



Coke deactivation and regeneration of HZSM-5 zeolite catalysts in the oligomerization of 1-butene

Marta Díaz, Eva Epelde*, José Valecillos*, Sepideh Izaddoust, Andrés T. Aguayo, Javier Bilbao

Department of Chemical Engineering, University of the Basque Country (UPV/EHU), P. O. Box 644, 48080, Bilbao, Spain

ARTICLE INFO

Keywords:

Oligomerization
1-butene
HZSM-5 zeolite
Coke deactivation
Regeneration

ABSTRACT

The deactivation phenomenon of HZSM-5 catalysts ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 30–280) in the 1-butene oligomerization has been studied. Experiments were performed in a fixed-bed reactor at 175–325 °C; 1.5–40 bar; and, 2–6 h mol^{-1} . Used catalysts were analyzed by: temperature-programmed sweeping with N_2 (TPS- N_2), soluble coke analysis by gas chromatography/mass spectrometry (GC/MS); Fourier-transform infrared spectroscopy (FTIR); temperature-programmed oxidation (TPO), and; combined TPO/FTIR. The main deactivation cause is the oligomer (soft coke) confinement in the catalyst matrix, which depends on the reaction conditions (temperature and pressure). Soft coke is removed by TPS- N_2 at 400 °C, whereas the remaining hard coke, by combustion. Two types of hard coke are distinguished, which are located in the catalyst matrix and in the zeolite micropores, being the second fraction more refractory to combustion. The low developed nature of soft coke facilitates catalyst regeneration, which is fully achieved by the combustion of hard coke at 500 °C.

1. Introduction

The oligomerization of C_2 – C_5 olefins is an attractive and versatile route to selectively produce environmentally friendly synthetic transportation fuels [1,2], especially if olefins are produced from sources alternative to conventional oil-based steam cracking and FCC units [3]. Among these routes for light olefin sustainable production, the conversion of oxygenates derived from biomass (methanol, dimethyl ether (DME), bioethanol or bio-oil) [4–7], wastes of consumer society (mainly polyolefins) [8–10], and CO_2 [11] are the most promising ones. Likewise, the direct synthesis of olefins from CH_4 [12] is receiving a great attention.

The products of olefin oligomerization are mainly composed of a mixture of alkenes, free of heteroatoms and sulphur, with low concentration of naphthenes and aromatics, which after a hydrogenation step can be used as gasoline, jet fuel and diesel fuel blending components [13–15]. In addition to oligomerization and co-oligomerization reactions, the reaction mechanism includes skeletal and double bond isomerization, hydrogen transfer, cracking and cyclization reactions [13,16,17]. Furthermore, the product distribution greatly depends on the operating conditions (pressure, temperature and space time) [18–22] and the catalyst properties (acidity and shape selectivity) [1,2,23–27]. A key target in the olefin oligomerization processes is the use of

active, selective and stable catalysts [1,2,15]. The HZSM-5 zeolite based catalysts meet these features, though the shape selectivity of the HZSM-5 zeolite (MFI structure) limits the formation of hydrocarbons in the fraction of middle distillates. The deactivation of the HZSM-5 zeolite is related to both acid site and pore blocking, where the confinement of oligomer products plays a substantial role, due to their internal diffusion limitations [18,23,28].

There are different strategies to improve activity-selectivity-stability of the catalysts based on HZSM-5 zeolite [14,23,25,26,29]. Corma et al. [23] studied the effect of several modifications of HZSM-5 zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ –80) for the oligomerization of propylene and pentene at 200 °C and 40 bar. They reported that high Brønsted acid site density and small crystallites improved both propylene conversion and catalyst stability. In the oligomerization of pentene, additional mesoporosity formed by several desilication treatments was crucial in order to greatly improve catalyst stability. Silva et al. [27] tested several MFI-based micro/mesoporous zeotypes prepared via bottom-up approaches in the oligomerization of 1-butene at 250 °C and 40 bar. Overall, the zeotypes provided with a regular morphology, nanocrystallites and with a high level of mesoporosity performed better than the commercial zeolites for the production of middle distillates. We recently explored the capacity of HZSM-5 zeolite based catalysts for the oligomerization of 1-butene at low pressure (1.5 bar) [21] and high pressure conditions [22], for maximizing naphtha (C_5 – C_{11}) and diesel (C_{12} – C_{20}) yields. The catalysts

* Corresponding authors.

E-mail addresses: eva.epelde@ehu.es (E. Epelde), jose.valecillos@ehu.es (J. Valecillos).

<https://doi.org/10.1016/j.apcatb.2021.120076>

Received 21 January 2021; Received in revised form 23 February 2021; Accepted 25 February 2021

Available online 1 March 2021

0926-3373/© 2021 The Authors.

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Nomenclature

C_c, C_{ci}	Total coke content and i coke fraction content in the catalyst, respectively (wt%)
E_i	Activation energy for the combustion of each i coke fraction (kJ mol^{-1})
f_i	Mass fraction of each i coke fraction (wt%)
k_1, k_2	Kinetic constants for the combustion of coke type I and II, respectively ($\text{atm}^{-1} \text{h}^{-1}$)
$S_{\text{BET}}, S_{\text{micro}}$	BET specific surface area and micropore surface area, respectively ($\text{m}^2 \text{g}^{-1}$)
TOS	Time on stream (h)
W	Catalyst mass (g)
W/F_0	Space time (g h mol_C^{-1})
X	Conversion (%)

were prepared with a hierarchical structure of the particle, by agglomerating the zeolite in a mesoporous matrix (which also provides mechanical strength). Under the wide range of operating conditions studied (temperature, pressure, space time and partial pressure of butene in the feed), the catalysts reached a pseudo-steady state after 10–20 h on stream, by keeping a remarkable remaining constant activity after a transient state of rapid deactivation.

The understanding of the deactivation phenomenon in olefin oligomerization reactions is challenging because the conventional mechanisms of coke formation (catalyzed by acid sites) [5,8,30–32] are conditioned by the confinement of oligomers, which block the micropores and restrict their accessibility. The coke deposition is related to the limited diffusion of formed liquid products, which are rapidly retained in the micropores [23,33]. The presence of mesopores favors the diffusion of products, giving way to a better catalytic performance and less coke content [23,26,34].

Furthermore, the presence of confined species masks the results obtained in the analysis of spent catalysts by using conventional techniques. Additionally, it hinders the interpretation of the results based on the effect of the reaction conditions (temperature and pressure), as the aggregation state of the oligomer products (as liquid or gas) changes, and this affects their confinement capacity. Likewise, the protocols for removing the trapped oligomers and deposited coke on the acid sites should be defined for the catalyst regeneration.

This work focuses on studying the deactivation and regeneration of HZSM-5 zeolite based catalysts in the oligomerization of 1-butene at low and high pressure conditions (1.5–40 bar) [21,22], with the aim of reasonably understanding these phenomena, by distinguishing between soft coke (confined oligomers) and hard coke (more developed carbonaceous species). The existence of these two coke fractions was already established by Corma et al. [23]. Likewise, we have established the suitable conditions for the removal of soft coke (by sweeping) and hard coke (by combustion) in order to recover the catalyst properties. For this purpose, we have studied the effect of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the HZSM-5 zeolite and of the most relevant reaction conditions (especially temperature and pressure) on the amount and composition of coke deposited on the catalyst. In order to observe the differences between soft and hard coke, we have sequentially used different analysis techniques: temperature-programmed sweeping with N_2 (TPS- N_2) of soft coke; gas chromatography/mass spectrometry (GC/MS) of soluble coke in CH_2Cl_2 ; Fourier transform infrared (FTIR) spectroscopy alone or combined with temperature-programmed oxidation (TPO) of total coke and hard coke (remained after sweeping soft coke); and, TPO analysis of hard coke, whose removal requires combustion. The deterioration of the physical and acid properties of the used catalysts has been studied by using N_2 and NH_3 adsorption-desorption, respectively. Additionally, reaction-regeneration cycles have been carried out to establish the

suitable conditions for coke sweeping or combustion in order to assure a total regeneration of the catalysts.

2. Experimental

2.1. Catalysts

HZSM-5 zeolite based catalysts with three different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (30, 80 and 280) provided with a hierarchical porous structure have been used in this study. The procedure for catalyst preparation and characterization, as well as their main physical and acid properties are detailed in Section S1 and Table S1 of the Supporting Information.

