

Benzofuran as deactivation precursor molecule: Improving the stability of acid zeolites in biomass pyrolysis by co-feeding propylene

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Abstract

Benzofuran (BZF) is produced during the biomass and waste pyrolysis, playing a key role in the catalytic deactivation in the processing of the resulting fractions, as well as in catalytic pyrolysis reactions. The transformation of this chemical over a typical pyrolysis catalyst (ZSM-5) is studied in this article. When this compound is processed alone, it presents a very high reactivity. At low temperature, the formation of large amount of coke precursors leads to a fast catalyst deactivation. As temperature increases, the weight of cracking reactions (yielding benzenes or naphthalenes) becomes more important, increasing the catalyst's stability, although new polyaromatic carbon species are detected.

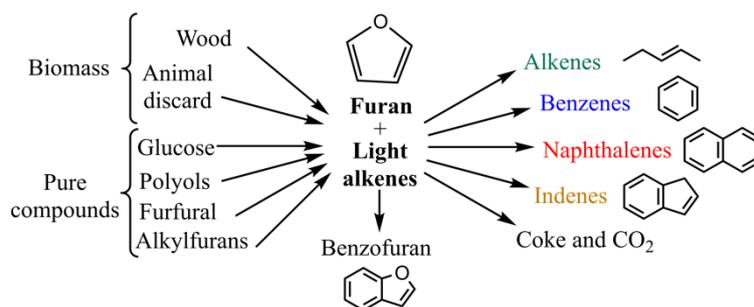
A new strategy to minimize the deactivation caused by this compound, consisting of co-feeding propylene, is proposed. The presence of an alkene leads to the formation of alkylated derivatives of Diels-Alder condensation products, hindering their oligomerization capacity and minimizing the formation of polyaromatic coke deposits. Different temperatures and alkene/BZF ratios were tested, concluding that increasing the alkene concentration and the reaction temperature monotonously increase the catalyst's stability in presence of BZF.

Key-words: coke formation; aromatics chemistry; Diels-Alder reaction; thermochemical biomass upgrading; aromatics alkylation

1. Introduction

Biomass pyrolysis is one of the most promising routes for the waste upgrading, considering that this process takes place in a single step reactor, without requiring any pretreatment or fractionation of the raw material. These requirements are the common drawbacks for all the liquid-phase alternatives proposed in the literature. By pyrolysis, the solid biomass is thermally converted in a complex mixture of oxygenated vapours, containing furans and alkanes, among others [1, 2]. If this pyrolysis is carried out in presence of an acidic catalyst (catalytic pyrolysis – CP), this decomposition is accompanied by different condensation reactions, highlighting the Diels-Alder reactions (a cycloaddition where a conjugated diene adds to an alkene to yield aromatic derivatives), obtaining aromatic compounds (benzene, naphthalene and indene families) with multiple applications at industrial scale [3-6].

Acid zeolites, such as ZSM-5, are proposed in the literature as optimum catalysts for this purpose, providing high activities for different lignocellulosic raw materials: pine sawdust, microalgae, seaweed, fish discard, wood and plastic-wood mixtures, etc. [7-11]. In addition, the specific pathway of Diels-Alder reaction has been studied considering pure compounds that could be obtained during the biomass pyrolysis: cellulose [12], glucose [11, 13-15], sorbitol, glycerol, tetrahydrofuran, methanol [14], ethylene glycol [15], furfural [16, 17], furfuryl alcohol [17], etc. The same kinds of products is obtained in all these cases, suggesting a complex process in which many secondary reactions are involved, including oligomerizations, alkylations/dealkylations, cyclizations, isomerizations, cracking (decarbonylation and hydrolysis) [9, 18]. Furan and light alkenes are identified as the precursors of most of these final compounds, being proposed as common products obtained in all the biomass pyrolysis, despite the raw material, as summarized in **Scheme 1**.



Scheme 1: Outline of the biomass and organic pure compounds produced during pyrolysis processes. Adapted from results of [7-17].

