_6^+ yields passed through a maximum at 400 °C while aromatic and paraffin yields increase from this temperature on. For paraffins a decrease is observed at 500 °C. For other contact times, the propylene yield also goes through a minimum at 400 °C. Butenes, C_5 and C_6^+ yields decreased throughout the temperature range. For aromatics, a significant increase in yield was observed with increasing temperature, while for paraffins yield an increase was significant only between 300 and 400 °C. Thus, aromatic/paraffin molar ratio increased with increasing temperature, as previously mentioned.

The minimum observed for propylene yield (400 or 450 °C) for all studied contact times is related to the multiple possible routes that propylene is involved in. At lower temperatures, propylene can be produced through the reaction between ethylene and carbene species, as proposed by Takahashi et al. [15]. Then, propylene reacts with ethylene to form five-carbon olefins or oligomerizes into larger olefins. At higher temperatures, propylene yield increases due to the cracking of heavier compounds (paraffins and olefins).

The increase in butenes, C_5, and C_6^+ yields up to 400 °C, observed for contact time of 0.15 g_{cat} h $g^{-1}_{ethylene}$ (Fig. 5), may be related to the ethylene dimerization, the reaction between ethylene and propylene, and the oligomerization of light olefins, respectively. Dimerization is an important step in most of the proposed mechanisms for the catalytic conversion of ethylene and is the initial step in the mechanisms that involve sequences of oligomerizations [14, 36, 37]. As temperature increases, these larger olefins can form aromatics and paraffins through the cyclization and hydrogen transfer reactions or aromatics through dehydrocyclization. These two routes are strongly influenced by temperature and higher temperatures apparently promote dehydrocyclization, which explains the lower paraffins yield at higher temperatures.

For higher contact times (Figs. 6, S9, S10), butenes, C_5, and C_6^+ yields decreased as temperature increases. This behavior is accompanied by the increase of paraffins and mainly aromatics yields. A maximum for the yield of lighter fractions is not noted probably due to the increase of the rate of the reactions involved as contact time increases.

The decrease of C_5 fraction yield suggests that these compounds can also react to form aromatics via dehydrocyclization through the reaction of pentenes with ethylene producing toluene, or with propylene producing xylenes.

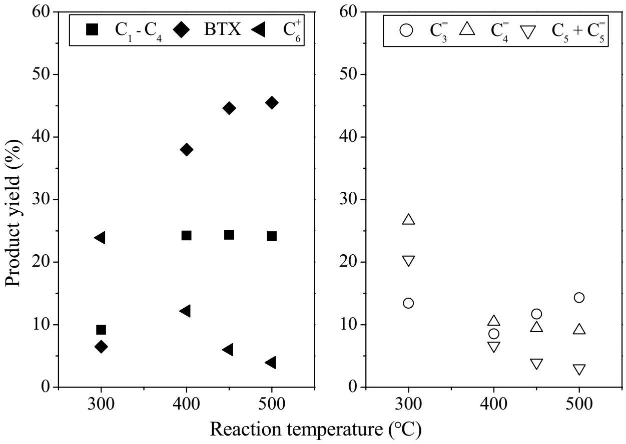


Fig. 6 Effect of reaction temperature on product yield for ethylene reaction into hydrocarbons using HZSM-5 zeolite. Experimental conditions: $\tau = 0.40$ g_{cat} h $g^{-1}_{ethylene}$; $p_{ethylene} = 0.12$ atm. C_1–C_4 (filled square), $C_3^=$ (open circle), $C_4^=$ (open triangle), $C_5+C_5^=$ (open inverted triangle), BTX (filled diamond), C_6^+ (filled left pointed triangle)

Considering all contact times (Figs. 5, 6, S9, S10), paraffins and aromatics yields increased as temperature increased from 300 to 400 °C, except for contact time of 0.15 g_{cat} h $g^{-1}_{ethylene}$. When the reaction temperature rises ($T \geq 400$ °C), the difference between paraffins and aromatics yields is accentuated and, except for contact time of 0.15 g_{cat} h $g^{-1}_{ethylene}$, aromatics yield becomes significantly higher than that of paraffins. In the shortest space time, the amount of aromatics exceeds that of paraffins only at 500 °C. These observations agree with the proposal that different reaction routes for the formation of aromatics are occurring.

The proposed mechanisms for aromatics formation from ethylene suggest that it occurs through cyclization reactions of olefins with six or more carbons followed by hydrogen transfer reactions, forming aromatics and paraffins, or by dehydrocyclization of smaller olefins derived from ethylene (propylene, butenes and pentenes), producing aromatics.

In this work, the dehydrocyclization reactions are favored at higher temperatures, which is consistent with the endothermic character of these reactions.

Similar results were reported in the literature [39] for the aromatization of ethylene using Ga/HZSM-5 catalysts. According to the authors, the high aromatics yield at higher temperatures has been attributed to high dehydrogenation catalytic activity associated with gallium species. At lower temperatures (300 °C), the catalyst showed little or no dehydrogenation activity and the formation of aromatic compounds has been associated to hydrogen transfer reactions. At intermediate temperatures, both reaction paths can produce aromatics.

Based on our results for the effect of contact time and reaction temperature on product yield, the reaction scheme shown in Fig. 7 is proposed.