2.2. Equipment and conditions for reaction and regeneration

Experimental runs were performed in an automated reaction system (PID Technol., Madrid, Spain) equipped with a stainless-steel fixed-bed reactor (internal diameter, 9 mm) and a piston pump (Gilson 307) for feeding 1-butene in liquid phase. A detailed description of the experimental setup used can be found elsewhere [21] and its flow diagram is shown in Fig. S1 (Section S2). Catalyst particles were mixed with inert SiC (particle diameter, 90 μm) so as to ensure a constant height (1.5–2 cm) and isothermal conditions in the catalytic bed [5]. Prior to reactions, catalysts were in situ pretreated at 450 °C for 3 h under atmospheric pressure in N_2 (50 $\text{cm}^3 \text{min}^{-1}$), in order to remove moisture from the catalyst. The following operating conditions were tested: 175–325 °C; 1.5–40 bar; space time, up to 6 $\text{g}_{\text{catalyst}} \text{h mol}_C^{-1}$ (as pressure is raised a lower space time is needed to reach the same conversion level); catalyst mass, 0.1–0.55 g; 1-butene (99 %, Air Liquide) diluted with inert gas N_2 (30 vol%.); and, time on stream (TOS) up to 20 h. In Section S3 of the Supplementary Information, the effect of the reaction pressure (1.5–40 bar) on the aggregation state (vapor or liquid) of the 1-butene feed (diluted in 30 vol% of N_2) and that of the most representative lumped products (non-converted butene, propylene, butane, $\text{C}_5\text{--C}_7$ olefins, $\text{C}_8\text{--C}_{11}$ olefins and C_{12+} olefins) has been analyzed at 225 °C (Table S2) and 275 °C (Table S3). The simulations have been carried out using PRO-II v.10 process simulation software using the Peng Robinson thermodynamic model to calculate the vapor and liquid molar fraction for each condition. The results shown in Table S2-S3 reveal that the 1-butene feed is in vapor phase under all the reaction conditions tested in our work. We can also predict that under high pressure conditions (above 10–20 bar) the oligomer products are partially present in liquid phase [24,35]. It should be noted that when the composition of the reaction medium comprises these oligomers, part of 1-butene will also be in liquid phase. The liquid state of a significant fraction of the reaction medium will condition the kinetic results (including product distribution and catalyst deactivation), as the oligomerization reaction steps will be limited by the diffusion of the different compounds of the reaction medium. Furthermore, the liquid state of the oligomers (especially of the heaviest ones) will facilitate their confinement, as part of soft coke. This situation also takes place in the aromatic alkylation reactions [36].

The procedure for product analysis and the reaction indices (conversion, yield and selectivity of each lumped products) are summarized in Section S4 of the Supporting Information.

With the aim of studying the catalyst regeneration, reaction-regeneration cycles were carried out following two steps for the in situ regeneration of the catalysts (after sweeping with N_2 at the reaction temperature): (1) sweeping with N_2 at 400 °C (1 h); and, (2) coke combustion with a continuous flow of air (40 $\text{cm}^3 \text{min}^{-1}$), following a heating ramp of 10 °C min^{-1} up to 500 °C, which was kept for 0.5 h.

2.3. Used catalyst characterization

Prior to characterization, all the used catalyst samples were firstly swept in the reactor with 30 $\text{cm}^3 \text{min}^{-1}$ of N_2 at the reaction temperature

for 20 min in order to ensure the reproducibility of analyses [37,38]. The deterioration of physical and acid properties of the coked catalyst samples were measured using the same methods applied for fresh catalyst characterization (Section S1). Temperature-programmed sweeping with N_2 (TPS- N_2) of confined oligomers (soft coke) and temperature-programmed oxidation (TPO) with air of remaining coke (hard coke) were carried out in a TGA Q5000TA thermobalance (Thermo Scientific) as previously reported [22]. For the TPS- N_2 analysis, ~15 mg of sample were rapidly treated with N_2 at 200 °C for 15 min in order to remove adsorbed water, and subsequently heated up to 400 °C (10 °C min^{-1}) in $40\text{ cm}^3\text{ min}^{-1}$ of N_2 and kept for 20 min. TPO analysis of remaining hard coke was carried out by introducing $40\text{ cm}^3\text{ min}^{-1}$ of air, with a heating ramp of 3 °C min^{-1} up to 575 °C, which was kept for 1 h (to ensure complete combustion of coke). The procedure for quantifying the amount of each fraction of hard coke and their combustion kinetics is summarized in Section S5 of the Supplementary Information.

In order to identify the total retained species (total coke) on the used catalysts, a soluble coke extraction with CH_2Cl_2 was carried out [39–42]. Firstly, ~100 mg of used catalyst sample were dissolved in HF (Merck, 40 %), with a sample/HF ratio of 10 g cm^{-3} in a Teflon container for 1 h. Afterward, the acid solution was neutralized with a NaOH solution. Secondly, the organic phase was extracted by adding ~ 3 cm^3 of CH_2Cl_2 (Sigma-Aldrich, 99.8 %). Finally, the liquid sample (extract) was analyzed in a GC-MS (Shimadzu QP2010) and GC-2010 gas chromatograph.

FTIR and combined FTIR-TPS- N_2 and FTIR-TPO spectroscopic measurements were carried out for the analysis of total and hard coke (after the sweeping treatment) in a Nicolet 6700 spectrophotometer (ThermoFisher Scientific) using a transmission cell (60 scans, and resolution of 4 cm^{-1}). The used catalyst samples (30 mg) were supported on a KBr (300 mg) disc and placed in the chamber, where they were outgassed at 200 °C under vacuum to remove water and adsorbed contaminants, and FTIR spectra were taken. For the TPS- N_2 , the sample was heated up to 400 °C at 10 °C min^{-1} with N_2 ($30\text{ cm}^3\text{ min}^{-1}$) and kept isothermally for 20 min. Subsequently, for the TPO, the sample was cooled down to 100 °C, the flow was switched to air ($60\text{ cm}^3\text{ min}^{-1}$) at 100 °C, and the temperature was raised up to 550 °C at 5 °C min^{-1} and kept isothermally for 1 h for the complete combustion of hard coke. For both TPS- N_2 and TPO measurements, FTIR spectra were recorded every 5 min; and, simultaneously, effluent gas was analyzed using a mass spectrometer (OmniStar ThermoStar) recording various mass per charge (m/z) signals related to hydrocarbons and CO_2 .

3. Results

The most significant results of this work focus on the characterization of coke, as the main responsible for catalyst deactivation; and, on the catalyst regeneration. The initial hypothesis, which is checked in this work, is that coke comprises two types of compounds, as previously established [23]: (1) soft coke, constituted by the oligomers confined in the catalyst porous structure (particularly in the matrix); and, (2) hard coke. This latter fraction of coke is more structured and will be formed by condensation and hydrogen transfer reactions, which are catalyzed by the acid sites of the HZSM-5 zeolite and will lead to the formation of polycyclic aromatic structures (mainly bicyclic and tricyclic aromatics) [33,43,44].

3.1. Effect of the reaction conditions on the catalyst deactivation

The effect of the reaction conditions on the butene conversion and product yield and selectivity has been extensively studied in previous works at low pressure [21] and high pressure [22] conditions. Herein, we briefly report in Section S6 of the Supporting Information the effect of the reaction conditions on the catalyst stability (deactivation) to contribute for a better understanding of the main causes of deactivation.

As an example of the extensive kinetic study, Fig. S2 shows the

evolution with time on stream of the conversion of 1-butene for the catalysts prepared with different SiO_2/Al_2O_3 ratios (graphs a and b, for low and high pressure, respectively) and tested under different temperatures (graph c) and pressures (graph d). The evolution with time on stream of the main oligomer yields ($C_8.C_{11}^-$, $C_5.C_7^-$ and C_{12}^+) under these conditions are shown in Figs. S3–S7. The interpretation of these results requires to firstly consider the effect of the variables studied on the reaction extent (which will affect the concentration of the compounds in the reaction medium) and on the aggregation state of the oligomer products as gas or liquid.

As shown in Figs. S2a (1.5 bar) and S2b (40 bar), the highest decrease in butene conversion is observed for the lowest SiO_2/Al_2O_3 ratio. This fact is attributed to the highest acid site density and acid strength of HZ-30 catalyst, which favors the formation of oligomers [21–23,45], which are partially confined in the catalyst. It should be noted that at low pressure conditions (Figure S2a), the deactivation level is lower at 325 °C than at 275 °C (Fig. S2c), which is related to a higher evaporation of oligomers; and, thus, to a lower confinement of these species in the catalyst. Furthermore, above 275 °C, secondary reactions (mainly cracking and hydrogen transfer) are favored, giving way to the formation of lighter oligomers and paraffins, as we previously reported [21]. The reaction pressure (Fig. S2d) also plays a significant role on the catalyst stability, being the decrease of the butene conversion higher as the pressure is raised, due to the higher concentration of heavier oligomers (as it will be seen later). Interestingly, the results for all the catalysts and tested conditions show a fast initial deactivation period, followed by a pseudo-steady state after 4–5 h on stream, in which an almost constant remaining activity is kept (except for 40 bar (Fig. S2d)). This behavior has also been reported in the literature [18,20,28], and it is associated with a deactivation mechanism in which a pseudo-equilibrium state is reached in the deposition of the species responsible for deactivation. The effect of pressure and temperature could be related to the aggregation state of components in the reaction medium. At 225 and 275 °C and above 10–20 bar, most of oligomers formed at the beginning of the reaction remain adsorbed in the catalyst in liquid phase, as previously checked by simulations in PRO II software (Table S2–S3). Such liquid oligomers will cause the blockage of the zeolite micropores and lead to a rapid deactivation at the beginning of the reaction.

3.2. Soft coke

The amount of soft coke in the spent catalysts has been determined by TPS- N_2 at 200–400 °C with a ramp of 10 °C min^{-1} . Under these conditions, the removed species are oligomers (soft coke) confined in the mesoporous matrix of the catalyst, whereas the most developed carbonaceous species (hard coke), mainly confined in the micropores of the zeolite, would require higher temperatures for sweeping or even a combustion step for their removal. Fig. 1 shows the TPS- N_2 profiles at different reaction pressures (Fig. 1a) and reaction temperatures (Fig. 1b). As seen, by increasing the reaction pressure the amount of soft coke notably increases from 5.7 wt% at 1.5 bar to 19.4 wt% at 40 bar, which could be related to the higher formation of heavy oligomers (Fig. S6) and to their lower volatility, which favor the confinement in the catalyst particle.