Despite the different reactants and the plethora of reaction products, there is a good agreement about the key role of benzofuran (BZF) in these transformations. This compound is directly obtained by the reaction between two furan molecules [19-22], being a ubiquitous chemical in these reaction media. Due to its high reactivity, it is considered as a relevant coke precursor its polymerization being suggested as the main deactivation cause [23, 24]. The poor stability as well as the low control on the selectivity distribution (benzene, toluene and xylene - BTX- identified as the most interesting compounds) are nowadays considered the main drawbacks of the catalytic pyrolysis approach [9, 25]. On the other hand, it has been observed that these deactivation mechanisms are largely affected by the temperature and the presence of other chemicals [22, 26]. In spite of the evidences of the key role of BZF on catalyst deactivation and the abovementioned sensibility to operation parameters, there is a lack of systematic studies about the deactivation mechanisms involving this intermediate.

This paper tries to fill this gap by studying the benzofuran pyrolysis catalysed by ZMS-5. This zeolite has been chosen as catalyst since it has been identified as the optimum material to produce aromatics from biomass since it has an ideal pore size to maximize the production of benzene, toluene and xylene (BTX), three of the most interesting aromatic compounds [21,27]. Special attention is paid to both the effect of the temperature and the effect of the presence of olefins in the reaction mixtures. Propylene is chosen as co-reactant since previous works

corroborate an activity significantly higher than the one obtained with other light alkenes, such as ethylene [17, 21, 28]. All these studies allow us proposing a detailed mechanism in which all the single steps derived from benzofuran reactivity are considered.

2. Experimental

2.1. Catalyst: NH₃-ZSM-5 zeolite (Si/Al: 11.5, Zeolyst) were used for this study. Before being used, it was calcined to H-ZSM-5 in air at 550°C for 12 h, being this temperature reached with a slope of 1°C/min. For sake of simplicity, this catalyst is labelled as ZSM-5 in this article. This catalyst has been previously used in our group, its characterization being deeply studied in a previous work [29]. According to these analyses, the ZSM-5 zeolite has a total surface of 353 m²/g (external and pores surfaces of 109 and 244 m²/g, respectively); a pore volume of 0.19 cm³/g (0.12 and 0.07 cm³/ of micro and mesoporous) and pore channels of 5.3 Å. Acidity was measured by programmed-temperature desorption using NH₃ as probe molecule, obtaining a total acidity of 15.6 mmol/g, with 6.0 mmol/g of them associated to strong acid sites (desorption temperature higher than 300°C). This methodology cannot distinguish between Lewis and Bronsted sites. However, according to the bibliography, this zeolite has a strong Bronsted acidity, discarding the presence of Lewis sites [24,30].

2.2. Reaction studies: Samples of 240 mg (250-355 µm) were disposed inside a 0.7 cm internal diameter U-shaped fixed-bed quartz reactor. The fixed-bed reactor is placed in an electric oven equipped with a thermocouple and a PID controller. All the pipes and fittings between the injection point and the analytic system were maintained at 250°C with heating blankets to prevent any condensation. Benzofuran (ThermoFisher, >99.5%) and propylene (Air Liquide, >99.5%) were fed diluted in helium (Air Liquide, >99.999%), reaching a total flow of 20 mL/min (s.t.p.) with 10 % of organics. Reaction temperature and ratios of compounds were variable between experiments, from 300 to 550°C, and from a 0/1 to 24/1 in reactions involving

propylene/benzofuran (P/BZF). Pressure was kept in 2.0 ± 0.1 bars, the pressure drop along all the system being lower than 0.2 bar.

To validate the accuracy of these studies, the fluid-dynamic of the system was empirically evaluated, analysing the signal distribution obtained after a pulse disturbance in the concentration of one compound, according to the Peclet number (Pe). Thus, 2.5 μL of furan were suddenly injected in the system in absence of catalyst and the evolution of the signal obtained with the GC-FID was analysed. Resident time distribution (RTD) were studied with the Wolf-Resnick's model [31]. A Peclet number of 56 was obtained, suggesting that the flow regime is turbulent. Considering the relationship between Pe and the Reynolds number ($Pe = Re \cdot Sc$), this Pe value guarantees a turbulent regime. The catalytic particle size was also chosen to allow a plug-flow regime. To corroborate the absence of diffusional limitations, the Carberry value were calculated obtaining a value of 0.014 at the less favourable conditions (highest reaction temperature), far from the thresholds and discarding the prevalence of external diffusional limitations. Thus, there are not relevant effects of mass transfer on the overall kinetics.