The effect of ethylene partial pressure on product yield at different reaction temperatures using contact time of 0.15 g_{cat} h $g^{-1}_{ethylene}$ was evaluated (Figs. 8, S11–S13). The same trend was observed for all studied contact time. Aromatics yield is clearly favored by the increase of reactant

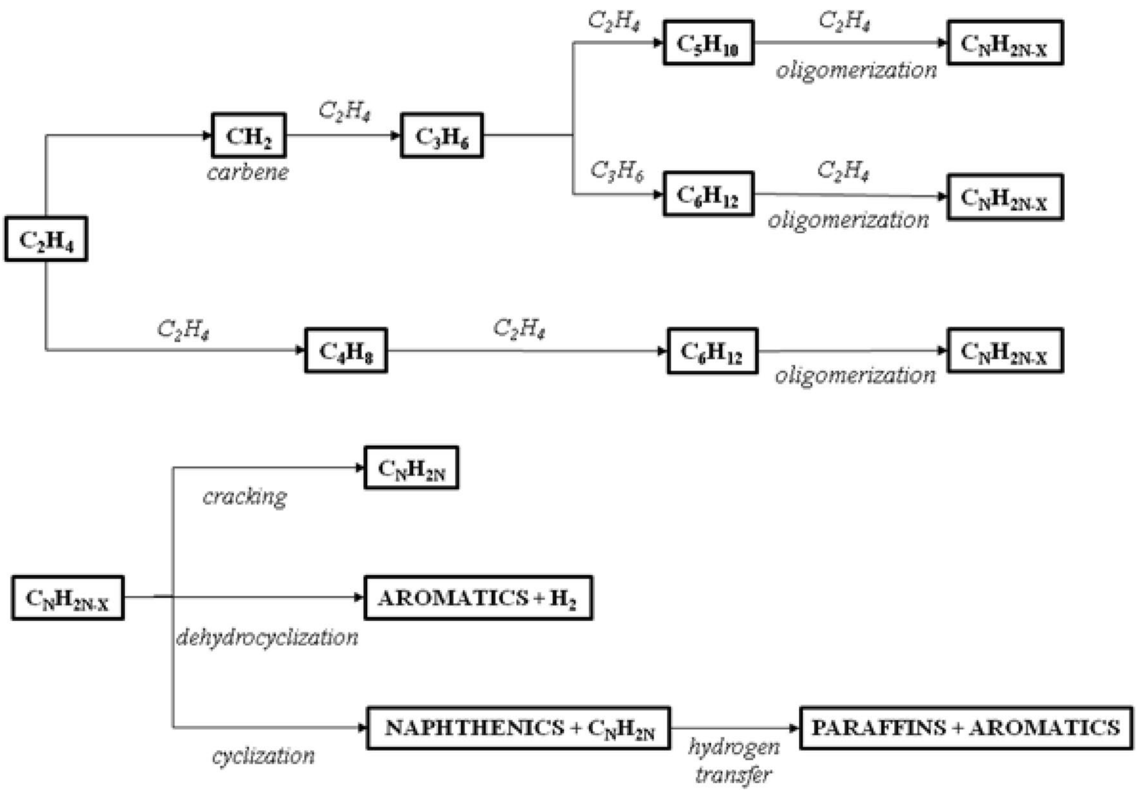


Fig. 7 Proposed reaction scheme for olefins and aromatics formation from ethylene

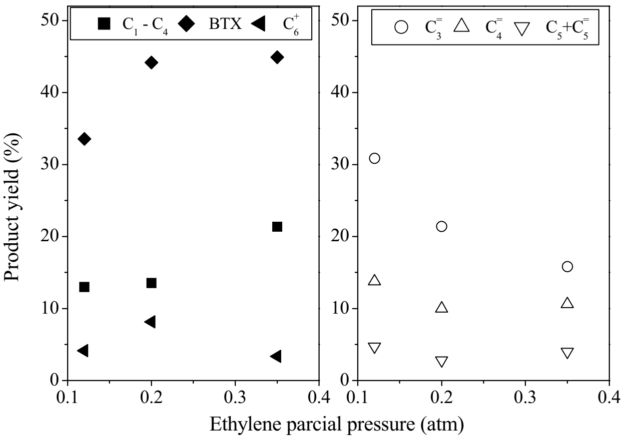


Fig. 8 Effect of ethylene partial pressure on product yield for ethylene reaction into hydrocarbons using HZSM-5 zeolite. Experimental conditions: $\tau = 0.15\ g_{cat}\ h\ g^{-1}_{ethylene}$; $T = 500$ °C. C_1–C_4 (filled square), $C_3^=$ (open circle), $C_4^=$ (open triangle), $C_5 + C_5^=$ (open inverted triangle), BTX (filled diamond), C_6^+ (filled left pointed triangle)

partial pressure at all studied temperatures, but aromatics formation is not always accompanied by paraffins production. This finding is a further indication that the formation of aromatic compounds can occur through different reaction paths, reinforcing the hypothesis that both hydrogen transfer (forming paraffins and aromatics) and dehydrocyclization (forming aromatics and hydrogen) are involved in the process.

For all studied temperatures, the increase in partial pressure is accompanied by a decrease in propylene yield, which is in agreement with the proposed reaction scheme (Fig. 7) in which propylene is a primary product of the reaction and is formed by the reaction between ethylene and the intermediate carbene species, but it is transformed into other species by consecutive reactions.

