Kinetics and reactor modeling of the conversion of n-pentane using HZSM-5 catalysts with different Si/Al ratio

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The production of olefins and aromatics from n-pentane has been modeled using the experimental results collected in an isothermal packed bed reactor with HZSM-5 zeolite catalysts with different Si/Al ratios (15 and 140) in the temperature range of 400–550 °C. In a first stage, a lump-based kinetic model has been established, evaluating the role of the Si/Al ratio in the kinetic parameters and therefore, in the conversion, product distribution and deactivation by coke. The effect of the catalyst acidity and the reaction conditions has been explained by analyzing the used catalysts by means of N₂ and *tert*-butylamine adsorption-desorption, temperature-programmed oxidation and confocal fluorescence microscopy. In a second stage, the kinetic parameters extracted for both catalysts have been used in simulations of an isothermal packed bed reactor in order to study the evolution of the reaction with the space time and time on stream. It has been found certain suitable conditions (550 °C and 3.5 g_{cat} h mol⁻¹) for maximizing the yield and selectivity of olefins (31 and 51 %, respectively, using the zeolite with Si/Al = 140) and aromatics (yield and selectivity of 53 %, using the one with Si/Al = 15) in the simulated range.

1. Introduction

Paraffins, which are one of the main byproducts in processes of fuel production, present great interest as potential candidates for being used as a source of commodities with increasing demand in the petrochemical industry, such as light olefins and aromatics. In this regard, there is a strong drive of the market in order to valorize paraffins, but the problem is the relatively unreactive C-H bond. The main current process for paraffins valorization is the steam cracking, where olefins (mainly ethylene) are produced with high amounts of energy requirement and considerably CO₂ emissions.^{1,2} In contrast, these two drawbacks are remarkably lessened in the catalytic cracking of paraffins, whereby the ability to selectively produce propylene is increased.^{1,3,4} Moreover, the catalytic aromatization of alkanes is one of the most encouraging ways for satisfying the current demand of BTX aromatics (benzene, toluene and xylenes),⁵ which are starting materials for manufacturing plastics, fibers or rubbers.⁶ Great attention is nowadays receiving co-aromatization reactions of long paraffins (C₄+) with ethane,⁷ or even methane from gas natural,^{8,9} in order to activate the stable C–H bond of short alkanes.

These catalytic cracking and aromatization processes are usually carried out over HZSM-5 zeolite (MFI structure) catalysts,¹⁰ where the presence of Al in its framework gives the

zeolite Brønsted acidity, which has been found crucial for the selective conversion of n-pentane into olefins.^{11–13} These olefins can also form aromatic compounds through oligomerization and cyclization-aromatization pathways in the zeolite acid sites.^{13–15} Remarkable yields of BTX aromatics have recently been reported using Zn- and Ga-modified ZSM-5,^{8,9} as well as the important role of the framework and extra-framework Al sites in aromatization reactions.¹⁶

Inevitably, olefins and aromatics finally condense to coke on the acid sites of the catalyst, thus leading to the catalyst deactivation.^{17,18} The mechanisms of coke formation and removal during different catalytic processes have been reported by Mahamulkar et al.,¹⁹ along with several techniques for coke characterization. The properties of the catalyst have been found to play a key role in these mechanisms. In this sense, (i) the framework of HZSM-5 zeolite has straight and perpendicularly crossed channels,²⁰ (ii) increasing the Si/Al ratio of the zeolite,²¹ and (iii) the agglomeration of the zeolite in a mesoporous matrix²² are proven strategies for limiting the coke formation during the reaction. But in this scenario, efforts must be conducted to the development of more stable catalysts²³ and kinetic models that allow predicting the performance of the catalysts during the conversion of alkanes into olefins and/or aromatics.²⁴

Most of the kinetic studies in this field are conducted to the crucial role of temperature and Si/Al ratio of zeolite in the initial steps of the mechanism of alkane conversion.^{25,26} Indeed, intrinsic kinetics have been proposed for the alkane adsorption over the acid sites,²⁷ as well as the effect of their carbon chain on the monomolecular cracking rates.²⁸ Nevertheless, catalyst deactivation have usually been disregarded in kinetic models due to its inherent empiricism and the hurdles of relating the formation of coke with the loss of the catalyst activity.^{29–32} Lump-based kinetic models offer

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the possibility of predicting the evolution of the catalyst performance with time in a computationally cheap way, by sacrificing the accurate thermodynamics consideration required in some microkinetic techniques.^{33,34} These models can however provide enough mechanistic information when the steps of the lump reaction scheme are well related to the different stages of the reaction mechanism.²⁴ These premises would lead to a rational design of reactors, such as isothermal packed bed reactors that are the most used configuration for kinetic studies on other widely reported catalytic processes as MTO^{35,36} or Fischer-Tropsch.^{37,38}

In this work, experimental runs of *n*-pentane catalytic cracking have been carried out using HZSM-5 zeolites with Si/Al ratios of 15 and 140, aiming the modeling of the kinetics, and afterwards the reactor, for the production of light olefins and aromatics. Due to the relevance of deactivation in the kinetic model, the effect of the Si/Al ratio and the reaction conditions on the deterioration of the catalyst properties has been analyzed using different techniques: N₂ and *tert*-butylamine adsorption-desorption, temperature-programmed oxidation and confocal fluorescence microscopy. According to the kinetics parameters, a comparison between the extents of each stage of the paraffin catalytic cracking mechanism has been made in order to quantify the role of Si/Al ratio of the zeolite. Then, these kinetic parameters for both catalysts have been incorporated in the simulations of an isothermal packed bed reactor for predicting the suitable conditions to selectively produce light olefins and aromatics while controlling the catalyst deactivation.

2. Experimental

2.1. Catalyst preparation

HZSM-5 zeolites (provided by Zeolyst) with two different Si/Al ratios (15 and 140) were used in order to prepare the catalysts. The catalysts were prepared by an agglomeration method for the sake of dispersing the zeolite crystals into an inert matrix with improved mechanical resistance. α -Al₂O₃ was used as the inert filler and pseudoboehmite was used as a binder. For the preparation, a colloidal dispersion of 20 wt% of α -Al₂O₃ (provided by Alfa Aesar) was mixed with the pseudoboehmite (70 wt% Al₂O₃, provided by Sasol). When the homogeneous mixture was reached, the zeolite was slowly added into the solution ensuring a correct mixture and dispersion in the slurry. Then, the mixture was extruded in cylinders of ca. 2 mm and dried during 12 h at room temperature. The relatively fragile extrudates were sieved to a particle size between 0.125–0.3 mm and the resulting particles were calcined in air at 550 °C during 2 h using a temperature ramp of 5 °C min⁻¹. During the calcination, pseudoboehmite is converted into γ -Al₂O₃, which is its stable phase at this temperature. The amounts of precursors were calculated in order to achieve a zeolite/ γ -Al₂O₃/ α -Al₂O₃ ratio of 50/30/20 (wt%) in the final catalyst. Tough particles are obtained after the calcination. Hence, this agglomeration of the zeolites provides the final catalyst with an improved mechanical resistance, but also with a hierarchical mesoporous structure (due to the presence of the γ -Al₂O₃ matrix) that favors the stability of the catalyst due to the favored diffusion of the coke

precursors outside the catalyst.³⁹ The procedure was repeated for the zeolite with different Si/Al ratio, and the catalysts were named after the Si/Al ratio of the used zeolite: Z15 (Si/Al = 15) and Z140 (Si/Al = 140). These two HZSM-5 zeolites were selected after a preliminary study about the influence of Si/Al ratio on the product distribution in the catalytic cracking of *n*-pentane.