2.3. Analysis: The qualitative analysis was carried out by gas chromatography-mass spectrometry (GC-MS Shimadzu QP 2010), once the effluent was condensed with an ice bath and dissolved in organic solvent. A capillary column is used as stationary phase (TRB 5MS, 30 m, 0.25 mm). Two solvents were used to dilute the samples and prevent saturation: acetone and octane in order to obtain the complete spectra of products involved, since the solvent signal masked the light or heavy products, respectively. Thus, the complete identification requires the double analysis. Isomers cannot be identified with enough accuracy, so they are considered together in any product.

The quantitative analysis of the reactor effluent was performed on-line using gas chromatograph with flame ionization detector (GC-FID HP 6890Plus), with the same column

and temperature program previously defined for the GC-MS. GC-FID chromatograph results were analysed with calibrations using commercial samples and response factors when these standards were not available [32,33]. The percentage of known compounds area were higher than 96%, assuming that the discrepancies in the carbon balances are due to char, coke, CO, CO₂ and/or condensed compounds. Equations used to express the results are summarized below:

$$\text{Selectivity (\%)} = \frac{n_i \cdot C_i}{\sum(n_i \cdot C_i)} \cdot 100 \quad [2]$$

$$\text{Molar yield (\%)} = \frac{m_{p,i}}{m_r} \cdot 100 \quad [3]$$

In these equations “C” is the concentration of “i” compound in the gas phase; “n” is the number of carbon atoms in the molecule; and “m_{p,i}” and “m_r”, the moles of the outgoing product and incoming reactant. Therefore, selectivity and molar yield are expressed in terms of moles of carbon and moles of compound, respectively.

2.4. Spent catalyst characterization: Temperature programmed oxidation analyses (TPO) were carried out to analyse the solid deposits on the catalytic surface of spent catalyst. These analyses were done in a Micromeritics Autochem II 2920. Firstly, the catalysts’ surface was cleaned with a helium flow (20 ml/min) at 150°C for 30 minutes. The coke combustion was carried out with a flux of 5% O₂ in helium (20 ml/min). The temperature was increased from room temperature to 950°C with a slope of 2.5°C/min. The gas effluents were analysed by mass spectrometry (Omnistar GSD 301).

3. Results and discussion

3.1. Benzofuran pyrolysis: reaction mechanism

Benzofuran was fed (2.5 v.% in He) into the fix-bed reactor, using 240 mg of ZMS-5 (WHSV = 0.66 h^{-1} , measured as the BZF mass flow divided by the catalytic mass). The catalytic cracking was studied at three different temperatures (450, 500 and 550 °C), these values being chosen according to the most typical temperatures reported in the literature. A blank experiment was carried out without observing any conversion in absence of catalyst. In presence of ZSM-5, total conversion of benzofuran was obtained, despite the temperature, as it could be anticipated due to its high activity, observing slight differences in the products distribution, both by and inside each family. These distributions are shown in **Figure 1**.