At 300 °C (Fig. S11), when the reactant partial pressure increases a maximum for butenes and C_5 fraction yields was observed at partial pressure of 0.20 atm. After that these yields decrease, while the yield of compounds with six or more (C_6^+) carbon atoms slightly increased with ethylene partial pressure increase. These behaviors are consistent with the proposed reaction scheme in which butenes, pentenes, and hexenes are products of ethylene oligomerization ($C_4^=$ and $C_6^=$) or of the reaction of ethylene with propylene ($C_5^=$), which are transformed into larger olefins/polyolefins by reacting with ethylene molecules. The reactions that form larger olefins/polyolefins and their transformation into aromatics are favored at higher temperatures (400–500 °C), while butenes, C_5, and C_6^+ yields showed a trend to decrease.

Another characteristic of the reaction carried out at 300 °C is that paraffins yield decreases with ethylene partial pressure increase and it is also higher or approximately equal to aromatics yield. This behavior confirms the favoring to hydrogen transfer reactions at this temperature when compared to dehydrocyclization reactions. The results indicated a favor to the formation of aromatics by dehydrocyclization when reaction temperature and ethylene partial pressure increases. Similar trends were observed by Choudhary et al. [39] using Ga/HZSM-5 as catalyst.

Similar results were reported by Lin et al. [13] when studying the effect of reagent partial pressure on the catalytic conversion of ethylene to propylene and butenes using HZSM-5 zeolite. The authors observed two distinct behaviors. At pressures below 0.11 atm, propylene can be obtained with high selectivity, but the increase in partial pressure causes an increase in conversion and a decrease in propylene yield, which is consistent with the results obtained in this work. For pressures above 0.39 atm, the increase in partial pressure results in the increase in conversion, the decrease in propylene yield, and the increase in aromatics yield. The same behavior was observed, when the reaction was carried out at higher ethylene pressure (0.35 atm) in this work.

3.2.4 Operational Conditions to Maximize Propylene and Aromatics Yields

The experimental parameters influence product yields and are directly related to the reaction mechanism proposed in Fig. 7. However, it is very important to identify the appropriated experimental conditions for the formation of a specific product that can be an intermediate or an end product. So, the results were analyzed in order to identify the most suitable conditions for the maximization of propylene and aromatics (BTX) yields.

The higher propylene yield was obtained at the higher reaction temperature, using lower values of contact time and ethylene partial pressure. Propylene is an intermediate in the proposed reaction scheme, and its subsequent transformations are not favored by low contact time and ethylene partial pressure that increase this product yield. Thus, the condition that provides the highest propylene yield is: ethylene partial pressure = 0.12 atm, reaction temperature = 500 °C, and contact time = 0.15 g_{cat} h $g_{ethylene}^{-1}$ (Fig. 9a).

On the other hand, aromatics (BTX) yield was favored by the following conditions: ethylene partial pressure = 0.35 atm, contact time = 0.20 g_{cat} h $g_{ethylene}^{-1}$, and reaction temperature = 400 °C (Fig. 9b). In this case, higher ethylene partial pressure, that is, greater amount of reagent available, promotes the formation of aromatics favoring the occurrence of consecutive reactions. The high selectivity to aromatics at intermediate reaction temperatures and contact times can be attributed to the fact that these compounds are precursors of coke, whose formation is favored by higher temperatures and contact times.

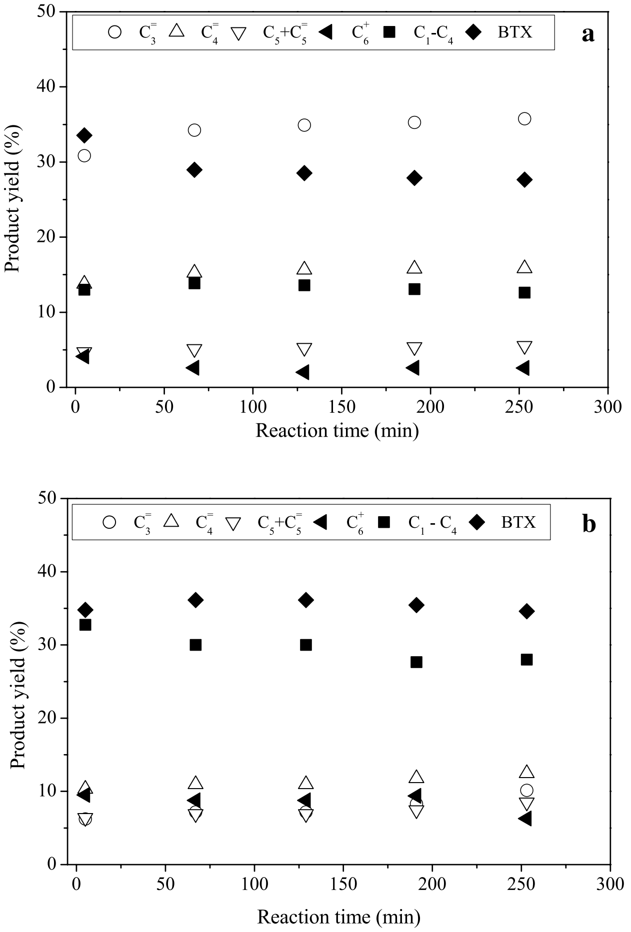


Fig. 9 Product yield with time on stream. Experimental conditions to maximize propylene: T = 500 °C; $p_{ethylene}$ = 0.12 atm; τ = 0.15 g_{cat} h $g_{ethylene}^{-1}$ (**a**), and aromatics: T = 400 °C; $p_{ethylene}$ = 0.35 atm; τ = 0.20 g_{cat} h $g_{ethylene}^{-1}$ (**b**)

To determinate the condition that maximizes aromatic yield, catalyst stability was also considered. A yield higher than that observed for the selected condition was obtained at the beginning of the reaction when it was carried out at 500 °C, employing ethylene partial pressure of 0.20 atm and contact time of 0.40 g_{cat} h $g_{ethylene}^{-1}$. However, when considering the reaction evolution over time, the yield decreased significantly, which is not interesting since catalyst stability is important.