2.2. Catalyst characterization

The morphology of the fresh and used catalysts was studied by confocal fluorescence microscopy (CFM) in a ZEISS LSM 800 Microscope, provided with a turbo pumped chamber, a motorized stage and multialkali, GaAsP and Airyscan detectors. The microscope is also provided with three excitation channels with diode lasers at 405, 488 and 561 nm, making the samples emit fluorescence in the wavelength of blue, green and red ranges, respectively. The used accelerating voltage was 20 kV. Reflection images of the samples were also obtained, being the particles submitted only to the 405 nm laser and the reflected beam collected by the detector. Images were formed by stacking 10–20 samples of different *z* axis (0–50 μ m deep on the particle surface).

The porous structure of the fresh and the used catalysts was characterized by means of N₂ adsorption-desorption at -196 °C in a Micromeritics ASAP 2010. Samples were degassed at 150 °C for 8 h for removing impurities and water adsorbed within the pores. From the N₂ adsorption-desorption isotherms, specific surface area was calculated using the BET equation (*S*_{BET}).

The acidity of the fresh and the used catalysts was measured by *tert*-butylamine (t-BA) adsorption-desorption, which was carried out in a Setaram DSC-111 calorimeter coupled in-line with a mass spectrometer (Balzers). After a pretreatment of the sample with He at 550 °C, t-BA was adsorbed at 100 °C. Physisorbed t-BA was removed with He and the remaining chemisorbed molecules were desorbed by increasing the temperature up to 500 °C using a temperature ramp of 5 °C min⁻¹. This temperature-programmed desorption (TPD) was monitored with the mass spectrometer by recording the signal of butene (*m/z* = 56), which is the main product of the t-BA cracking. From the results, the total acidity of the catalyst for cracking reactions was calculated.

The total coke content and its nature and location were measured by temperature-programmed oxidation (TPO) in a TGA Q5000 IR thermobalance from TA Instruments. Each used catalyst sample was submitted to a sweeping pretreatment at the reaction temperature (10 °C min⁻¹) during 30 min and subsequently temperature was decreased to 50 °C. TPO experiments were carried out under a continuous air flow of 50 cm³ min⁻¹ raising the temperature from 50 to 550 °C at a temperature rate of 5 °C min⁻¹. The final temperature was maintained isothermal during 2 h, after which it was decreased to room temperature.

2.3. Experimental reaction runs

Catalytic cracking reactions of n-pentane (99.9%, Merck) were carried out in a stainless steel fixed bed reactor (internal diameter, 9 mm) heated by a ceramic oven (PID Eng & Tech) and provided with a syringe pump (Harvard PHD 4400) for feeding the reactant. Catalyst particles were mixed with SiC (particle diameter, 0.4–0.6 mm) as inert solid in order to use a constant catalytic bed height and ensure its isothermal condition. Prior to the reaction, the catalyst was pretreated with air at 550 °C during 2 h, removing impurities and adsorbed water within its pores. The catalytic bed was cooled down to the reaction temperature (measured by thermocouples) and n-pentane was fed into the reactor (partial pressure, 0.9). The used reaction conditions were: 400–550 °C, 1.4 bar, space time up to 5 g_{cat} h mol⁻¹, time on stream up to 15 h. After the reaction, the catalytic bed was submitted to a continuous flow of N₂ during 20 min and it was cooled down to room temperature.

Reaction products were analyzed *in-situ* in a gas chromatograph (Agilent 300A Micro GC) coupled in-line with the reactor. The gas chromatograph is provided with different columns to identify and quantify methane (MS-5 column), C_{2–4} paraffins and olefins (Alumina column), C_{5–8} hydrocarbons and BTX aromatics (Stabilwax column). In all cases, the carbon mass balance closure was higher than 95 wt% with respect to the n-pentane feed. For analyzing the obtained results, products were grouped in different lumps according to their similar structure and behavior in the reaction mechanism. In such a way, C_{2–4} olefins were grouped in the olefin lump (O, primary product), C_{2–4} paraffins were included in the light paraffins lump (P), C_{5–8} hydrocarbons were grouped in the long hydrocarbon lump (C₅₊) and benzene, toluene and xylenes form the BTX lump (BTX). The catalytic cracking of n-pentane was monitored by using different indexes, conversion (X), selectivity (S_i) and yield (Y_i) of each lump, which were defined as a function of the carbon molar flow rate of these lumps:

$$X = \frac{F - F_{nC_5}}{F} 100 \quad (1)$$

$$S_i = \frac{F_i}{F - F_{nC_5}} 100 \quad (2)$$

$$Y_i = \frac{F_i}{F} 100 \quad (3)$$

where F is the total carbon molar flow rate and F_{nC_5} and F_i are the carbon molar flow rate at the outlet of the reactor of n-pentane (reactant) and of each i lump (products), respectively.

3. Results and discussion

3.1. Role of the Si/Al ratio in the catalyst performance

The morphology of the agglomerated zeolite was firstly characterized by means of confocal fluorescence microscopy and the results are presented in Fig. 1. The fluorescence of the fresh catalyst is limited. However, we have been able to locate small domains of the zeolite well dispersed in the matrix material by reflection (Fig. 1a). This is an analogous technique to the scanning electron microscopy (SEM) but using a laser beam of 405 nm instead of irradiating the sample with electrons. By reflection, the images provide relatively low information of the dispersion of the zeolite due to the scarce penetration within the catalytic particles, and particularly into the matrix made by γ -Al₂O₃ formed during the calcination of the pseudoboehmite. The presence of this matrix provides the

catalyst with a hierarchical porous structure mainly dominated by the mesopores of the matrix, since HZSM-5 is a microporous zeolite with a MFI framework.⁴⁰ For this reason, both zeolite-based catalysts (Z15, Si/Al = 15 and Z140, Si/Al = 140) present similar structural parameters, registering BET surface areas (S_{BET}) of 285 and 271 m² g⁻¹ for Z15 and Z140 catalysts, respectively (Table 1). Then, it is worth of mentioning that the main difference between both catalysts is the acidity of each one, which is given by the Si/Al ratio of the zeolite (Table 1, 0.43 and 0.16 mmol_{t-B}A g⁻¹ for Z15 and Z140 catalysts, respectively).

After reactions, some coke structures were deposited on the surface of the catalysts. The conjugated dienes and aromatics of coke are very fluorescent under the type of radiation used in the microscope.^{22,41} This methodology is then able to faithfully analyze the zeolite or coke domains within the catalyst bodies.⁴² Fig 1b shows a representative particle of an used Z15 catalyst at certain conditions. Small and well-dispersed domains of high fluorescence intensity are observed, which correspond to the zeolite crystals, in which the reaction takes place. This CFM result indicates the good performance of the agglomeration method in order to prepare the catalyst. Similar ones were previously reported for agglomerated catalysts,^{42,43} where these zeolite domains were also clearly differentiated in this type of catalyst particles.