Likewise, an increase in the reaction temperature (Fig. 1b) gives way to an increase of the soft coke content, from 9.5 wt% at 150 °C to 19.5 wt% at 275 °C. This effect is more significant above 200 °C, which is coherent with the higher amount of heavier oligomers formed at higher temperature (Fig. S7). Interestingly, the maximum temperature of the desorption peak shifts toward higher temperature (from 277.8 °C for 150 °C to 317.7 °C for 275 °C) as the reaction temperature is raised. This could be related to the higher molecular weight of heavy oligomers that need higher temperatures for their sweeping [24].

In order to explore the nature of the removed species, we carried out the TPS- N_2 of soft coke in a used HZ-30 catalyst sample (deactivated at

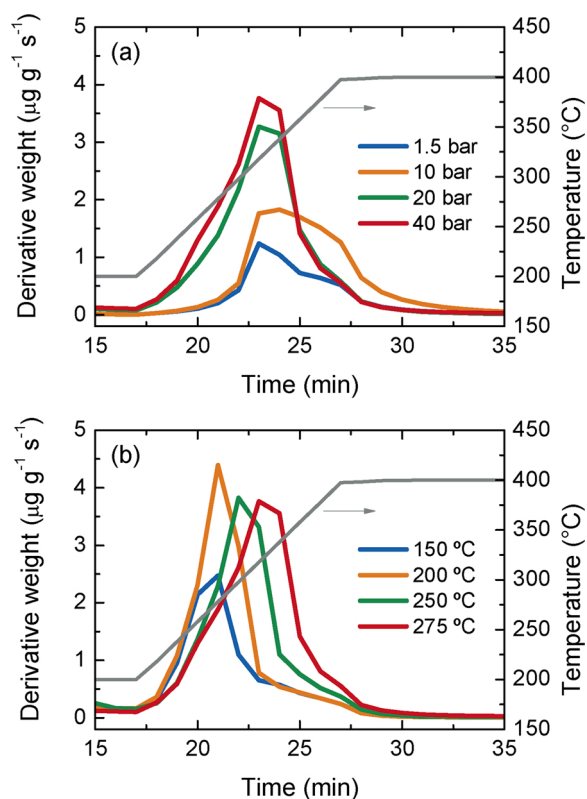


Fig. 1. Effect of pressure (a) and temperature (b) on the TPS-N₂ profiles for the used HZ-30 catalyst. Reaction conditions: space time, 2 g_{catalyst} h mol_C⁻¹; (a) 275 °C; (b) 30 bar.

275 °C and 10 bar) using in situ FTIR spectroscopy of the used catalyst with simultaneous analysis of the gaseous effluent using MS. This sweeping treatment at the reaction temperature aims to simulate the sweeping of soft coke throughout the reaction. The evolution with increasing temperatures of the differential FTIR spectra (the spectrum of the deactivated catalyst is subtracted) is shown in Fig. S8. The main FTIR bands that show an evolution with increasing temperatures are those related to oligomers (1378, 1461, 1608, 2856, 2871, 2923, 2930, 2960 cm⁻¹) and some bands also related to monocyclic aromatics (1504 and 1608 cm⁻¹) [43]. The most prominent MS signals (Fig. 2a) correspond to characteristic fragments of oligomers ($m/z = 28, 41, 43, 55, 57$), while there is a slight presence of MS signals related to alkylated aromatics ($m/z = 78, 91$). The evolution with time (and increasing temperatures) of the derivative of the maximum intensity (dl/dt) of selected FTIR bands (1462, 1608, 2871 and 2960 cm⁻¹) (Fig. 2b) indicates the removal of these species and matches the evolution of the MS signals very satisfactorily.

The results in Figs. 1 and 2 make evident that the majority of the carbonaceous materials on the catalysts are confined oligomers (soft coke), whose presence provides the coke with a high degree of heterogeneity and thermal instability, making difficult the analysis of coke and used catalysts. Thus, when we compare the physical properties of the used catalysts (Table 1) with those of fresh catalysts (Table S1) we observe an apparent severe deterioration of the catalyst properties that does not correspond to the deactivation behavior shown in Fig. S2. An apparent full blockage of the micropores is observed for the HZ-30 and HZ-80 catalysts, and an almost full blockage for the HZ-280 catalyst after 10–20 h on stream. Mesopore volume is also reduced, but to a lesser extent, suggesting that the pore blockage by coke formation is more pronounced in the micropores rather than in the mesopores, which is common in the zeolite based catalysts [26,33,35]. Thus, a substantial decrease in BET surface is observed for the used catalysts. It must be highlighted that the degree of pore blocking on HZSM-5 zeolite observed

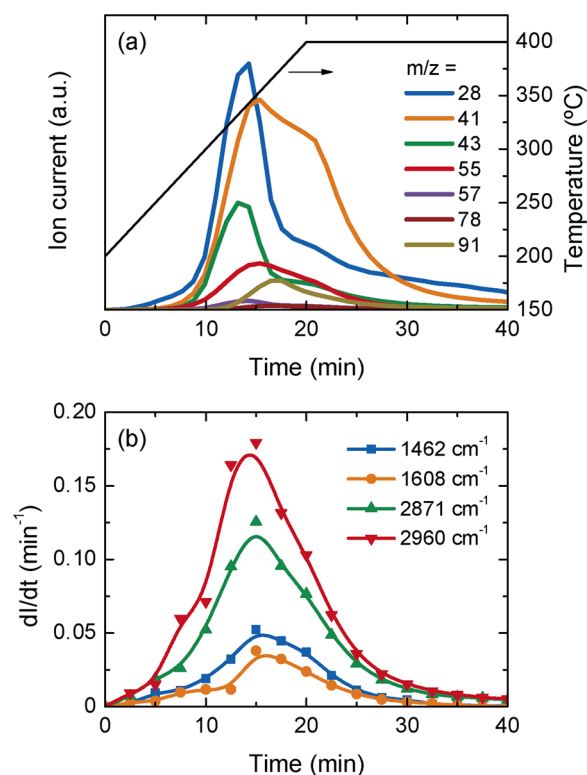


Fig. 2. Evolution with time (and increasing temperatures) during the TPS-N₂ of soft coke of the: (a) MS signals related to oligomers ($m/z = 28, 41, 43, 55, 57$) and alkylated aromatics ($m/z = 78, 91$). (b) Derivative of the maximum intensity (dl/dt) of selected FTIR bands (1462, 1608, 2871 and 2960 cm⁻¹). Reaction conditions: HZ-30 catalyst; 275 °C; 10 bar; space time, 2 g_{catalyst} h mol_C⁻¹.

Table 1

Physical properties of the catalysts used under different conditions. Reaction temperature, 275 °C. Sweeping conditions in the reactor before analysis: 275 °C (reaction temperature), 20 min.

SiO ₂ / Al ₂ O ₃ molar ratio	Reaction conditions			S _{BET} (m ² g ⁻¹)	S _{micro} (m ² g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)
	P (bar)	W/ F ₀ ^a	TOS (h)				
30	1.5	6	20	73	0	0.22	0
	40	2	10	37	0	0.15	0
80	1.5	6	20	91	0	0.27	0
	40	2	10	50	0	0.16	0
280	1.5	6	20	100	6	0.27	0.003
	40	2	10	66	0	0.22	0

^a in g_{catalyst} h mol_C⁻¹.

is not common for this zeolite in the conversion of hydrocarbons [46, 47], oxygenates [5] and polyolefins [31,44], unless for full deactivation conditions. However, our catalysts have shown a stable remaining catalytic activity (Fig. S2). Therefore, this apparent pore blockage could be related to the presence of soft coke [33,35] that, under the conditions of the N₂ adsorption-desorption analyses (-194 °C), have blocked the access of N₂. However, under the reaction conditions, the remaining catalytic activity can be related with a certain degree of soft coke mobility, which could facilitate the access of butene to the acid sites. The difficulty on the analysis of spent catalysts in the presence of soft coke has also been reported by Henry et al. [48].

Likewise, the determination of the remaining acid properties in the used catalysts by using TPD-NH₃ (Fig. 3) evidences that the presence of soft coke affects the measurements. The catalysts exhibit a sharp decrease in their total acidity respect to the one of fresh catalyst, where

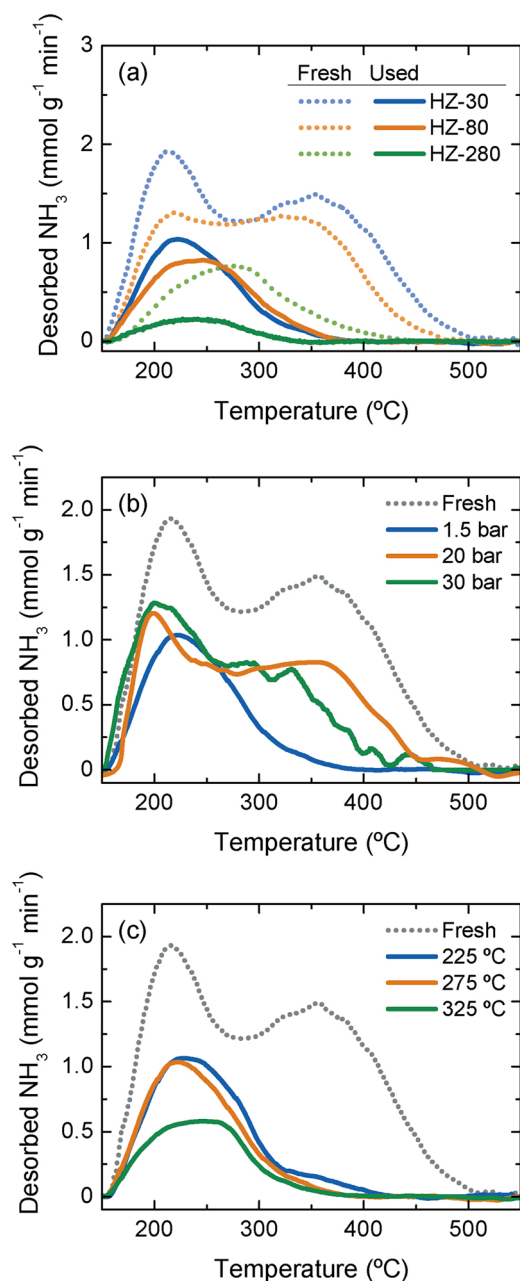


Fig. 3. Deterioration of the acidity (TPD-NH₃ profiles) of the catalysts used under different conditions. (a) Different SiO₂/Al₂O₃ of the zeolite, 275 °C, 1.5 bar, 6 g_{catalyst} h mol_C⁻¹. (b) Different pressure, 275 °C, 2 g_{catalyst} h mol_C⁻¹. (c) Different temperature, 1.5 bar, 6 g_{catalyst} h mol_C⁻¹. Sweeping conditions before analysis: 275 °C (reaction temperature), 20 min.