3.2.5 Catalyst Stability

Catalyst stability, that is, activity and selectivity performance, is an important characteristic to choose a suitable catalyst for a specific reaction. For example, some catalysts, such as ZSM-5 [1] and SSZ-13 [14] zeolites, and SAPO-34 [29] were tested for the ethylene conversion into hydrocarbons; however, the stability of these materials is very different. Catalyst stability was evaluated using long-term tests (1200 min) carried out under the conditions previously selected as the most suitable for the maximization of propylene and aromatics yields using HZSM-5 zeolite.

For both conditions, ethylene conversion (Fig. 10) remains nearly constant in the first 400 min. From this time on, it decreases continuously and gradually. After 1200 min, there was a decrease of 37% and 44% in ethylene conversion at propylene and aromatics experimental conditions, respectively. This deactivation can be associated with coke formation and was favored in the experimental conditions for higher aromatics yield.

According to Guisnet et al. [40] in most catalytic processes using zeolites a progressive decrease in their catalytic activity due to the deposition of bulky organic compounds, known as coke, inside micropores or on crystal surface is noted. Coke formation is a complex process and involves successive reactions, such as intramolecular and intermolecular cyclization, and condensation between reactants and/or products.

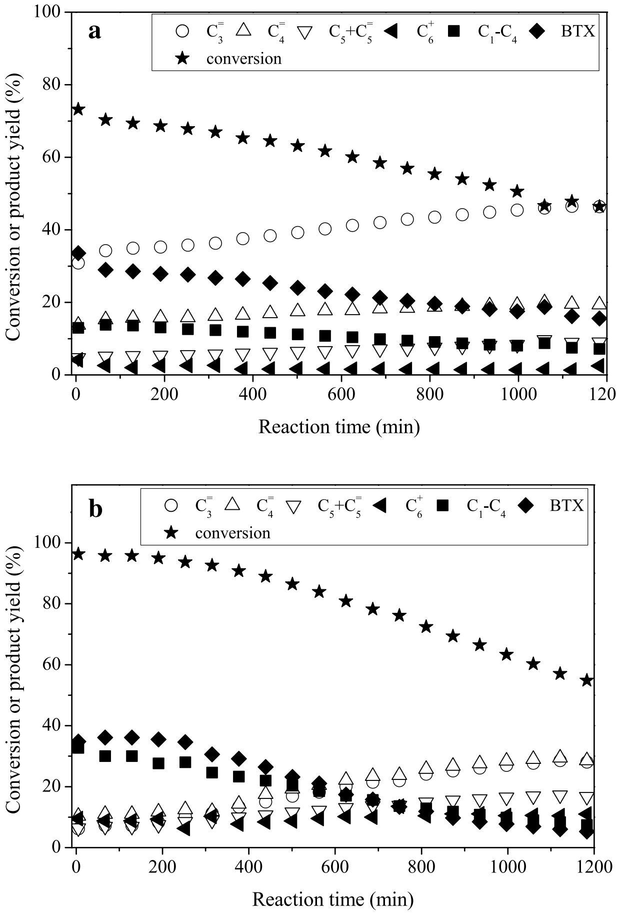


Fig. 10 Ethylene conversion and product yield with time on stream for long-term tests. Experimental conditions to maximize propylene: T = 500 °C; $p_{ethylene} = 0.12$ atm; $\tau = 0.15\ g_{cat}\ h\ g^{-1}_{ethylene}$ (**a**), and aromatics: T = 400 °C; $p_{ethylene} = 0.35$ atm; $\tau = 0.20\ g_{cat}\ h\ g^{-1}_{ethylene}$ (**b**)

The variation of product yield with time on stream was also investigated in long-term reactions, and the results are presented in Fig. 10. The change in product yield becomes more significant after 400 min of reaction. These changes indicate a reduction in aromatics yield and an increase in propylene and C_4–C_5 olefins yields. These results suggest that coke mainly affects the strongest acid sites that are active for cyclization, hydrogen transfer, and aromatic condensation reactions where as weak and intermediate acid sites are those active for the initial steps of the reaction (carbene formation and dimerization). Similar behavior was observed by Li et al. [13] that studied the conversion of ethylene into hydrocarbons using an HZSM-5 zeolite with SAR equal to 76 for a long time on stream (90 h) at 450 °C. Ethylene conversion decreased gradually throughout time on stream, while propylene selectivity slightly increased.

For both reaction conditions, butenes and propylene yields showed the same trend, that is, they increase as BTX and paraffins yields decrease that reinforces once again the proposed reaction mechanism in which aromatic and heavier compounds are formed from light olefins.