Fig. 1. CFM images of (a) the fresh Z15 catalyst (reflection) and (b) a used Z15 catalyst (excitation wavelength, 488 and 561 nm)

These catalysts were tested in the catalytic cracking of n-pentane, and the initial values of conversion and selectivity of the main products (olefins, paraffins, BTX aromatics and C₅₊ hydrocarbons) are depicted in the Fig. S1. At 500 °C, the more

acid Z15 catalyst mainly yields paraffins, with n-pentane conversions higher than 45% using a space time of $0.15 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$ (**Fig. S1a**). When conversion is increased up to 90%

Table 1. Total coke content, specific surface area and total acidity of the fresh and used catalysts at 500 and 550 °C (space time, $1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$)

	Coke content (wt%)	S_{BET} ($\text{m}^2 \text{ g}_{\text{cat}}^{-1}$)	Total acidity ($\text{mmol}_{\text{t-BA}} \text{ g}_{\text{cat}}^{-1}$)
Z15	-	285	0.43
500 °C	3.9	205	0.24
550 °C	7.4	167	0.21
Z140	-	271	0.16
500 °C	0.2	250	0.15
550 °C	0.8	238	0.15

(space time, $1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$), values of selectivity of BTX aromatics higher than 20% are observed. On the contrary, olefins are the main products obtained with Z140 catalyst at the same space time value. An increase in the temperature up to 550 °C (**Fig. S1b**) promotes the selective production of olefins and reduces the selectivity of paraffins in all cases. Olefins/paraffins ratio is then boosted using both catalysts and Z140 catalyst achieves a maximum selectivity of olefins of 65% ($0.30 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$), whereas BTX aromatics reach a maximum selectivity value of 24% with Z15 catalyst (space time, $1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$).

During the reaction, the catalysts were progressively deactivated due to the deposition of coke that causes the blockage of the active sites. This loss of activity can be quantified following the evolution of the reaction with time on stream (TOS). In all cases of **Fig. 2**, the rapidity of conversion drop is directly related to the catalyst activity, and therefore, the higher the n-pentane conversion is, the faster deactivation is observed. At 500 °C, almost linear trends are shown by the two catalysts and conditions (**Fig. 2a**), reaching a maximum slope using Z15 catalyst and $1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$ (initial conversion of 92%). Although similar values of conversion are yielded by both catalysts at certain conditions, Z140 seems to be deactivated slightly slower. Indeed, at very low values of conversion, this catalyst shows a stable performance, maintaining a constant conversion during 15 h on stream. These behaviors are emphasized at 550 °C (**Fig. 2b**), where linear decays of the conversion are no longer observed. At the highest value of space time ($1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$), Z15 catalyst shows an initial period of slow deactivation that is followed by a fast drop of the conversion (68% after 15 h). Opposite to that, decreasing the space time or the catalyst acidity (Z140 catalyst) the initial fast deactivation tends to a steady state upon increasing the TOS, particularly at 500 °C (**Fig. 2b**).

The activity drop due to the coke formation and deposition is then directly related to the catalyst acidity (Si/Al ratio of the zeolite), the temperature and the space time, which also affects the composition of the reaction medium.^{39,44} The evolutions of the yield of products with TOS at 550 °C, corresponding to the experiments of **Fig. 2b**, are displayed in **Fig. 3**. As previously mentioned, the higher conversions attained with Z15 catalyst produce olefins, paraffins (35 and 25 wt%, respectively **Fig. 3a**) and remarkable yields of BTX

aromatics at $1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$ (24 wt%, **Fig. 3b**). However, the fastest observed deactivation mainly affects the two latter, thus observing remarkable decreases in the yields of paraffins and BTX aromatics. The yield of olefins slightly decreases at

Fig. 2. Evolution with time on stream of the conversion using Z15 and Z140 catalysts and different values of space time at (a) 500 °C and (b) 550 °C

low values of space time and even increases upon increasing the TOS at $1.00 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$ (**Fig. 3b**). Otherwise, a negligible decay of the reaction products is observed at conditions of low conversions with Z140 catalyst when the reactant is the main component of the reaction medium (**Fig. 3c**). Here, low but constant yields of all product are observed during 15 h on stream, being olefins the main obtained products (4 wt%). Finally, regarding those conditions of similar conversions with both catalysts (**Fig. 3a** and **Fig. 3d**), a yield of olefins of ca. 24% is achieved in both cases. However, a faster decay of the yields of olefins and particularly paraffins is observed with the more acid Z15 catalyst.

The coke deposited during the reaction was quantified and characterized through TPO analysis and its effect on the catalyst porous structure and acidity is summarized in **Table 1**. The TPO profiles of the used Z15 and Z140 catalyst at 500 and 550 °C are depicted in **Fig. S2**, whereas the N_2 adsorption-desorption isotherms and the *tert*-butylamine (t-BA) TPD profiles of the fresh and used catalyst are respectively shown in **Fig. S3a** and **Fig. S3b**.

Fig. 3. Evolution with time on stream of product yields using Z15 catalyst and space time values of (a) 0.15 and (b) 1.00 $\text{g}_{\text{cat}} \text{h mol}_{\text{C}}^{-1}$, and using Z140 catalyst and space time values of (c) 0.30 and (d) 4.00 $\text{g}_{\text{cat}} \text{h mol}_{\text{C}}^{-1}$ at 550 °C

Two main peaks are observed at 490 and 550 °C (peak I and II, respectively) in the TPO profile of used Z15 catalysts at 500 °C and a space time value of 1.00 $\text{g}_{\text{cat}} \text{h mol}_{\text{C}}^{-1}$ (**Fig. 4a**). These peaks could be related to the combustion of two different coke fractions. According to its lower combustion temperature, the peak I is associated with carbon species easier to burn off, presumably aliphatic structures located on the mesoporous structure of the $\gamma\text{-Al}_2\text{O}_3$ matrix. On the other hand, higher combustion temperature (peak II) is required in order to burn off more developed structures deposited within the micropores of the zeolite or their mouths.^{22,39} The presence of this two coke fractions is consistent with the more intense fluorescence observed in the zeolite domains in **Fig. 1b**. An increase in the catalyst acidity and/or temperature promotes the formation of coke (maximum of 7.4 wt% with Z15 catalyst at 550 °C, **Table 1**), and particularly the fraction located outside the zeolite. Nevertheless, significant amounts of coke deposited within the zeolite pores are not registered on Z140 catalyst, which could be ascribed to the lower acidity of this zeolite ($\text{Si}/\text{Al} = 140$) and then, a lower activity for condensing carbon structures.