the strong acid sites (peak at high temperature), related to the Brønsted acid sites and preferentially located in the interior of the zeolite micropores [26], are practically blocked. A substantial decrease in the acid sites of moderate and weak acidity (broad peak at lower temperature), which are present in the matrix, is also observed, but to a lesser extent in comparison to the strong acid sites. For the HZ-280 catalyst, with a low amount of acid sites, the remaining total acidity is very low.

It should be noted that the apparent blockage of the acid sites is lower than the one observed for the micropore volume (Table 1). This difference could be explained because the diffusion of NH₃ at the adsorption temperature (150 °C) will be presumably higher than that of N₂ at -196 °C.

3.3. Analysis of total coke

3.3.1. GC/MS of soluble coke

The chromatograms of the compounds extracted with CH₂Cl₂ from the total coke of used HZ-30 catalyst at 1.5 and 40 bar are depicted in Fig. S9. Under both reaction pressures, the identified compounds are mainly olefins and some methylated monocyclic aromatics. These results are in good agreement with those species identified by TPS-N₂/MS (Fig. 2). Particularly, at 40 bar, a high amount of retained hydrocarbons is observed, which consist of long chain alkenes up to C₂₀, whose formation is favored at high pressure. In addition, the coke deposited at 1.5 bar shows a higher amount of aromatic compounds, which can be formed by secondary reactions (cracking, hydrogen transfer) from shorter hydrocarbon chains than those formed at high pressure.

3.3.2. FTIR spectroscopy

Fig. 4 shows the two most important regions of bond vibration in the FTIR spectra of total coke deposited on the HZ-30 catalysts at 1.5 and 40 bar. The vibrations in the region of 3200–2700 cm⁻¹ mostly correspond to olefins (asymmetric and symmetric stretching) and monocyclic aromatics, while the vibrations in the region of 1650–1350 cm⁻¹ correspond to aromatics and some bending modes of aliphatics (olefins). A detail assignment of the observed bands based on the literature [31,32,43,49,50], is summarized in Table S4.

An increase in reaction pressure gives way to a strong growth of CH₂ and CH₃ absorption bands at 2960, 2927, 2870 cm⁻¹, 1462 and 1450 cm⁻¹, corresponding especially to olefins [44,48,49,51]. Under both conditions, an intense band at 1608 cm⁻¹ is observed, which is characteristic of olefins too [44]. In the case of coke deposited at 1.5 bar, the bands at 1508 and 1572 cm⁻¹ are more pronounced, which is indicative of aromatic species present in the soluble fraction of hard coke, due to the secondary cracking and hydrogen transfer reactions. However, under both pressure conditions, the stretching bands of C–H for aromatics (3000–3200 cm⁻¹) are not significant, which means that the aromatic structures should be highly alkylated [48].

Fig. 5 shows the FTIR spectra of coke deposited on the HZ-30 catalysts at 10 bar, before and after sweeping with N₂ at 550 °C. As we previously reported using TPS-N₂ of the used catalysts (Section 3.2), a great amount of retained oligomers (soft coke) are removed after this sweeping treatment, which is evidenced by the decrease in the intensities of the CH₂ and CH₃ absorption bands assigned to these species (2960, 2927, 2870 cm⁻¹, 1462 and 1450 cm⁻¹). Interestingly, a broad band at ~1570–1590 cm⁻¹ is observed after sweeping, characteristic of more evolved polycyclic aromatic compounds remained as hard coke [8,47,50,52]. Although sweeping at high temperature (550 °C) is sufficient for removing soft coke, this procedure also modifies the structure of the remaining species, as a consequence of the phenomenon of coke aging in

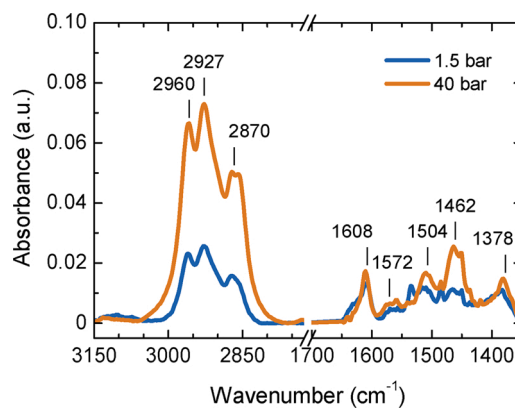


Fig. 4. Effect of pressure on the FTIR spectra of the used HZ-30 catalyst. Reaction conditions: 275 °C; space time, 6 g_{catalyst} h mol_C⁻¹. Sweeping of the catalyst before analysis: 275 °C (reaction temperature), 20 min.

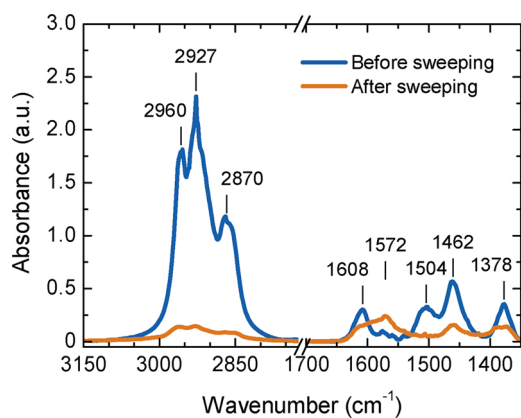


Fig. 5. Effect of sweeping treatment with N_2 ($550\text{ }^\circ\text{C}$) on the FTIR spectra of the used HZ-30 catalysts. Operating conditions: $275\text{ }^\circ\text{C}$, 10 bar, $2\text{ g}_{\text{catalyst}}\text{ h mol}_C^{-1}$. Sweeping conditions before analysis: $275\text{ }^\circ\text{C}$ (reaction temperature), 20 min.

which dehydrogenation and polymerization reactions take place [38, 52]. These results highlight the importance of coke aging in the step of sweeping of soft coke, which should be taken into consideration for the catalyst regeneration. The notable recovery of the specific surface of the catalyst ($238\text{ m}^2\text{ g}^{-1}$ after the sweeping treatment and $266\text{ m}^2\text{ g}^{-1}$ for the fresh catalyst) and its acidity ($0.34\text{ mmol}_{\text{NH}_3}\text{ g}^{-1}$ and $0.38\text{ mmol}_{\text{NH}_3}\text{ g}^{-1}$, respectively) gives evidence of the impact of soft coke on the catalyst activity loss. The main cause for not achieving a complete recovery of the physical and acid properties is the presence of hard coke on the acid sites. In addition, we have also checked that the H/C ratio of coke before this high temperature sweeping treatment shows values of ~ 1.9 , which is coherent with the high content of oligomers (soft coke). After the sweeping treatment, the H/C ratio values decreases down to ~ 0.75 .

3.4. Analysis of hard coke

The amount of hard coke was determined by the TPO of the remaining species after the TPS- N_2 (Section 3.2), and, therefore, after the removal of soft coke. Fig. 6 shows the effect of the reaction temperature on the TPO profiles for the HZ-30 catalyst used at 1.5 bar (Fig. 6a) and 40 bar (Fig. 6b). Two fractions of hard coke are distinguished according to the combustion temperature: coke I, burning at low temperature ($420\text{--}440\text{ }^\circ\text{C}$), and coke II, burning at higher temperature ($520\text{--}550\text{ }^\circ\text{C}$). The presence of these coke fractions is common in different reactions catalyzed by HZSM-5 zeolites. Coke I is deposited in the catalyst matrix (mesoporous structure), which facilitates its combustion at lower temperatures, whereas coke II is deposited in the micropores, and, therefore, its combustion takes place at higher temperatures because of the constraints imposed by shape selectivity [5, 31,32].

It is important to highlight the high content of hard coke at 1.5 bar (Fig. 6a) coinciding with the low content of soft coke at this low pressure (Fig. 1a), which indicates that low pressures favor the formation of hard coke, due to secondary reactions of cracking and hydrogen transfer. At low pressure conditions (1.5 bar, Fig. 6a) it is noteworthy to mention the increase in total coke content and, particularly, in the amount of coke II as the temperature is raised, which is consistent with the higher velocity of oligomerization reactions and secondary reactions to form hard coke. The latter effect is especially relevant, in view of the increase in the peak of coke II observed while increasing temperature. This effect is also observed at 40 bar (Fig. 6b), but the lower coke content obtained under these conditions makes this comparison difficult.