According to the literature [14, 29, 36, 41], SAPO-34 and SSZ-13 show high ethylene conversion and propylene selectivity in the ethylene to propylene conversion due to shape selectivity caused by the small pores of the CHA zeolite structure [36], although SSZ-13 zeolite had relatively high propylene selectivity compared to SAPO-34 zeolite, SSZ-13 deactivates very fast. Dai et al. [14] have studied dealuminated H-SSZ-13 zeolite for ethylene to propylene conversion. They observed high ethylene conversion and propylene selectivity for this catalyst, but after 12 h on stream the zeolite was not active anymore at 400 °C probably due to coke formation. On the other hand, Kim et al. [29] have synthesized SAPO-34 zeolite with different crystal size and acidity to catalyze the ethylene to propylene conversion, but their best catalyst lost 81% of its activity after 16 h on stream.

The changes in ethylene conversion and product yield were not important in the first 400 min of reaction, for both studied conditions, and they gradually became more significant for longer reaction times. This behavior is consistent with coke deactivation model proposed in the literature [40] for HZSM-5, whose porous structure allows three-dimensional circulation of molecules and does not have cavities. Thus, for shorter reaction times, in which coke amount is lower, deactivation occurs by covering active sites. As the reaction proceeds, there is a gradual increase in coke content, thereby blocking access to sites at channel intersections where coke molecules are located. Finally, for higher coke levels, limitation or block of reactant access to active sites located in the channels, where there are no coke molecules, occurs. This process is more deleterious for zeolite activity, because the number of sites inactivated is much larger than the number of molecules of coke. It should be mentioned that the deactivation effect is more important on strong acid sites which are those that catalyze reactions that lead to coke formation.

3.2.5.1 Influence of Water Vapor in Ethylene Conversion into Propylene and Aromatics In the catalytic transformation of ethanol into hydrocarbons in the presence of acid catalysts, the first step is the formation of ethylene and water (molar ratio = 1:1) at high rates. The presence of water in the reaction medium influences the catalytic activity, the product distribution, and the catalyst deactivation. The presence of water attenuates deactivation at moderate temperatures because it reduces coke deposition. On the other hand, it reduces catalytic activity at high temperatures, as it causes zeolite framework dealumination reducing acid site density [1, 7].

Considering that ethylene is the primary product in ethanol conversion into hydrocarbons, it can be assumed that these hydrocarbons are formed through a reaction pathway that has ethylene as reactant. Thus, understanding the effect of water on ethylene conversion reactions can bring important information to the overall ethanol conversion process.

The influence of water in the performance of a HZSM-5 zeolite in ethylene conversion was evaluated under the experimental conditions previously selected as the most suitable for the maximization of the yield of propylene and aromatics feeding ethylene and water vapor at the same time (0, 18, and 36 vol% of water vapor). As observed in Fig. 11, the presence of water has little effect on ethylene conversion at the beginning of the reaction (5 min). For longer reaction times, the deactivation process is more pronounced in the presence of water vapor. This behavior suggests that in the studied conditions, particularly at 500 °C, the water vapor is promoting the zeolite framework dealumination with acid site reduction. This effect is more important than a possible reduction of coke formation by water vapor presence.

In order to evaluate the effects of water vapor in the zeolite framework, the HZSM-5 zeolite was exposed to water vapor at reaction temperature before ethylene was fed to the reactor. For higher temperature (500 °C), the ethylene conversion decreased and only a slight deactivation was observed during time on stream. Although the catalyst was less active after the water vapor treatment, it was stable throughout 1200 min. When a zeolite is exposed to water vapor at high temperatures a dealumination process occurs and the acidity and textural properties are changed. On the other hand, for lower reaction temperature (400 °C), no change in the activity or stability of the catalyst was noted indicating that no significant modification occurred during the water vapor treatment. So, the deactivation of the catalyst during the reaction at 400 °C in the presence of water was due to the modification of the reaction mechanism and not to the modification of the zeolite structure. These results suggest that acid sites reduction due to dealumination promoted by water vapor predominates over coke inhibition at 500 °C. This acid site density reduction decreased catalyst activity (Fig. 11a).