Regarding the effect of this deposition of coke on the catalyst properties, a more pronounced drop of S_{BET} is registered for the more acid Z15 catalyst as the reaction temperature is increased (**Table 1**). A maximum decay up to 167 $\text{m}^2 \text{g}^{-1}$ is reached by this catalyst at 550 °C (41% loss) in comparison to the 12% decrease in S_{BET} shown by Z140 catalyst. This is the result of the higher ability to form coke of

Z15 than that of Z140 catalyst (3.9 and 7.4 wt% vs. 0.2 and 0.8 wt% of coke at 500 and 550 °C, respectively, **Table 1**). The same tendency is observed for the catalyst acidity, with values of 0.24 and 0.21 $\text{mmol}_{\text{t-BA}} \text{g}_{\text{cat}}^{-1}$ for the used Z15 catalysts at 500 and 550 °C, respectively and negligible drop for the used Z140 catalysts (**Table 1**). Since the desorption of t-BA yields butene as the main product, TPD results indicate the required temperature for cracking t-BA.⁴⁵ In this sense, two peaks are observed in **Fig. S3b** (peaks S and W) which are associated with strong and weak acid sites, respectively. Indeed, we have found a linear correlation between the cracking temperature and the acid strength.⁴⁶ The pore blockage by coke mainly leads to a loss of the weak acid sites, which is consistent with the previously discussed preferential deposition of coke on the mesopores of the matrix, thus blocking the weak acid sites of the $\gamma\text{-Al}_2\text{O}_3$.

3.2. Kinetic modeling

The complexity of the reaction scheme should be taken into account for discussing the results and modeling the catalytic cracking of n-pentane. A simplification of the complex scheme can be achieved with the lump-based reaction scheme depicted in **Fig. 4**, which is described by 6 lumps and 10 reaction steps (and an additional one corresponding to the deactivation). The kinetic model was defined according to a total carbon atom balance, and the assignation of the number of carbon of each lump was weighted as a function of the experimental composition: Olefin (O) and Paraffin (P) lumps

are assumed to have 3 carbon atoms; C_{5+} hydrocarbon lump is considered to have 6 carbon atoms (C_{8+} hydrocarbon concentration was almost negligible), and BTX lump is assumed to be a 7 carbon atom lump, being toluene its main compound. In the reaction scheme of Fig. 4, Olefins (O) are the main intermediates of the reaction scheme and are produced from two different reactions: (i) the direct cracking of n-pentane (nC_5 , reactant) or the ones of the produced paraffins (P) and C_{5+} hydrocarbons (with the kinetic constants k_1 , k_2 and

Fig. 4. Reaction scheme for the catalytic cracking of n-pentane considering the formation of coke

k_3 , respectively, green arrow in Fig. 4); and (ii) the autocatalytic reactions (k_4 , k_5 and k_6) for the formation of olefins from these three lumps (orange arrow). Note that olefins are twice depicted for pointing out their role in the autocatalytic reaction although both are the same lump. Then, olefins yield C_{5+} hydrocarbons (C_{5+}), paraffins and BTX aromatics (BTX) through oligomerization-cracking (k_7), hydride transfer (k_8) and cyclization-aromatization (k_9) pathways, respectively. These secondary reactions are depicted with blue arrows in Fig. 4. Finally, the production of methane through the thermal cracking pathway is also considered (k_{10} , grey arrow). All these lump-based reactions are based on the widely studied and reported mechanistic considerations of paraffin catalytic cracking, protolytic cracking and oligomerization cracking.⁴⁷

According to the previously discussed results, a deactivation mechanism in series is proposed for the catalytic cracking of n-pentane. The formation of coke can be considered as a side reaction. Then, aromatization and condensation pathways finally produce polyaromatic structures of coke that block the active sites of the HZSM-5 zeolite.¹³ Based on these, coke could presumably be formed from products as olefins and BTX aromatics and thus, the higher their concentrations are in the reaction medium, the faster will be the catalyst deactivation. This is in agreement with our negligible observed deactivation when the conversion is low and the reaction medium is mainly formed by n-pentane reactant (Fig. 2). Therefore, it can be assumed that paraffins with lower carbon chain neither contributes to catalyst deactivation. The more acid Z15 catalyst leads to higher overall olefins + BTX aromatics (Fig. 3), even at conditions of same conversion levels. This suggests that olefins and BTX aromatics are the main precursors of coke (Fig. 4) and explains the slower deactivation of Z140 catalyst (Fig. 3), the lower amount of coke formed on this catalyst (Table 1) and the lower deterioration of its properties during the reaction (Fig. S3).

Moreover, the reaction scheme of Fig. 4 also explains the decrease in the yields of paraffins and BTX aromatics and the increase in the one of olefins since deactivation primarily affects the secondary reactions, and their extent should be limited as the catalyst activity drops.

The proposed equations describing the model assume that all the steps of the reaction scheme are considered elementary and the concentration of each reactant (R) was quantified with its partial pressure (P_R). Moreover, all the steps are affected by the catalyst deactivation, except for the thermal production of methane, whose production was observed independent on the catalyst deactivation:

$$r_j = \begin{cases} k_j \prod_R P_R a, & j = 1, \dots, 9 \\ k_j \prod_R P_R, & j = 10 \end{cases} \quad (4)$$

where r_j is the reaction rate of each j step of the reaction scheme and k_j is its kinetic constant. Deactivation was described with a non-selective model, in which the catalyst activity (a) depends on the partial pressure of the precursors of coke: olefins (P_O) and BTX aromatics (P_{BTX}):

$$-\frac{da}{dt} = k_d (P_O + P_{BTX}) a^d \quad (5)$$

where k_d is the deactivation kinetic constant and d is the deactivation order. These two parameters are simultaneously estimated with the ones referred to the zero time on stream kinetics (k_j). In Eqs. (4) and (5) the activity parameter (a) is defined as a ratio between the reaction rate at a given t time (r_j) and zero time ($r_{j,0}$) but at the same reaction conditions:

$$a = \frac{r_j}{r_{j,0}} \quad (6)$$

being $0 < a < 1$.

All the kinetic constants (k , including k_j and k_d) are defined by using the reparameterized form of the Arrhenius equation:

$$k = k^* \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (7)$$

where k^* is the kinetic constant at the reference temperature (T^*), E is the activation energy, R is the universal gas constant and T is the temperature.

Based on our previously proposed methodology,²⁴ the values of k^* and E were estimated by solving the conservation equations for each i lump, considering that the formation rate of each i lump (r_i) is related to each r_j by a carbon balance coefficient matrix ($A_{i,j}$):

$$r_i = A_{i,j} r_j \quad (8)$$

Table S1 lists the values of the kinetic constants of the model for Z15 and Z140 catalysts at the reference temperature of 500 °C (k^*) and the activation energy (E) for each reaction step shown in Fig. 4. The accuracy of the fit is also shown, being the confidence intervals calculated from the discrepancies of predicted and experimental data (confidence intervals at 95%). A worse fit is only obtained for reactions involving lumps with very low concentrations in the reaction medium. Fig. 5 shows the comparison of the experimental data and those estimated with the kinetic model for both catalysts at selected reaction conditions. As can be observed, the model accurately predicts the evolution of the product molar fractions with space time (τ , Fig. 5a-c) and time on stream (TOS, Fig. 5d-f) in a wide range of operation conditions.