The amount of two coke fractions has been quantified by TPO analysis (Section S5). The results summarized in Table 2 give evidence of the higher reactivity of coke I (higher kinetic constant and lower

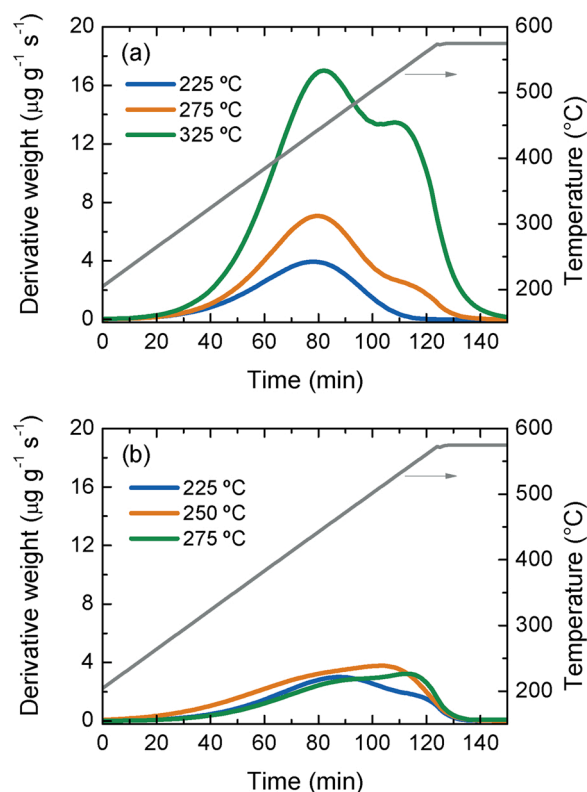


Fig. 6. Effect of reaction temperature on the TPO profiles for the combustion of the hard coke deposited on HZ-30 catalyst. Reaction conditions: (a) 1.5 bar, $6\text{ g}_{\text{catalyst}}\text{ h mol}_C^{-1}$, TOS = 10 h. (b) 40 bar, $2\text{ g}_{\text{catalyst}}\text{ h mol}_C^{-1}$, TOS = 20 h. Sweeping conditions before analysis: $400\text{ }^\circ\text{C}$, 20 min.

Table 2

Effect of the reaction temperature on the hard coke content (C_c), coke I fraction (f_{c1}) and on the kinetic parameters of the combustion of each hard coke fraction deposited on the HZ-30 catalyst at 1.5 bar and 40 bar and different reaction temperatures. The results correspond to the TPO profiles plotted in Fig. 6.

T ($^\circ\text{C}$)	C_c (wt %)	f_{c1} (%)	Coke I		Coke II	
			k_1 (atm^{-1} h^{-1})	E_1 (kJ mol^{-1})	k_2 (atm^{-1} h^{-1})	E_2 (kJ mol^{-1})
1.5 bar^a						
225	1.39	88.8	21 ± 3	45 ± 1	7 ± 1	162 ± 18
275	2.13	78.2	22 ± 2	55 ± 1	9 ± 1	217 ± 12
325	6.21	52.2	48 ± 3	62 ± 1	9 ± 0	119 ± 4
40 bar^b						
225	1.05	87.5	25 ± 3	68 ± 5	3 ± 1	244 ± 33
250	1.13	71.9	22 ± 5	58 ± 4	4 ± 1	230 ± 13
275	1.52	73.4	21 ± 4	68 ± 9	4 ± 1	221 ± 13

^a space time, $6\text{ g}_{\text{catalyst}}\text{ h mol}_C^{-1}$.

^b space time, $2\text{ g}_{\text{catalyst}}\text{ h mol}_C^{-1}$.

apparent activation energy) in comparison to coke II. The increase in the activation energy of the combustion of coke I deposited at 1.5 bar as the reaction temperature is raised could be explained by the higher extent of the condensation reactions. This effect is not observed for coke II. The maximum apparent activation energy at $250\text{ }^\circ\text{C}$ may indicate that above this temperature, and for the formation of this coke fraction, the presence of light oligomers accessing the microporous structure rather than their higher condensation rate is more important. The effect of temperature on the volatility of coke precursors is attenuated at 40 bar, and, thus, at high pressure conditions, the kinetic parameters of coke combustion, and presumably coke composition, slightly vary in the $225\text{--}275\text{ }^\circ\text{C}$ temperature range.

Fig. 7 shows the TPO profiles corresponding to the combustion of

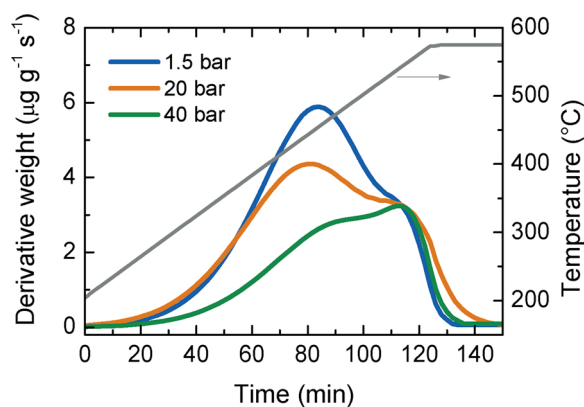


Fig. 7. Effect of pressure reaction on the TPO profiles for the coke deposited on HZ-30 catalyst. Reaction conditions: 275 °C, 2 g_{catalyst} h mol_C⁻¹; TOS = 20 h. Sweeping conditions before analysis: 400 °C, 20 min.

hard coke deposited on the HZ-30 catalyst under different pressure conditions. A raise in pressure gives way to a decrease in hard coke deposition, as summarized in Table 3, from 2.91 wt% (1.5 bar) to 1.52 wt% (40 bar). This could be linked to the lower concentration of butene and volatile light oligomers in the reaction medium, which are presumably more active in the formation of hard coke. Furthermore, the higher content of soft coke would partially suppress the reactions of hard coke formation, as the diffusion of butene and volatile light oligomers and their contact on acid sites will be hindered by the components in liquid phase.

It must be noted that the hard coke content in Tables 2 and 3 is lower than that reported by Coelho et al. [18] for the oligomerization of 1-butene on a HZSM-5 zeolite of SiO₂/Al₂O₃ = 30 for TOS of 21 min and a butene partial pressure of 0.5 bar. This could be related to the agglomeration of the zeolite (50 wt%) on a matrix, while they used a pure zeolite as catalyst. Moreover, the severe conditions of the sweeping step (TPS-N₂) prior to the TPO measurements in this work condition the composition of remaining hard coke and its combustion.

The TPO of hard coke in the HZ-30 catalyst (deactivated at 275 °C and 10 bar and swept by TPS-N₂) was also studied by using *in situ* FTIR spectroscopy and with simultaneous analysis of the gaseous effluent using MS. During this experiment, we observed the evolution of the FTIR bands related to aromatics (1462 and 1572 cm⁻¹) and some aliphatics corresponding to oligomers or substituents of aromatics (1378, 2871, 2930, 2960 cm⁻¹). Fig. 8 shows the evolution with time (and increasing temperature) of the MS signal corresponding to CO₂ (*m/z* = 44) (Fig. 8a) and of the derivative of the maximum intensity (*dI/dt*) of selected FTIR bands (1378, 1462, 1572 and 2871 cm⁻¹) (Fig. 8b). Regarding the evolution of these bands, first, the lighter components of hard coke (2871 cm⁻¹) are removed by combustion at lower temperatures giving rise to the CO₂ signal. These components have an aliphatic nature and may be attributed to remaining oligomers or substituents of aromatics that are easily removed at the TPO conditions. Second, the bands characteristics of aromatics (1378, 1462 and 1572 cm⁻¹) show a negative evolution at lower temperatures (at the time that the lighter species

Table 3

Effect of reaction pressure on the hard coke content (*C_c*), coke I fraction (*f_{c1}*) and on the kinetic parameters of the combustion of each coke fraction deposited on the HZ-30 catalyst. The results correspond to the TPO profiles plotted in Fig. 7.

Pressure (bar)	<i>C_c</i> (wt %)	<i>f_{c1}</i> (wt %)	Coke I		Coke II	
			<i>k₁</i> (atm ⁻¹ h ⁻¹)	<i>E₁</i> (kJ mol ⁻¹)	<i>k₂</i> (atm ⁻¹ h ⁻¹)	<i>E₂</i> (kJ mol ⁻¹)
1.5	2.91	78.2	22 ± 2	55 ± 1	9 ± 1	217 ± 12
20	1.83	85.8	34 ± 5	48 ± 2	7 ± 1	230 ± 11
40	1.52	73.4	21 ± 4	68 ± 9	4 ± 1	221 ± 13

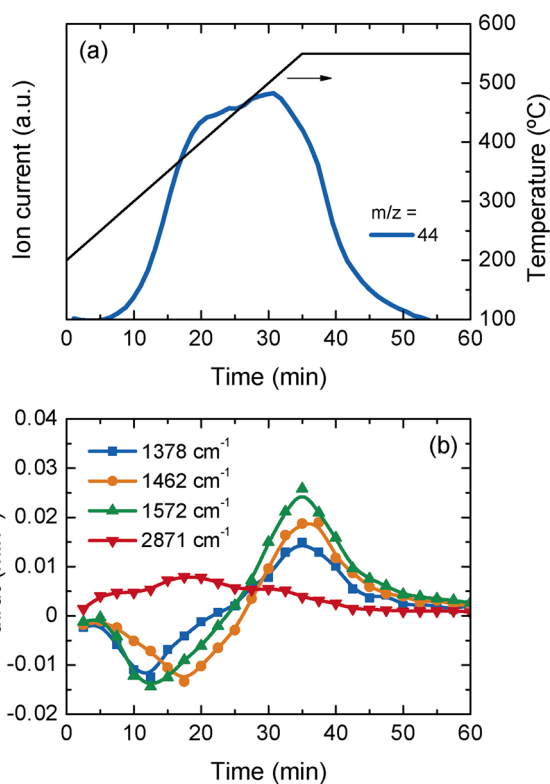


Fig. 8. Evolution with time (and increasing temperatures) of the: (a) CO₂ MS signal. (b) Derivative of the maximum intensity (*dI/dt*) of selected FTIR bands, during the TPO analysis of the hard coke deposited on HZ-30 catalyst. Reaction conditions: 275 °C, 10 bar, 2 g_{catalyst} h mol_C⁻¹, TOS = 20 h. Sweeping conditions before analysis: 400 °C, 20 min.

are removed) and a positive evolution at higher temperatures. The negative evolution indicates that these species partially evolve in the catalyst without being removed yet, indicating the occurrence of an aging process that leads to the formation of more developed/condensed polycyclic aromatics [38,52]. Upon further increases of the temperature (heating ramp), these species show a positive evolution indicating that they are eventually removed by combustion.