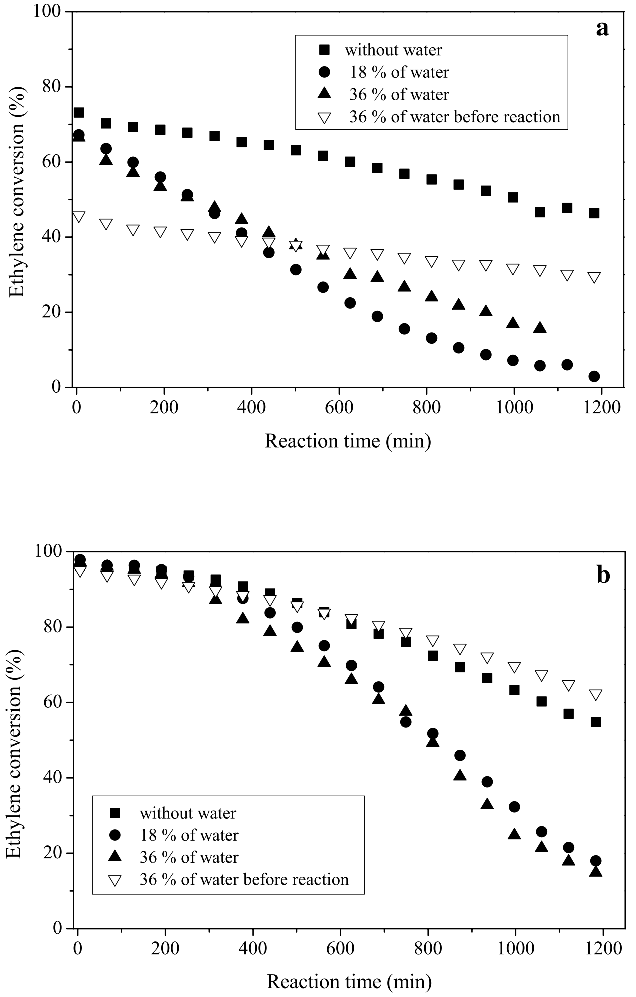


Fig. 11 Effect of water presence on ethylene conversion with time on stream. Experimental conditions to maximize propylene: T = 500 °C; $p_{ethylene} = 0.12$ atm; $\tau = 0.15$ g_{cat} h $g_{ethylene}^{-1}$ (**a**), and aromatics: T = 400 °C; $p_{ethylene} = 0.35$ atm; $\tau = 0.20$ g_{cat} h $g_{ethylene}^{-1}$ (**b**)

The effects of the presence of water vapor on product yield are illustrated in Fig. 12 for propylene and aromatics. For propylene yield, it was noted that despite of the water content in the feed or the water vapor treatment before the reaction there is a slightly increase of propylene yield. These results suggest that the framework dealumination promoted by water vapor mainly affects the strong acid sites which are those that are active for the reaction involved on the conversion of propylene into higher hydrocarbons (cyclization, hydrogen transfer, and aromatization reactions). On the other hand, for aromatics yield different effects were observed mainly for reaction time lower than 200 min. The lower amount of water vapor (18 vol%)

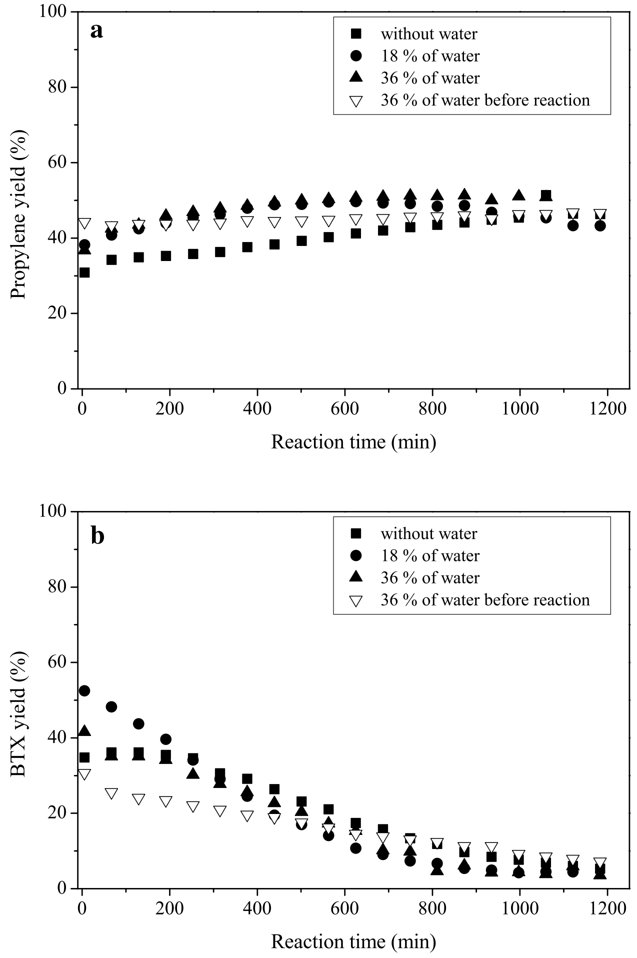


Fig. 12 Effect of water presence on product yield with time on stream. Experimental conditions to maximize propylene: T = 500 °C; $p_{ethylene} = 0.12$ atm; $\tau = 0.15$ g_{cat} h $g^{-1}_{ethylene}$ (**a**), and aromatics: T = 400 °C; $p_{ethylene} = 0.35$ atm; $\tau = 0.20$ g_{cat} h $g^{-1}_{ethylene}$ (**b**)

improved aromatics yield, while the higher amount did not influence the formation of aromatics. The preliminary water vapor treatment resulted in a decrease of aromatics yield. This behavior indicates that water vapor plays a role in the mechanism of the reaction as ethylene conversion did not change due to water presence at least before 400 min on stream. However, under the studied conditions the results did not allow us to understand how water vapour acts on the mechanism.

The influence of the water vapor on catalyst activity was less significant at 400 °C than at 500 °C. Two proposals can be presented in an attempt to justify these results: (i) insignificant or non-existent framework dealumination at 400 °C, and (ii) higher ethylene partial pressure and longer contact time employed in the reaction at 400 °C would exert a leveling off effect so that possible changes in zeolite acid properties were less noticeable.