Fig. 5. Comparison of the experimental data (dots) and those estimated with the kinetic model (lines) for the evolution with (a-c) space time and (d-f) time on stream of the molar fractions at selected conditions: (a) Z15, 400 °C, 0 h; (b) Z15, 550 °C, 0 h; (c) Z140, 550 °C, 0 h; (d) Z15, 500 °C, 0.14 $\text{g}_{\text{cat}} \text{h mol}_{\text{C}}^{-1}$; (e) Z15, 550 °C, 0.56 $\text{g}_{\text{cat}} \text{h mol}_{\text{C}}^{-1}$; (f) Z140, 550 °C, 3.85 $\text{g}_{\text{cat}} \text{h mol}_{\text{C}}^{-1}$

Table 2. Average kinetic constant at 500 °C and activation energy values and kinetic parameter ratios for Z15 and Z140 catalysts

	Z15	Z140	$R_{\text{Z15/Z140}}$
Kinetic rates			
k_{1-3}^* ($\text{mol}_{\text{C}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1} \text{atm}^{-1}$)	$(6.52 \pm 0.41) 10^{-1}$	$(3.46 \pm 2.21) 10^{-2}$	18.84
k_{4-6}^* ($\text{mol}_{\text{C}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1} \text{atm}^{-2}$)	$(3.20 \pm 0.97) 10^0$	$(2.64 \pm 0.59) 10^{-1}$	12.15
k_{7-9}^* ($\text{mol}_{\text{C}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1} \text{atm}^{-1}$)	$(1.54 \pm 0.05) 10^0$	$(6.94 \pm 2.99) 10^{-2}$	22.25
k_{10}^* ($\text{mol}_{\text{C}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1} \text{atm}^{-1}$)	$(1.05 \pm 0.41) 10^{-3}$	$(1.07 \pm 0.95) 10^{-3}$	0.98
E_{1-3} (kJ mol^{-1})	$(5.69 \pm 0.98) 10^1$	$(5.96 \pm 1.33) 10^1$	0.95
E_{4-6} (kJ mol^{-1})	$(3.38 \pm 0.91) 10^1$	$(3.43 \pm 0.91) 10^1$	0.98
E_{7-9} (kJ mol^{-1})	$(1.74 \pm 0.16) 10^1$	$(1.80 \pm 0.61) 10^1$	0.96
E_{10} (kJ mol^{-1})	$(2.36 \pm 0.31) 10^1$	$(2.29 \pm 1.07) 10^1$	1.03
Deactivation rate			
k_d ($\text{h}^{-1} \text{atm}^{-1}$)	$(3.14 \pm 0.06) 10^{-1}$	$(1.05 \pm 0.29) 10^{-1}$	2.99
E_d (kJ mol^{-1})	$(3.00 \pm 0.15) 10^1$	$(3.21 \pm 0.78) 10^1$	0.93

Regarding the fitting of experimental data, the model allows obtaining reproducible values of the experimental runs previously presented in this work. Conditions of high and low conversions and of fast and slow deactivation with both catalysts can be relatively well-predicted by the model considering our deactivation equation (Eq. (5)) and a deactivation order near to 1 in both cases (Table S1). Relating the steps of the Fig. 4 to the extent of the reactions, the kinetic constants can be divided in three different groups, including the initiation reactions (k_{1-3}), the autocatalytic formation of olefins (k_{4-6}) and the secondary reactions (k_{7-9}).

The average values of k^* and E for each of these groups are displayed in Table 2. For comparing the results, the ratios between the kinetic parameters of both catalysts ($R_{\text{Z15/Z140}}$) are also calculated and depicted in the Table 2. Values higher than unity are observed for these three groups of reactions (18.84, 12.15 and 22.25 for k_{1-3} , k_{4-6} and k_{7-9} , respectively), thus pointing out a promotion of all of them with Z15 catalyst. Consequently, the initiation of the catalytic mechanism through a paraffinic C–C bond cleavage is almost 20 times faster using the most acid Z15 catalyst (k_{1-3}). At the same time, the higher increase in the $R_{\text{Z15/Z140}}$ ratio for secondary reactions

(k_{7-9}) than that for olefins formation reactions (k_{4-6}) is consistent with the higher selectivity of olefins observed using the Z140 catalyst (Fig. S1) and those of aromatics and paraffins using the Z15 catalyst.

The values of the activation energy are very similar for all the steps of the reaction scheme using both catalysts. In all cases, activation energy values are in the range of ca. 10.0 and 72.4 kJ mol⁻¹, being the minimum and maximum $R_{Z15/Z140}$ ratios of 0.95 (E_{1-3}) and 1.03 (E_{10}) (Table 2). These results indicate the coherence on defining the reaction steps of Fig. 4 according to the reaction mechanism. The general trend is a decrease in the activation energy with the more active catalyst, which is the expected result in catalytic processes.

A similar tendency is observed comparing the deactivation kinetic parameters obtained for each catalyst. A threefold value of the deactivation kinetic constant is observed for the Z15 catalyst, whereas the value of activation energy is slightly lower (practically with the same deactivation order, considered 1). This behavior is in accordance with the well-established role of the HZSM-5 zeolite acidity in activating the condensation reactions of olefins and BTX aromatics towards polyaromatics structures of coke.^{44,48}

3.3. Reactor simulation for olefin and aromatic productions

The kinetic parameters summarized in Table S1 were used in the simulation of an isothermal packed bed reactor in order to establish the optimal operation conditions (temperature, space time) and maximize the yields of olefins and BTX aromatics with the Z15 and Z140 catalysts. The simulations consist of solving the conservation equations for the molar fraction of each i lump in Fig. 4 (y_i , in terms of carbon). This is a direct application of the convection-dispersion-reaction equation of a gas flow through a cylindrical reactor (where the catalyst is package), considering one-dimensional flow direction. Then, the evolution of y_i with the catalytic bed length (l) and with the time on stream (t) can be described as:

$$\varepsilon_b \frac{\partial y_i}{\partial t} = -\frac{\partial}{\partial l} \left(v y_i - D \frac{\partial y_i}{\partial l} \right) + \frac{RT}{P N_C} \rho_b r_i \quad (9)$$

defined for $t > 0$ and $0 < l < L$, and where ε_b is the effective bed-particle porosity, v is the linear velocity of the gas, D is the effective dispersion coefficient of the gas, P the total pressure, N_C the (carbon molar flow rate)/(total molar flow rate) ratio, ρ_b the catalytic bed density and L the total catalytic bed length. The formation rate of each i lump (r_i) is calculated from Eq. (8) and the gas dispersion is assumed negligible in comparison to the gas convection. Nevertheless, the dispersion term is required in order to ensure the stability of the stiff problem resolution using an implicit Runge-Kutta method based on the numerical differentiation formulas of orders 1–5 (*ode15s* in MATLAB). The computation of the differential equation system in Eq. (9) also requires a simultaneous calculation of the Eq. (5) for considering the catalyst deactivation in the formation rate of each i lump and the following initial and boundary conditions:

$$\begin{cases} y_i(l, 0) = 1; & i = nC_5 \\ y_i(l, 0) = 0; & i \neq nC_5 \\ a(l, 0) = 1 \end{cases} \quad (10)$$

$$\begin{cases} y_i(0, t) = y_i(l, 0) + \frac{D}{v} \frac{\partial}{\partial l} y_i(0, t) \\ \frac{\partial}{\partial l} y_i(L, t) = 0 \end{cases} \quad (11)$$

Please note that the feed is assumed to be diluted in N₂ ($P = 1.5$ atm and $P_{nC5} = 0.9$ atm) but y_i is defined in terms of carbon. The isothermal packed bed reactor was simulated considering the conditions of experimental runs, within the temperature range of 450–550 °C and space time values up to 5 g_{cat} h mol⁻¹. First, the results obtained for catalyst activity values of 1 (TOS = 0) are shown in Fig. 6. Fig. 6a displays the evolution of the maximum yield of olefins obtained at certain space time values, and the one of BTX aromatics are depicted in Fig. 6b. From a commercial point of view, these two products are the most interesting alternatives for valorizing paraffins such as n-pentane. As observed, Z15 catalyst allows obtaining higher yields of olefins at 450 °C than Z140 catalyst (Fig. 6a). However, Z140 catalyst is clearly the best catalyst for producing olefins at higher temperatures. Otherwise, this catalyst does not practically show significant yields of BTX aromatics at any condition whereas higher yields than 50% can be achieved with Z15 catalyst (Fig. 6b). In any case, the increase in the temperature up to 550 °C enhances the production of olefins and BTX aromatics with both catalysts.