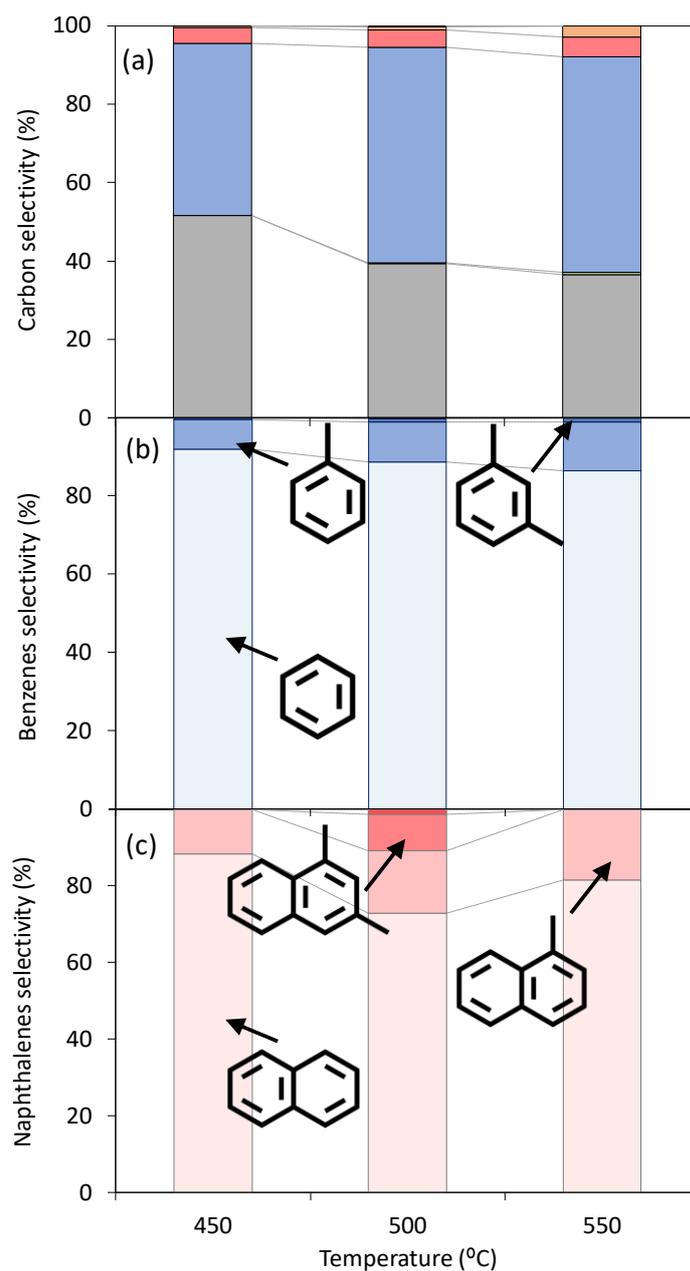


Figure 1: (a) Product distribution in BZF cracking (2.5 v.%) as function on temperature. Symbols: (■) indenes, (■) naphthalenes, (■) benzenes and (■) CO₂ and coke. Selectivities in (b) benzenes and (c) naphthalenes families

Benzenes are the main products detected in the gas phase, reaching selectivities of 55 % at 500 and 550°C. This value is 25 % relatively higher than the selectivity obtained at 450 °C. The prevalence of benzene as the main product of this family slightly decreases with the temperature, from 92 to 87 %, in favour of the production of toluene, which increases from 8

to 12 % in the same temperature range. The presence of monocyclic aromatics is mainly explained by the benzofuran decarbonylation, previously suggested in the literature [22], releasing CO as co-product. A similar reaction, but with a different breakdown of the benzofuran molecule could also justify the presence, in lower amount, of toluene. Other authors suggest that monocyclic aromatics could also be produced by the Diels-Alder reaction between propylene and furan, obtaining toluene as the main product [34]. Toluene would be in disproportionation equilibrium with benzene, also justifying the presence of xylene. These reactants could be obtained by benzofuran cracking, mainly by inverse Diels-Alder reaction and hydrolysis [19]. This path is discarded as the main route based on the high benzene/toluene carbon ratios obtained as well as the absence of evidences about the previous requirements (benzofuran inverse Diels-Alder and hydrolysis), since neither furan nor propylene are detected in the gas-phase. The almost total absence of dialkylbenzenes supports the prevalence of decarbonylation; since benzene formation from toluene disproportionation would lead to the formation of equimolar amounts of benzene and dialkylbenzene. However, a slight relevance cannot be discarded at the highest temperatures, since the benzene/toluene carbon ratio decreases from 11.5 to 7.3 (**Fig. 1b**). This is in good agreement with the positive effect of temperature in cracking reactions. At these temperatures, side reactions could involve the dialkylbenzenes, justifying the absence of xylene in the product mixture. In any case, this would be a minority effect since experimental results suggest benzofuran decarbonylation as the main route, the benzene being the primary reaction product of the benzofuran pyrolysis.