4 Conclusion

HZSM-5 zeolite is an efficient catalyst for the direct conversion of ethylene into propylene and aromatics. The results showed that reaction conditions affected both ethylene conversion and product yield. The formation of propylene occurred through one carbene species produced from ethylene with another molecule of ethylene. Higher molecular weight olefins were formed by the dimerization of ethylene and propylene, and the reactions between propylene and ethylene, and between butene and ethylene. For the formation of aromatics and paraffins, different mechanisms were observed depending on reaction temperature. These mechanisms are the dehydrocyclization of C_6^+ olefins that releases hydrogen in the reaction medium causing the formation of paraffinic compounds by hydrogenation, and the hydrogen transfer between naphthenic compounds and olefins generating aromatic compounds and paraffins. In the conditions used in this work, the results point to the dehydrocyclization reactions, which are favorable at higher temperatures. For long-term reactions, ethylene conversion and products yield changed after 400 min. This deactivation can be associated with coke formation. A reduction in aromatics yield and an increase in propylene yield suggest that coke mainly affects the strongest acid sites that are active for cyclization, hydrogen transfer, and aromatic condensation reactions. The presence of water vapor resulted in a deactivation process at 500 °C due to zeolite framework dealumination with acid site reduction and at 400 °C due to modification in reaction mechanism.

Acknowledgements Débora S. Fernandes thanks CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil – Finance Code 001) for M.Sc. scholarship and financial support. Cristiane A. Henriques thanks CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and Prociencia program (Universidade do Estado do Rio de Janeiro) for her research scholarship and financial support.

Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

References

1. Takahashi A, Xia W, Nakamura I, Shimada H, Fujitani T (2012) Effects of added phosphorus on conversion of ethanol to propylene over ZSM-5 catalysts. Appl Catal A 423–424:162–167
2. Gayubo A, Alonso A, Valle B, Aguayo A, Olazar M, Bilbao J (2011) Kinetic modelling for the transformation of bioethanol into olefins on a hydrothermally stable Ni–HZSM-5 catalyst considering the deactivation by coke. Chem Eng J 167:262–277