Thereby, 550 °C was selected as the suitable temperature for studying the process and the simulated contour maps of activity with the space time (τ) and time on stream (TOS) for Z15 and Z140 catalysts are displayed in Fig. 7a and Fig. 7b,

respectively.

Fig. 6. Simulated maximum yields of (a) olefins and (b) BTX aromatics respectively obtained with Z15 and Z140 catalysts at different temperatures

Fig. 7. Predicted contour maps of activity with space time and time on stream for (a) Z15 and (b) Z140 catalysts at 550 °C, and their projections onto the X axis (τ projection) for (c) Z15 and (d) Z140 catalysts and onto the Y axis (TOS projection) for (e) Z15 and (f) Z140 catalysts

As the equation system of **Eq. (9)** is defined as a function of the time on stream and the catalytic bed length, the simulated space time values were calculated as:

$$\tau = \frac{\rho_b S}{F} l \quad (11)$$

where S is the section of the reactor. For an easier visualization of the results, **Fig. 7** also provides the projections onto the X axis (τ projection) for selected values of TOS (**Fig. 7c** and **Fig. 7d**) and onto the Y axis (TOS projection) for selected values of τ (**Fig. 7e** and **Fig. 7f**). A more abrupt decay of the activity with the space time is observed for Z15 (**Fig. 7a**) than Z140 catalyst (**Fig. 7b**), that leads to a minimum value in the range of 0.5–1.0 $\text{g}_{\text{cat}} \text{h mol}_c^{-1}$. This means that Z15 catalyst undergoes a more severe deactivation near to the inlet of the reactor regarding the activity profiles in the packed bed reactor (τ projection in **Fig. 7c**). This profile is obviously reproduced at lower values of activity upon increasing the TOS. A softer activity profile is observed for Z140 catalyst, finding the minimum activity value at the outlet of the reactor in all cases (τ projection in **Fig. 7d**). Apart from the different activity profiles of each catalyst, a faster deactivation is also predicted for Z15 catalyst and values lower than 0.2 are estimated in all the reactor positions after 15 h on stream (TOS projection in **Fig. 7e**). Otherwise, the drop of the activity for Z140 catalyst depends on the reactor position (TOS projection in **Fig. 7f**). Activity values from 0.7 to 0.35 are respectively estimated for space time values of 1.0 and 5.0 $\text{g}_{\text{cat}} \text{h mol}_c^{-1}$,

respectively. This is in agreement with the above discussed experimental results and goes hand in hand with the product distribution in each case. Then, a higher activity for the transformation of n-pentane also leads to more abrupt activity profiles and faster deactivation rates.

Considering these evolution of the activity for each catalyst, **Fig. 8** displays the contour maps of the evolution with the TOS and the space time of the olefin and BTX aromatic yields for both catalysts. As previously stated (**Fig. 2** and **Fig. 3**), Z15 catalyst is more active and also shows a faster deactivation with TOS. The main consequence of deactivation is the progressive decrease in the yield of BTX aromatics with the TOS (**Fig. 8b**). This slowing down of secondary reaction upon increasing the TOS leads to a maximum of olefins after 5–15 h (23.5%). Then, for higher values of TOS, reactions of olefin production are also affected by deactivation and its yield decreases (**Fig. 8a**). A clearly differentiated evolution of the yields of olefins (**Fig. 8c**) and BTX aromatics (**Fig. 8d**) is predicted for the Z140 catalyst. The lower acidity of this catalyst and thus the restricted extent of secondary reactions can explain its performance. BTX aromatics are negligible in the whole range of studied conditions, and contrary to the performance of Z15 catalyst, the maximum yield of olefins (31%) is obtained at the highest space time value with a remarkably slower deactivation with the TOS (**Fig. 7**). This allows having a relatively wide range of olefin yields between 25 and 31% from 0 to 10 h on stream.

Fig. 8. Simulated contour maps for (a, b) Z15 and (c, d) Z140 catalysts of the evolution with the time on stream and space time of the (a, c) olefin and (b, d) BTX aromatic yields at 550 °C

As these two product lumps are considered as coke precursors and Eq. (5) assumes that the evolution of the activity with time is a function of the sum of their concentration, the maxima location of the sum of their concentration will determine the activity profile in the reactor. Coherent results are therefore obtained for both catalysts, and the minimum activity values (Fig. 7) correspond to the maximum concentration of precursors of coke (Fig. 8). Additional experimental runs were carried out for corroborating the yields of olefins and BTX aromatics predicted by the model. Fig. S5 displays the comparison of these results for both catalysts and two selected values of space time (1 and 3.5 $\text{g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$) at 500 °C. As can be observed, the predicted values are quite close to the experimental ones, which manifests that the model predictions are accurate enough for assuming the reliability of the model.

In terms of production, the olefin and BTX aromatic selectivities are also important indexes, aiming the best insulation of the desired products. Using the conversion contour maps of Fig. S6, the selectivity contour maps of the evolution with the TOS and the space time for both catalysts are calculated (Fig. 9). The maximum olefin selectivity is located at very low values of space time with the Z15 catalyst (Fig. 9a), which was expected as primary product of the reaction scheme (Fig. 4). This however is not a favorable situation because the maximum yield of olefins (Fig. 8a) does not coincide with its maximum selectivity (Fig. 9a). This situation can be achieved for BTX aromatic yield and selectivity (both 53%) at full conversion conditions (Fig. 9b). The most encouraging result in terms of selectivity is achieved with Z140 catalyst. In all the studied range, values of olefin selectivities of 44–51% are predicted (Fig. 9c) with negligible BTX aromatic

ones (Fig. 9d). This result is slightly lower than those reported by Hou et al.¹³ in the catalytic cracking of n-pentane with modified HZSM-5 zeolites, which suggests the satisfactory performance of this zeolites for the valorization of this paraffin.