3.5. Catalyst regeneration

A key factor in the feasibility of the butene oligomerization is the catalyst regeneration for the use in successive reaction-regeneration cycles with a reproducible behavior. Although a complete combustion of deposited coke has been observed at 575 °C in the TPO analysis (Section 3.3), the total recovery of the catalytic activity (catalyst regeneration) must be checked. Hence, reaction-regeneration cycles have been performed, following the procedures described in Section 2.2

According to the TPS-N₂ results of the used catalysts (Section 3.2), soft coke can be easily removed after sweeping. Hence, a regeneration strategy based on sweeping with N₂ (40 cm³ min⁻¹) at 400 °C for 1 h has been analyzed. We have checked that this is the minimum temperature for totally removing soft coke, in agreement with the TPS-N₂ profiles shown in Fig. 3. This sweeping is a prior step to coke combustion, aiming to remove most of the compounds confined within the catalyst porous structure, whose uncontrolled combustion may generate hot spots and irreversible deterioration of catalyst acidity. The results corresponding to the reaction-sweeping cycles for a HZ-30 catalyst under severe deactivation conditions are plotted in Fig. 9. As observed, by removing confined oligomers the initial activity is almost recovered as well as the initial product yield. This observation reveals that the main cause of the catalyst deactivation observed in the early stages of the reaction is the

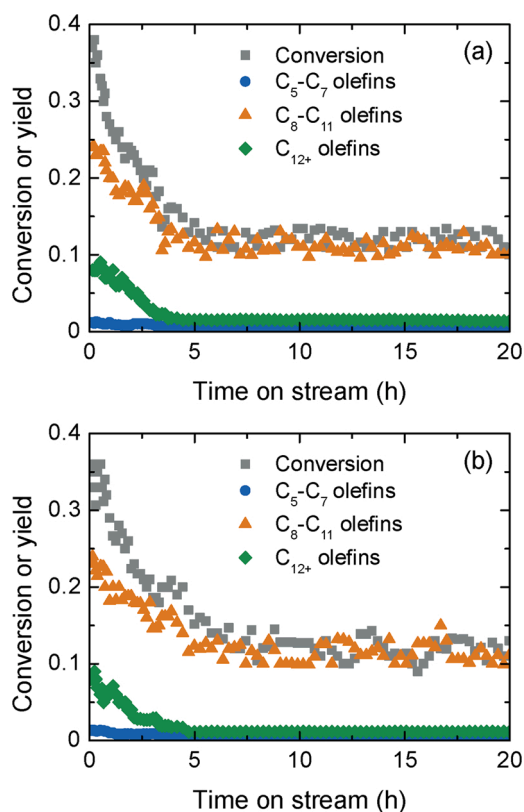


Fig. 9. Evolution of butene conversion and C₅-C₇, C₈-C₁₁ and C₁₂⁺ fraction yield with time on stream in a reaction-sweeping cycle on HZ-30 catalyst. (a) First reaction (fresh catalyst); (b) Second reaction (regenerated catalyst). Reaction conditions: 250 °C, 40 bar, 1 g_{catalyst} h mol⁻¹. Regeneration conditions: Sweeping with a continuous flow of N₂ at 400 °C (40 cm³ min⁻¹).

confinement of oligomers (soft coke). Around 90 % of the carbonaceous species retained on the spent catalysts can be attributed to this soft coke. The incomplete recovery of the initial activity may be caused by the presence of hard coke formed during the reaction and by the aging of soft coke to form hard coke under sweeping at high temperature [38, 52]. Thus, hard coke that remains after sweeping (Section 3.3) will require a subsequent combustion step for its complete removal.

Fig. 10 shows the evolution with time on stream of butene conversion and of the yields corresponding to the main olefin fractions (C₅-C₇, C₈-C₁₁ and C₁₂⁺) with the fresh catalyst (Fig. 10a) and after a regeneration treatment (Fig. 10b) based on the combustion of coke with a continuous flow of air (40 cm³ min⁻¹), following a heating ramp of 10 °C min⁻¹ from 275 °C up to 500 °C (at which the CO₂ formation is negligible). As seen, the catalyst recovers its activity and the evolution of conversion and olefin yields with time on stream with the regenerated catalyst are similar to those obtained with the fresh catalyst. These results give also evidence of the high hydrothermal stability of this catalyst. It must be pointed out that the degradation of the acidic sites in the regeneration (by dehydroxylation of Brønsted sites to Lewis) is avoided, as the catalyst calcination temperature for its equilibration (575 °C) is not exceeded during regeneration (at 500 °C) [53,54]. Furthermore, the agglomeration of the zeolite with a matrix favors the dissipation of the heat generated during the coke combustion.

4. Conclusions

The use of different techniques for the analysis of the spent catalysts in a wide range of reaction conditions has allowed us to obtain a general view of the complex phenomenon of catalyst deactivation in the oligomerization of olefins. The results presented in this work correspond to

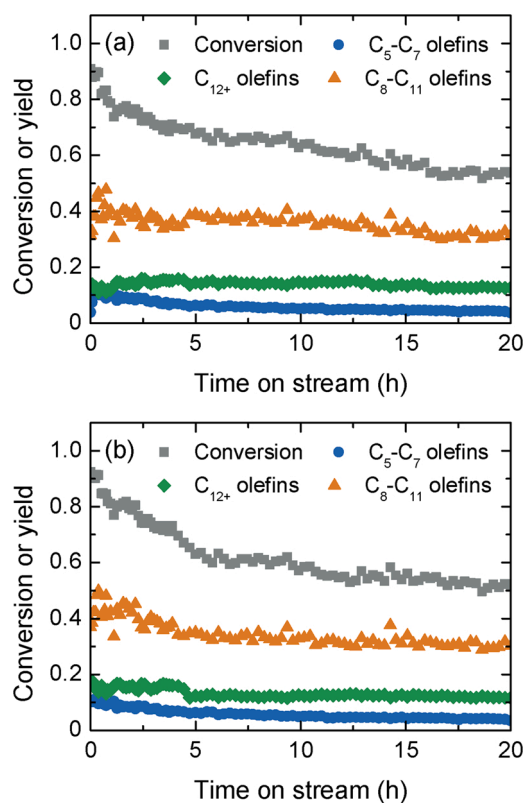


Fig. 10. Evolution of butene conversion and C₅-C₇, C₈-C₁₁ and C₁₂⁺ fraction yield with time on stream in a reaction-regeneration cycle on HZ-30 catalyst. (a) First reaction (fresh catalyst); (b) Second reaction (regenerated catalyst). Reaction conditions: 275 °C, 40 bar, 2 g_{catalyst} h mol⁻¹. Regeneration conditions: Coke combustion with a continuous flow of air (40 cm³ min⁻¹), following a heating ramp of 10 °C min⁻¹ from 275 °C up to 500 °C.

the oligomerization of 1-butene on HZSM-5 zeolites embedded in a mesoporous matrix of γ -Al₂O₃ and α -Al₂O₃, but the conclusions are of general interest for making progress on the improvement of the catalyst stability for the oligomerization of other olefins.

The main cause of catalyst deactivation is the blockage of the pores of the matrix and the zeolite by soft coke that is composed of oligomers that are the primary reaction products. The reaction pressure and temperature influence the formation rate, composition and aggregation states (liquid or gas) of these oligomers, which affects their capacity of being confined in the porous structure. Furthermore, it also contributes to the catalyst deactivation the presence in the matrix and in the zeolite micropores of hard coke. This coke is constituted by olefinic and aromatic species that are formed by secondary reactions catalyzed by the acid sites (in which the hydrogen transfer reaction plays a key role). The sweeping of soft coke with an inert gas (N₂) at high temperature also contributes to the formation of this hard coke by an aging phenomenon. The combustion of the hard coke fraction in the catalyst matrix is favored by the accessibility of air into the mesoporous structure and probably by the more hydrogenated and less structured nature of this coke. The amount of hard coke deposited in the zeolite micropores is lower (which is characteristic for HZSM-5 zeolites), and as a higher combustion temperature, a lower kinetic constant and a higher apparent activation energy for its combustion in comparison to the combustion of hard coke deposited in the matrix.