3. Madeira F, Gnep N, Magnoux P, Maury S, Cadran N (2009) Ethanol transformation over HFAU, HBEA and HMFI zeolites presenting similar Brønsted acidity. Appl Catal A 367:39–46
4. Song Z, Takahashi A, Mimura N, Fujitani T (2009) Production of propylene from ethanol over ZSM-5 zeolites. Catal Lett 131:364–369
5. Inaba M, Murata K, Saito M, Takahara I (2006) Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts. React Kinet Catal Lett 88:135–141
6. Sousa Z, Veloso C, Henriques C, da Silva V (2016) Ethanol conversion into olefins and aromatics over HZSM-5 zeolite: Influence of reaction conditions and surface reaction studies. J Mol Catal A 422:266–274
7. Aguayo A, Gayubo A, Atutxa A, Olazar M, Bilbao J (2002) Catalyst deactivation by coke in the transformation of aqueous ethanol into hydrocarbons. Kinetic modeling and acidity deterioration of the catalyst. Ind Eng Chem Res 41:4216–4224
8. Ghashghaee M (2018) Heterogeneous catalysts for gas-phase conversion of ethylene to higher olefins. Rev Chem Eng 34:595–655
9. Hulea V (2018) Toward platform chemicals from bio-based ethylene: heterogeneous catalysts and processes. ACS Catal 8:3263–3279
10. Li X, Kant A, He Y, Thakkar H, Atanga M, Rezaei F, Ludlow D, Rownaghi A (2016) Light olefins from renewable resources: selective catalytic dehydration of bioethanol to propylene over zeolite and transition metal oxide catalysts. Catal Today 276:62–77
11. Epelde E, Aguayo A, Olazar M, Bilbao J, Gayubo A (2014) Modifications in the HZSM-5 zeolite for the selective transformation of ethylene into propylene. Appl Catal A 479:17–25
12. Batchu R, Galvita V, Alexopoulos K, van der Borght K, Poelman H, Reyniers M-F, Marin G (2017) Role of intermediates in reaction pathways from ethene to hydrocarbons over H-ZSM-5. Appl Catal A 538:207–220
13. Lin B, Zhang Q, Wang Y (2009) Catalytic conversion of ethylene to propylene and butenes over H – ZSM-5. Ind Eng Chem Res 48:10788–10795
14. Dai W, Sun X, Tang B, Wu G, Li L, Guan N, Hunger M (2014) Verifying the mechanism of the ethene-to-propene conversion on zeolite H-SSZ-13. J Catal 314:10–20
15. Takahashi A, Xia W, Wu Q, Furukawa T, Nakamura I, Shimada H, Fujitani T (2013) Difference between the mechanisms of propylene production from methanol and ethanol over ZSM-5 catalysts. Appl Catal A 467:380–385
16. Gayubo A, Tarrío A, Aguayo A, Olazar M, Bilbao J (2001) Kinetic modelling of the transformation of aqueous ethanol into hydrocarbons on a HZSM-5 zeolite. Ind Eng Chem Res 40:3467–3474
17. Johansson R, Hruby S, Rass-Hansen J, Christensen C (2009) The hydrocarbon pool in ethanol-to-gasoline over HZSM-5 catalysts. Catal Lett 127:1–6
18. van der Borght K, Batchu R, Galvita V, Alexopoulos K, Reyniers M-F, Thybaut J, Marin G (2016) Insights into the Reaction Mechanism of ethanol conversion into hydrocarbons on H-ZSM-5. Angew Chem Int Ed 55:12817–12821
19. Allotta P, Stair P (2012) Time-resolved studies of ethylene and propylene reactions in zeolite H-MFI by in situ fast IR heating and UV raman spectroscopy. ACS Catal 2:2424–2432
20. Ferreira Madeira F, Gnepa N, Magnoux P, Vezin H, Maury S, Cadran N (2010) Mechanistic insights on the ethanol transformation into hydrocarbons over HZSM-5 zeolite. Chem Eng J 161:403–408
21. Ferreira Madeira F, Vezin H, Gnep N, Magnoux P, Maury S, Cadran N (2011) Radical species detection and their nature evolution with catalyst deactivation in the ethanol-to-hydrocarbon reaction over HZSM-5 zeolite. ACS Catal 1:417–424
22. Chang C, Silvestri A (1977) The conversion of methanol and other *O*-compounds to hydrocarbons over zeolite catalysts. J Catal 47:249–259
23. Yamazaki H, Shima H, Imai H, Yokoi T, Tatsumi T, Kondo J (2012) Direct production of propene from methoxy species and dimethyl ether over H-ZSM-5. J Phys Chem C 116:24091–24097
24. Yamazaki H, Shima H, Imai H, Yokoi T, Tatsumi T, Kondo J (2011) Evidence for a "Carbene-like" intermediate during the reaction of methoxy species with light alkenes on H-ZSM-5. Angew Chem Int Ed 50:1853–1856
25. Costa E, Uguina A, Aguado J, Hernández P (1985) Ethanol to gasoline process: effect of variables, mechanism, and kinetics. Ind Eng Chem Process Des Dev 24:239–244
26. Derouane E, Nagy J, Dejaifve P, van Hooff J, Spekman B, Vedrine J, Naccache C (1978) Elucidation of the mechanism of conversion of methanol and ethanol to hydrocarbons on a new type of synthetic zeolite. J Catal 53:40–55
27. Spoto G, Bordiga S, Ricchiardi G, Scarano D, Zecchina A, Borello E (1994) IR study of ethene and propene oligomerization on H-ZSM-5: hydrogen-bonded precursor formation, initiation and propagation mechanisms and structure of the entrapped oligomers. J Chem Soc Faraday Trans 90:2827–2835
28. Bolis V, Vedrine J, van De Berg J, Wolthuizen J, Derouane E (1980) Adsorption and activation of ethene by zeolite-H-ZSM-5. J Chem Soc Faraday Trans 1(76):1606–1616
29. Kim H, Kim J-W, Kim N, Kim T-W, Jhung S, Kim C-U (2017) Controlling size and acidity of SAPO-34 catalyst for efficient ethylene to propylene transformation. Mol Catal 438:86–92
30. Chu Y, Han B, Zheng A, Deng F (2012) Influence of acid strength and confinement effect on the ethylene dimerization reaction over solid acid catalysts: a theoretical calculation study. J Phys Chem C 116:12687–12695
31. Katada N, Igi H, Kim J-H, Niwa M (1997) Determination of the acidic properties of zeolites by theoretical analysis of temperature-programmed desorption of ammonia based on adsorption equilibrium. J Phys Chem B 101:5969–5977
32. Katada N, Miyamoto T, Begum H, Naito N, Niwa M, Matsumoto A, Tsutsumi K (2000) Strong acidity of MFI-type ferrisilicate determined by temperature-programmed desorption of ammonia. J Phys Chem B 104:5511–5518
33. Epelde E, Ibañez M, Aguayo AT, Gayubo AG, Bilbao J, Castaño P (2014) Differences among the deactivation pathway of HZSM-5 zeolite and SAPO-34 in the transformation of ethylene or 1-butene to propylene. Microporous Mesoporous Mater 195:284–293
34. Blasco T, Corma A, Martínez-Triguero J (2006) Hydrothermal stabilization of ZSM-5 catalytic-cracking additives by phosphorus addition. J Catal 237:267–277
35. Beran S, Jirú P, Kubelková L (1981) Quantum chemical study of the interaction of ethylene and propylene with the hydroxyl groups of zeolites. J Mol Catal 12:341–349
36. Oikawa H, Shibata Y, Inazu K, Iwase Y, Murai K, Hyodo S, Kobayashi G, Baba T (2006) Highly selective conversion of ethene to propene over SAPO-34 as a solid acid catalyst. Appl Catal A 312:181–185
37. Ingram C, Lancashire R (1995) On the formation of C3 hydrocarbons during the conversion of ethanol using H-ZSM-5 catalyst. Catal Lett 31:395–403
38. Lin L, Qiu C, Zhuo Z, Zhang D, Zhao S, Wu H, Liu Y, He M (2014) Acid strength controlled reaction pathways for the catalytic cracking of 1-butene to propene over ZSM-5. J Catal 309:136–145
39. Choudhary V, Banerjee S, Panjala D (2002) Influence of temperature on the product selectivity and distribution of aromatics and C8 aromatic isomers in the conversion of dilute ethene over H-Galloaluminosilicate (ZSM-5 type) zeolite. J Catal 205:398–403

40. Guisnet M, Costa L, Ribeiro F (2009) Prevention of zeolite deactivation by coking. J Mol Catal A 305:69–83
41. Jun J-W, Khan N, Seo P, Kim C-U, Kim H, Jhung S (2016) Conversion of Y into SSZ-13 zeolites and ethylene-to-propylene reactions over the obtained SSZ-13 zeolites. Chem Eng J 303:667–674