Taking into account the contour maps of yields and selectivities regarding the production of BTX aromatics and olefins, an operational map can be constructed from the results of Fig. 8 and Fig. 9. In order to minimize the amount of catalyst, space time values of 4.0 $\text{g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$ should be enough for being within the maxima production region of aromatics and olefins with Z15 and Z140 catalysts, respectively. Nevertheless, this should require the regeneration of the Z15 catalyst after less than 1 h on stream (yield and selectivity >45%) and of the Z140 catalyst after 3 h on stream (yield >25% and selectivity >45%). Due to the different deactivation rates of each catalyst, increasing the space time up to 5.0 $\text{g}_{\text{cat}} \text{ h mol}_{\text{C}}^{-1}$ allows 10 h of operation of the Z140 catalyst but only being within the optimum selectivity zone after 2.5 h on stream (Fig. 9c).

According to the simulation results, some of the interesting operation conditions are located at the extreme studied points of temperature or space time. It is worth of mentioning that higher values than those depicted could allow reaching higher maxima of olefin and BTX aromatic yields/selectivities. Nevertheless, temperature is restricted by the catalyst stability (550 °C) in order to avoid the dealumination of the HZSM-5 zeolite.⁴⁹ In our study, the space time was also limited by the experimental reactor size, which could hypothetically be solved with a scale-up of the process. Based on the quality of the kinetic model, the results could also be useful to study different reactor configurations (moving-bed or fluidized bed reactors with catalyst recirculation) in the strategy of

scaling up the catalytic conversion of paraffins into olefins and/or BTX aromatics.

Conclusions

Aiming the progress in the industrial implementation of a catalytic process for valorizing paraffins, agglomerated HZSM-5 catalysts with Si/Al ratios of 15 (Z15) and 140 (Z140) have shown attractive performances in the production of BTX aromatics and light olefins, respectively. The feasibility of these processes is limited by the catalyst deactivation, which have been taken into account for the development of a lump-based kinetic model for n-pentane conversion.

Comparing the kinetic parameters computed for each catalyst, a marked influence of the Si/Al ratio of the zeolite is observed in all the steps of the reaction scheme: the olefin formation reactions, the main secondary reactions (hydride transfer, oligomerization-cracking and cyclization-aromatization) and also the catalyst deactivation, with a kinetic constant three times higher for the Z15 catalyst (with high acidity).

The simulation of the packed bed reactor allows for optimizing the operation conditions at which the yields and selectivities of olefins and BTX aromatics are maximized. Maximum values of olefin yield and selectivity of 31 and 51% are respectively estimated with the Z140 catalyst, whereas Z15 catalyst allows achieving maxima of both aromatic yield and selectivity of 53% at 550 °C.

High productions of the desired products inevitably favor the formation of coke and the drop of the catalyst activity because olefins and BTX aromatics are also the main precursors of coke (deactivation in series). In this regard, the Z140 catalyst offers the possibility of producing olefins with the highest registered yield and selectivity and considerably reducing the catalyst deactivation due to its lower acidity (lower the deactivation kinetic constant). The used catalyst analyses indicate that this faster deactivation of Z15 catalyst is attributed to its higher and stronger acidity that promotes the condensation reactions of coke. However, in both cases, the presence of a mesoporous γ -Al₂O₃ matrix favors the diffusion of this coke towards outside the catalyst particle, which helps to attenuate the catalyst deactivation.

Nomenclature

- a Catalyst activity
- $A_{i,j}$ C balance coefficient matrix
- BTX, C₅₊, O, P Lumps of BTX aromatics (benzene, toluene, xylenes), long chained hydrocarbons, olefins and paraffins
- D Effective dispersion coefficient of the gas, m² h⁻¹
- d Deactivation order
- E Activation energy, kJ mol⁻¹
- F Total carbon molar flow rate, mol_C h⁻¹

Fig. 9. Simulated contour maps for (a, b) Z15 and (c, d) Z140 catalysts of the evolution with the time on stream and space time of the (a, c) olefin and (b, d) BTX aromatic yields at 550 °C

- F_i, F_{nC5} Carbon molar flow rate at the outlet of the reactor of each i lump and of n-pentane, respectively
- k^* Kinetic constant at the reference temperature
- k_d Deactivation kinetic constant, $\text{h}^{-1} \text{atm}^{-1}$
- k_j Kinetic constant of each j step of the reaction scheme
- l Catalytic bed length, m
- L Total catalytic bed length, m
- N_C (carbon molar flow rate)/(total molar flow rate) ratio, $\text{mol}_C \text{mol}^{-1}$
- nC_5 n-Pentane
- P Total pressure, atm
- P_i Partial pressure of each lump, atm
- $R_{Z15/Z140}$ Kinetic parameter ratios of Z15 and Z140 catalysts
- r_i Formation rate of each i lump, $\text{mol}_C \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$
- $r_j, r_{j,0}$ Rates of each j step of the reaction scheme at t and zero time on stream, $\text{mol}_C \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$
- S Reactor section, m^2
- S_i, Y_i Selectivity and Yield of each i lump, $\text{mol}_C\%$
- S_{BET} BET specific surface area, $\text{m}^2 \text{g}^{-1}$
- T Temperature, K
- T^* Reference temperature, K
- t Time, h
- TOS Time on stream, h
- t-BA *tert*-Butylamine
- v Linear velocity of the gas, m h^{-1}
- X Conversion of n-Pentane, $\text{mol}_C\%$
- y_i molar fraction of each i lump, $\text{mol}_C \text{mol}_C^{-1}$

Greek symbols

- ε_b Effective bed-particle porosity
- ρ_b Catalytic bed density, kg m^{-3}
- τ Space time, $\text{g}_{\text{cat}} \text{h mol}_C^{-1}$