A catalyst regeneration procedure based on sweeping with an inert gas at high temperature almost totally recovers the catalyst activity. However, a complete catalyst regeneration requires the combustion of coke with air at a relative low temperature (500 °C). Hence, a reproducible behavior of the catalytic performance in successive reaction-regeneration cycles has been achieved in the oligomerization of 1-

butene.

CRedit authorship contribution statement

Marta Díaz: Conceptualization, Methodology, Investigation, Data curation. **Eva Epelde:** Formal analysis, Validation, Data curation, Writing - original draft. **José Valecillos:** Methodology, Visualization, Investigation, Writing - original draft. **Sepideh Izaddoust:** Investigation, Formal analysis, Writing - review & editing. **Andrés T. Aguayo:** Software, Resources, Supervision, Project administration, Funding acquisition. **Javier Bilbao:** Conceptualization, Supervision, Writing - original draft, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgments

This work has been carried out with the financial support of the Ministry of Economy and Competitiveness of the Spanish Government (Projects PID2019/108448RB-I00 and CTQ2016-79646-P), the ERDF funds and the Basque Government (Project IT1218-19). M. Díaz is grateful for the PhD grant from the Department of Education, University and Research of the Basque Government (PRE_2014_1_344). J. Valecillos and S. Izaddoust are thankful to the Ministry of Economy, Industry and Competitiveness of the Spanish Government for their grants BES-2014-069980 and BES-2017-080077, respectively. The authors also thank for technical and human support provided by IZO- SGiker of UPV/EHU and European funding (ERDF and ESF).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2021.120076>.

References

- C.P. Nicholas, Applications of light olefin oligomerization to the production of fuels and chemicals, *Appl. Catal. A Gen.* 543 (2017) 82–97, <https://doi.org/10.1016/j.apcata.2017.06.011>.
- A.V. Lavrenov, T.R. Karpova, E.A. Buluchevskii, E.N. Bogdanets, Heterogeneous oligomerization of light alkenes: 80 years in oil refining, *Catal. Ind.* 8 (2016) 316–327, <https://doi.org/10.1134/S2070050416040061>.
- I. Amghizar, L.A. Vandewalle, K.M. Van Geem, G.B. Marin, New trends in olefin production, *Engineering*. 3 (2017) 171–178, <https://doi.org/10.1016/j.eng.2017.02.006>.
- P. Tian, Y. Wei, M. Ye, Z. Liu, Methanol to olefins (MTO): from fundamentals to commercialization, *ACS Catal.* 5 (2015) 1922–1938, <https://doi.org/10.1021/acscatal.5b00007>.
- T. Cordero-Lanzac, A. Ateka, P. Pérez-Urriarte, P. Castaño, A.T. Aguayo, J. Bilbao, Insight into the deactivation and regeneration of HZSM-5 zeolite catalysts in the conversion of dimethyl ether to olefins, *Ind. Eng. Chem. Res.* 57 (2018) 13689–13702, <https://doi.org/10.1021/acs.iecr.8b03308>.
- A.G. Gayubo, A. Alonso, B. Valle, A.T. Aguayo, J. Bilbao, Selective production of olefins from bioethanol on HZSM-5 zeolite catalysts treated with NaOH, *Appl. Catal. B Environ.* 97 (2010) 299–306, <https://doi.org/10.1016/j.apcatb.2010.04.021>.
- B. Valle, A. Remiro, N. García-Gómez, A.G. Gayubo, J. Bilbao, Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review, *J. Chem. Technol. Biotechnol.* 94 (2019) 670–689, <https://doi.org/10.1002/jctb.5758>.
- P. Castaño, G. Elordi, M. Ibáñez, M. Olazar, J. Bilbao, Pathways of coke formation on an MFI catalyst during the cracking of waste polyolefins, *Catal. Sci. Technol.* 2 (2012) 504–508, <https://doi.org/10.1039/c2cy00434h>.
- G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals, A review, *Renew. Sustain. Energy Rev.* 73 (2017) 346–368, <https://doi.org/10.1016/j.rser.2017.01.142>.
- M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao, M. Olazar, Light olefins from HDPE cracking in a two-step thermal and catalytic process, *Chem. Eng. J.* 207–208 (2012) 27–34, <https://doi.org/10.1016/j.cej.2012.06.105>.
- W. Zhou, K. Cheng, J. Kang, C. Zhou, V. Subramanian, Q. Zhang, Y. Wang, New horizon in C₁ chemistry: breaking the selectivity limitation in transformation of syngas and hydrogenation of CO₂ into hydrocarbon chemicals and fuels, *Chem. Soc. Rev.* 48 (2019) 3193–3228, <https://doi.org/10.1039/c8cs00502h>.
- W. Taifan, J. Baltrusaitis, CH₄ conversion to value added products: Potential, limitations and extensions of a single step heterogeneous catalysis, *Appl. Catal. B Environ.* 198 (2016) 525–547, <https://doi.org/10.1016/j.apcatb.2016.05.081>.
- G. Bellussi, F. Mizia, V. Calemma, P. Pollesel, R. Millini, Oligomerization of olefins from light cracking naphtha over zeolite-based catalyst for the production of high quality diesel fuel, *Microporous Mesoporous Mater.* 164 (2012) 127–134, <https://doi.org/10.1016/j.micromeso.2012.07.020>.
- A.F. Silva, A. Fernandes, M.M. Antunes, M.F. Ribeiro, C.M. Silva, A.A. Valente, Catalytic conversion of 1-butene over modified versions of commercial ZSM-5 to produce clean fuels and chemicals, *ChemCatChem*. 11 (2019) 4196–4209, <https://doi.org/10.1002/cctc.201801975>.
- V.L. Dagle, J.S. Lopez, A. Cooper, J. Luecke, M. Swita, R.A. Dagle, D. Gaspar, Production and fuel properties of iso-olefins with controlled molecular structure and obtained from butene oligomerization, *Fuel*. 277 (2020), 118147, <https://doi.org/10.1016/j.fuel.2020.118147>.
- R.J. Quann, L.A. Green, S.A. Tabak, F.J. Krambeck, Chemistry of olefin oligomerization over ZSM-5 catalyst, *Ind. Eng. Chem. Res.* 27 (1988) 565–570, <https://doi.org/10.1021/ie00076a006>.
- A.F. Silva, P. Neves, S.M. Rocha, C.M. Silva, A.A. Valente, Optimization of continuous-flow heterogeneous catalytic oligomerization of 1-butene by design of experiments and response surface methodology, *Fuel*. 259 (2020), 116256, <https://doi.org/10.1016/j.fuel.2019.116256>.
- A. Coelho, G. Caeiro, M.A.N.D. A.N.D.A. Lemos, F. Lemos, F.R. Ribeiro, 1-Butene oligomerization over ZSM-5 zeolite: part 1 - Effect of reaction conditions, *Fuel*. 111 (2013) 449–460, <https://doi.org/10.1016/j.fuel.2013.03.066>.
- E. Kriván, S. Tomasek, J. Hancsók, Application possibilities of zeolite catalysts in oligomerization of light olefins, *Period. Polytech. Chem. Eng.* 58 (2014) 149–156, <https://doi.org/10.3311/PPCh.7204>.
- A.F. Silva, A. Fernandes, M.M. Antunes, P. Neves, S.M. Rocha, M.F. Ribeiro, M. Pillinger, J. Ribeiro, C.M. Silva, A.A. Valente, TUD-1 type aluminosilicate acid catalysts for 1-butene oligomerisation, *Fuel*. 209 (2017) 371–382, <https://doi.org/10.1016/j.fuel.2017.08.017>.
- M. Díaz, E. Epelde, A.T. Aguayo, J. Bilbao, Low-pressure oligomerization of 1-butene to liquid fuels on HZSM-5 zeolite catalysts: effect of operating conditions, *J. Ind. Eng. Chem.* 87 (2020) 234–241, <https://doi.org/10.1016/j.jiec.2020.04.006>.
- M. Díaz, E. Epelde, Z. Tabernilla, A. Ateka, A.T. Aguayo, J. Bilbao, Operating conditions to maximize clean liquid fuels yield by oligomerization of 1-butene on HZSM-5 zeolite catalysts, *Energy*. 15 (2020), 118317.
- A. Corma, C. Martínez, E. Doskocil, Designing MFI-based catalysts with improved catalyst life for C₃ and C₅ oligomerization to high-quality liquid fuels, *J. Catal.* 300 (2013) 183–196, <https://doi.org/10.1016/j.jcat.2012.12.029>.
- M.R. Díaz-Rey, C. Paris, R. Martínez-Franco, M. Moliner, C. Martínez, A. Corma, Efficient oligomerization of pentene into liquid fuels on nanocrystalline Beta zeolites, *ACS Catal.* 7 (2017) 6170–6178, <https://doi.org/10.1021/acscatal.7b00817>.
- L. Zhang, M. Ke, Z. Song, Y. Liu, W. Shan, Q. Wang, C. Xia, C. Li, C. He, Improvement of the catalytic efficiency of butene oligomerization using alkali metal hydroxide-modified hierarchical zsm-5 catalysts, *Catalysts*. 8 (2018) 298, <https://doi.org/10.3390/catal8080298>.
- W. Monama, E. Mohiuddin, B. Thangaraj, M.M. Mdleleni, D. Key, Oligomerization of lower olefins to fuel range hydrocarbons over texturally enhanced ZSM-5 catalyst, *Catal. Today* 342 (2019) 167–177, <https://doi.org/10.1016/j.cattod.2019.02.061>.
- A.F. Silva, A. Fernandes, M.M. Antunes, M.F. Ribeiro, C.M. Silva, A.A. Valente, Olefin oligomerisation over nanocrystalline MFI-based micro/mesoporous zeotypes synthesised via bottom-up approaches, *Renew. Energy* 138 (2019) 820–832, <https://doi.org/10.1016/j.renene.2019.02.019>.
- R. Henry, M. Komurcu, Y. Ganjkanlou, R.Y. Brogaard, L. Lu, K.J. Jens, G. Berlier, U. Olsbye, Ethene oligomerization on nickel microporous and mesoporous-supported catalysts: investigation of the active sites, *Catal. Today* 299 (2018) 154–163, <https://doi.org/10.1016/j.cattod.2017.04.029>.
- A.G. Popov, V.S. Pavlov, I.I. Ivanova, Effect of crystal size on butenes oligomerization over MFI catalysts, *J. Catal.* 335 (2016) 155–164, <https://doi.org/10.1016/j.jcat.2015.12.008>.
- G. Elordi, M. Olazar, G. Lopez, P. Castaño, J. Bilbao, Role of pore structure in the deactivation of zeolites (HZSM-5, H β and HY) by coke in the pyrolysis of polyethylene in a conical spouted bed reactor, *Appl. Catal. B Environ.* 102 (2011) 224–231, <https://doi.org/10.1016/j.apcatb.2010.12.002>.
- M. Ibáñez, M. Artetxe, G. Lopez, G. Elordi, J. Bilbao, M. Olazar, P. Castaño, Identification of the coke deposited on an HZSM-5 zeolite catalyst during the sequenced pyrolysis-cracking of HDPE, *Appl. Catal. B Environ.* 148–149 (2014) 436–445, <https://doi.org/10.1016/j.apcatb.2013.11.023>.
- M. Ibáñez, P. Pérez-Urriarte, M. Sánchez-Contador, T. Cordero-Lanzac, A.T. Aguayo, J. Bilbao, P. Castaño, Nature and location of carbonaceous species in a composite HZSM-5 zeolite catalyst during the conversion of dimethyl ether into light olefins, *Catalysts*. 7 (2017) 254, <https://doi.org/10.3390/catal7090254>.
- X. Wang, X. Hu, C. Song, K.W. Lux, M. Namazian, T. Imam, Oligomerization of biomass-derived light olefins to liquid fuel: effect of alkali treatment on the HZSM-5 catalyst, *Ind. Eng. Chem. Res.* 56 (2017) 12046–12055, <https://doi.org/10.1021/acs.iecr.7b02316>.
- F. Zhou, Y. Gao, G. Wu, F. Ma, C. Liu, Improved catalytic performance and decreased coke formation in post-treated ZSM-5 zeolites for methanol

- aromatization, *Microporous Mesoporous Mater.* 240 (2017) 96–107, <https://doi.org/10.1016/j.micromeso.2016.11.014>.
- [35] O. Jan, K. Song, A. Dichiaro, F.L.P. Resende, Ethylene oligomerization over Ni-H β heterogeneous catalysts, *Ind. Eng. Chem. Res.* 57 (2018) 10241–10250, <https://doi.org/10.1021/acs.iecr.8b01902>.
- [36] A. Corma, F.J. Llopis, C. Martínez, G. Sastre, S. Valencia, The benefit of multipore zeolites: catalytic behaviour of zeolites with intersecting channels of different sizes for alkylation reactions, *J. Catal.* 268 (2009) 9–17, <https://doi.org/10.1016/j.jcat.2009.08.012>.
- [37] R.D. Andrei, E. Borodina, D. Minoux, N. Nesterenko, J.-P. Dath, C. Cammarano, V. Hulea, Ethylene oligomerization from diluted stream over Ni-containing heterogeneous catalysts, *Ind. Eng. Chem. Res.* 59 (2020) 1746–1752, <https://doi.org/10.1021/acs.iecr.9b05576>.
- [38] A.T. Aguayo, A.G. Gayubo, J. Ereña, A. Atutxa, J. Bilbao, Coke aging and its incidence on catalyst regeneration, *Ind. Eng. Chem. Res.* 42 (2003) 3914–3921, <https://doi.org/10.1021/ie030085n>.
- [39] J. Valecillos, E. Epelde, J. Albo, A.T. Aguayo, J. Bilbao, P. Castaño, Slowing down the deactivation of H-ZSM-5 zeolite catalyst in the methanol-to-olefin (MTO) reaction by P or Zn modifications, *Catal. Today* 348 (2020) 243–256, <https://doi.org/10.1016/j.cattod.2019.07.059>.
- [40] P. Magnoux, P. Roger, C. Canaff, V. Fouche, N.S. Gnep, M. Guisnet, New technique for the characterization of carbonaceous compounds responsible for zeolite deactivation, *Stud. Surf. Sci. Catal.* (1987) 317–330, [https://doi.org/10.1016/S0167-2991\(09\)60370-0](https://doi.org/10.1016/S0167-2991(09)60370-0).
- [41] J. Valecillos, Z. Tabernilla, E. Epelde, E. Sastre, A.T. Aguayo, P. Castaño, Quenching the deactivation in the methanol-to-olefin reaction by using tandem fixed-beds of ZSM-5 and SAPO-18 catalysts, *Ind. Eng. Chem. Res.* 59 (2020) 13892–13905, <https://doi.org/10.1021/acs.iecr.0c01616>.
- [42] M.J. Wulfers, F.C. Jentoft, Identification of carbonaceous deposits formed on H-mordenite during alkane isomerization, *J. Catal.* 307 (2013) 204–213, <https://doi.org/10.1016/j.jcat.2013.07.011>.
- [43] M. Bjørgen, K.P. Lillerud, U. Olsbye, S. Bordiga, A. Zecchina, 1-butene oligomerization in Brønsted acidic zeolites: mechanistic insights from low-temperature in situ FTIR spectroscopy, *J. Phys. Chem. B* 108 (2004) 7862–7870, <https://doi.org/10.1021/jp0377836>.
- [44] P. Castaño, G. Elordi, M. Olazar, A.T. Aguayo, B. Pawelec, J. Bilbao, Insights into the coke deposited on HZSM-5, H β and HY zeolites during the cracking of polyethylene, *Appl. Catal. B Environ.* 104 (2011) 91–100, <https://doi.org/10.1016/j.apcatb.2011.02.024>.
- [45] M. Guisnet, P. Magnoux, Organic chemistry of coke formation, *Appl. Catal. A Gen.* 212 (2001) 83–96, [https://doi.org/10.1016/S0926-860X\(00\)00845-0](https://doi.org/10.1016/S0926-860X(00)00845-0).
- [46] E. Epelde, J.I. Santos, P. Florian, A.T. Aguayo, A.G. Gayubo, J. Bilbao, P. Castaño, Controlling coke deactivation and cracking selectivity of MFI zeolite by H $_3$ PO $_4$ or KOH modification, *Appl. Catal. A Gen.* 505 (2015) 105–115, <https://doi.org/10.1016/j.apcata.2015.07.022>.
- [47] E. Epelde, M. Ibáñez, A.T. Aguayo, A.G. Gayubo, J. Bilbao, P. Castaño, 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 (2014) 284–293, <https://doi.org/10.1016/j.micromeso.2014.04.040>.
- [48] M. Henry, M. Bulut, W. Vermandel, B. Sels, P. Jacobs, D. Minoux, N. Nesterenko, S. Van Donk, J.P. Dath, Low temperature conversion of linear C $_4$ olefins with acid ZSM-5 zeolites of homogeneous composition, *Appl. Catal. A Gen.* 413–414 (2012) 62–77, <https://doi.org/10.1016/j.apcata.2011.10.043>.
- [49] D. Eisenbach, E. Gallei, Infrared spectroscopic investigations relating to coke formation on zeolites: I. Adsorption of hexene-1 and n-hexane on zeolites of type Y, *J. Catal.* 56 (1979) 377–389, [https://doi.org/10.1016/0021-9517\(79\)90130-1](https://doi.org/10.1016/0021-9517(79)90130-1).
- [50] B. Valle, P. Castaño, M. Olazar, J. Bilbao, A.G. Gayubo, Deactivating species in the transformation of crude bio-oil with methanol into hydrocarbons on a HZSM-5 catalyst, *J. Catal.* 285 (2012) 304–314, <https://doi.org/10.1016/j.jcat.2011.10.004>.
- [51] A.N. Mlinar, P.M. Zimmerman, F.E. Celik, M. Head-Gordon, A.T. Bell, Effects of Brønsted-acid site proximity on the oligomerization of propene in H-MFI, *J. Catal.* 288 (2012) 65–73, <https://doi.org/10.1016/j.jcat.2012.01.002>.
- [52] P. Magnoux, H.S. Cerqueira, M. Guisnet, Evolution of coke composition during ageing under nitrogen, *Appl. Catal. A Gen.* 235 (2002) 93–99, [https://doi.org/10.1016/S0926-860X\(02\)00242-9](https://doi.org/10.1016/S0926-860X(02)00242-9).
- [53] P.L. Benito, A.T. Aguayo, A.G. Gayubo, J. Bilbao, Catalyst equilibration for transformation of methanol into hydrocarbons by reaction-regeneration cycles, *Ind. Eng. Chem. Res.* 35 (1996) 2177–2182, <https://doi.org/10.1021/ie950493u>.
- [54] A.G. Gayubo, A.T. Aguayo, M. Olazar, R. Vivanco, J. Bilbao, Kinetics of the irreversible deactivation of the HZSM-5 catalyst in the MTO process, *Chem. Eng. Sci.* 58 (2003) 5239–5249, <https://doi.org/10.1016/j.ces.2003.08.020>.