Subscripts

- d Deactivation
- i Lump i
- j Step j of the reaction scheme
- R Reactant

Conflicts of interest

There are no conflicts to declare

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References

- 1 N. Rahimi and R. Karimzadeh, *Appl. Catal. A Gen.*, 2011, **398**, 1–17.
- 2 S. M. Sadrameli, *Fuel*, 2015, **140**, 102–115.
- 3 S. M. Sadrameli, *Fuel*, 2016, **173**, 285–297.
- 4 Y. Ji, H. Yang and W. Yan, *Mol. Catal.*, 2018, **448**, 91–99.
- 5 K. Yang, Y. Yin, S. Lai, L. Zhu, J. Zhang, W. Lai, Y. Lian and W. Fang, *Catal. Lett.*, 2018, **148**, 3570–3582.
- 6 J. Liu, N. He, Y. Zhao, L. Lin, W. Zhou, G. Xiong, H. Xie and H. Guo, *Catal. Lett.*, 2018, **148**, 2069–2081.
- 7 A. Samanta, X. Bai, B. Robinson, H. Chen and J. Hu, *Ind. Eng. Chem. Res.*, 2017, **56**, 11006–11012.
- 8 Q. Li, F. Zhang, J. Jarvis, P. He, M. M. Yung, A. Wang, K. Zhao and H. Song, *Fuel*, 2018, **219**, 331–339.
- 9 Q. Li, P. He, J. Jarvis, A. Bhattacharya, X. Mao, A. Wang, G. M. Bernard, V. K. Michaelis, H. Zeng, L. Liu and H. Song, *Appl. Catal. B Environ.*, 2018, **236**, 13–24.
- 10 A. Corma, E. Corresa, Y. Matthieu, L. Sauvinaud, S. Al-Bogami, M. Ghrami and A. Bourane, *Catal. Sci. Technol.*, 2017, **7**, 12–46.
- 11 X. Hou, Y. Qiu, Y. Tian, Z. Diao, X. Zhang and G. Liu, *Chem. Eng. J.*, 2018, **349**, 297–308.
- 12 X. Hou, Y. Qiu, E. Yuan, F. Li, Z. Li, S. Ji, Z. Yang, G. Liu and X. Zhang, *Appl. Catal. A Gen.*, 2017, **543**, 51–60.
- 13 X. Hou, Y. Qiu, X. Zhang and G. Liu, *Chem. Eng. J.*, 2017, **307**, 372–381.
- 14 E. Epelde, M. Ibañez, A. T. Aguayo, A. G. Gayubo, J. Bilbao and P. Castaño, *Microporous Mesoporous Mater.*, 2014, **195**, 284–293.
- 15 B. Valle, A. G. Gayubo, A. T. Aguayo, M. Olazar and J. Bilbao, *Energy Fuels*, 2010, **24**, 2060–2070.
- 16 P. He, A. Wang, S. Meng, G. M. Bernard, L. Liu, V. K. Michaelis and H. Song, *Catal. Today*, 2018, **323**, 94–104.
- 17 M. Guisnet and P. Magnoux, *Appl. Catal. A Gen.*, 2001, **212**, 83–96.
- 18 K. Kubo, T. Takahashi, H. Iida, S. Namba and A. Igarashi, *Appl. Catal. A Gen.*, 2014, **482**, 370–376.
- 19 S. Mahamulkar, K. Yin, P. K. Agrawal, R. J. Davis, C. W. Jones, A. Malek and H. Shibata, *Ind. Eng. Chem. Res.*, 2016, **55**, 9760–9818.
- 20 E. Epelde, A. T. Aguayo, M. Olazar, J. Bilbao and A. G. Gayubo, *Appl. Catal. A Gen.*, 2014, **479**, 17–25.
- 21 A. S. Al-Dughaiter and H. de Lasa, *Ind. Eng. Chem. Res.*, 2014, **53**, 15303–15316.

- 22 M. Ibañez, P. Pérez-Urriarte, M. Sánchez-Contador, T. Cordero-Lanzac, A. T. Aguayo, J. Bilbao and P. Castaño, *Catalysts*, 2017, **7**, 254–266.
- 23 Y. Jiao, X. Ou, J. Zhang and X. Fan, *React. Chem. Eng.*, 2019, **4**, 427–435.
- 24 T. Cordero-Lanzac, A. T. Aguayo, A. G. Gayubo, P. Castaño and J. Bilbao, *Chem. Eng. J.*, 2018, **331**, 818–830.
- 25 S. Schallmoser, T. Ikuno, M. F. Wagenhofer, R. Kolvenbach, G. L. Haller, M. Sanchez-Sanchez and J. A. Lercher, *J. Catal.*, 2014, **316**, 93–102.
- 26 C. Song, Y. Chu, M. Wang, H. Shi, L. Zhao, X. Guo, W. Yang, J. Shen, N. Xue, L. Peng and W. Ding, *J. Catal.*, 2017, **349**, 163–174.
- 27 A. Janda, B. Vlaisavljevich, L. C. Lin, S. Mallikarjun Sharada, B. Smit, M. Head-Gordon and A. T. Bell, *J. Phys. Chem. C*, 2015, **119**, 10427–10438.
- 28 H. Li, S. A. Kadam, A. Vimont, R. F. Wormsbecher and A. Travert, *ACS Catal.*, 2016, **6**, 4536–4548.
- 29 G. F. Froment, *Catal. Rev.*, 2005, **47**, 83–124.
- 30 K. Toch, J. W. Thybaut and G. B. Marin, *AIChE J.*, 2015, **61**, 880–892.
- 31 T. von Aretin, S. Standl, M. Tonigold and O. Hinrichsen, *Chem. Eng. J.*, 2017, **309**, 873–885.
- 32 J. H. Miller, L. Bui and A. Bhan, *React. Chem. Eng.*, 2019, **4**, 784–805.
- 33 P. J. Becker, N. Serrand, B. Celse, D. Guillaume and H. Dulot, *Fuel*, 2016, **165**, 306–315.
- 34 P. Pérez-Urriarte, A. Ateka, A. G. Gayubo, T. Cordero-Lanzac, A. T. Aguayo and J. Bilbao, *Chem. Eng. J.*, 2017, **311**, 367–377.
- 35 X. Huang, H. Li, H. Li and W. De Xiao, *Fuel Process. Technol.*, 2016, **150**, 104–116.
- 36 W. Guo, W. Xiao and M. Luo, *Chem. Eng. J.*, 2012, **207–208**, 734–745.
- 37 M. Stamenic, V. Dikic, M. Mandic, B. Todric, D. B. Bukur and N. M. Nikacevic, *Ind. Eng. Chem. Res.*, 2017, **56**, 9964–9979.
- 38 A. Rai, M. Anand, S. A. Farooqui, M. G. Sibi and A. K. Sinha, *React. Chem. Eng.*, 2018, **3**, 319–332.
- 39 T. Cordero-Lanzac, A. Ateka, P. Pérez-Urriarte, P. Castaño, A. T. Aguayo and J. Bilbao, *Ind. Eng. Chem. Res.*, 2018, **57**, 13689–13702.
- 40 P. Pérez-Urriarte, M. Gamero, A. Ateka, M. Díaz, A. T. Aguayo and J. Bilbao, *Ind. Eng. Chem. Res.*, 2016, **55**, 1513–1521.
- 41 P. M. Allotta and P. C. Stair, *ACS Catal.*, 2012, **2**, 2424–2432.
- 42 P. Castaño, J. Ruiz-Martínez, E. Epelde, A. G. Gayubo and B. M. Weckhuysen, *ChemCatChem*, 2013, **5**, 2827–2831.
- 43 G. T. Whiting, F. Meirer, M. M. Mertens, A.-J. Bons, B. M. Weiss, P. A. Stevens, E. de Smit and B. M. Weckhuysen, *ChemCatChem*, 2015, **7**, 1312–1321.
- 44 G. Caeiro, R. H. Carvalho, X. Wang, M. A. N. D. A. Lemos, F. Lemos, M. Guisnet and F. Ramôa Ribeiro, *J. Mol. Catal. A Chem.*, 2006, **255**, 131–158.
- 45 I. Hita, T. Cordero-Lanzac, A. Gallardo, J. M. Arandes, J. Rodríguez-Mirasol, J. Bilbao, T. Cordero and P. Castaño, *Catal. Commun.*, 2016, **78**, 48–51.
- 46 E. Epelde, J. I. Santos, P. Florian, A. T. Aguayo, A. G. Gayubo, J. Bilbao and P. Castaño, *Appl. Catal. A Gen.*, 2015, **505**, 105–115.
- 47 S. Kotrel, H. Knözinger and B. C. Gates, *Microporous Mesoporous Mater.*, 2000, **35–36**, 11–20.
- 48 M. Guisnet, L. Costa and F. R. Ribeiro, *J. Mol. Catal. A Chem.*, 2009, **305**, 69–83.
- 49 A. G. Gayubo, A. Alonso, B. Valle, A. T. Aguayo, M. Olazar and J. Bilbao, *Fuel*, 2010, **89**, 3365–3372.