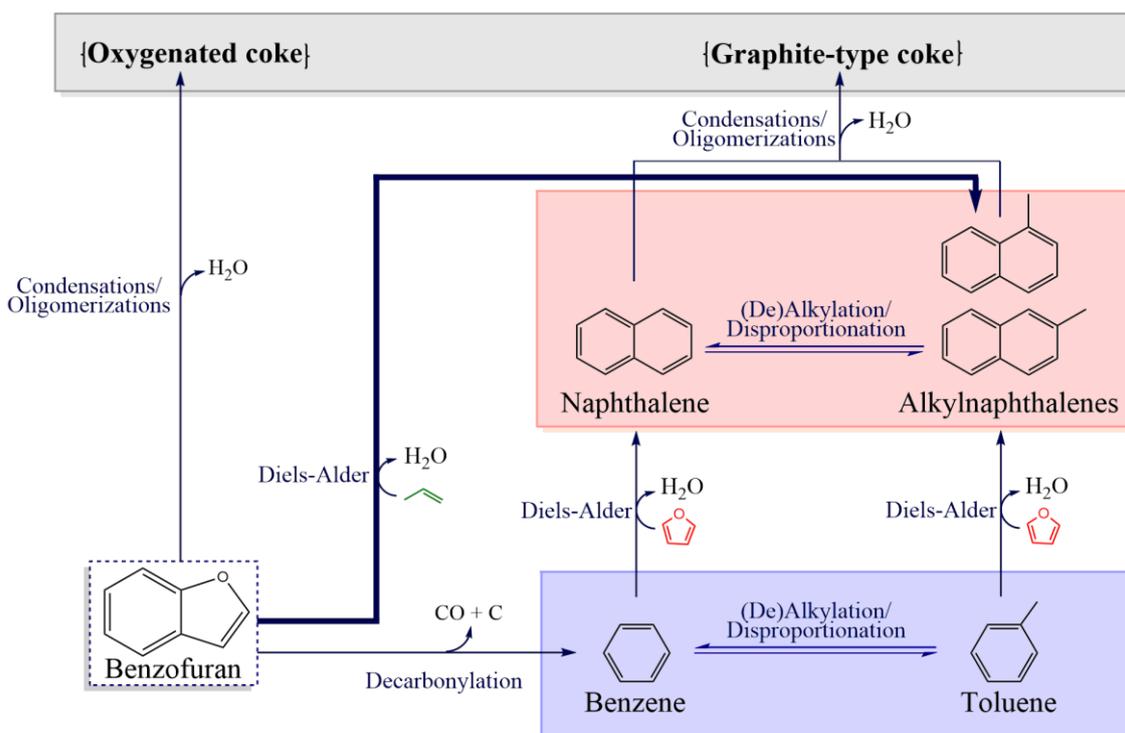
Naphthalenes (bicyclic aromatics) are the heaviest compounds detected in the gas phase, considering that subsequent oligomerizations lead to polyaromatics deposited on the catalyst surface (coke precursors). Their selectivities increase from 3.9 to 5.1 % in the considered temperature range. Naphthalene is the main compound observed (being 82 % of these compounds at 550°C), with significant amounts of alkylnaphthalenes (from 12 to 18 %) and an

almost absence of dialkylated derivatives, except at intermediate temperature, with 10 % of selectivity. The literature suggests that naphthalenes could be produced by Diels-Alder reaction between furan and an (alkyl)benzenes [17]. The lack of furan fed in the stream suggests that this compound is *in situ* obtained from benzofuran. This furan is so reactive that is consumed immediately after its production. Thus, it is not detected in the gas phase analysis, the presence of naphthalene and alkylnaphthalene being the only proof of the formation of this compound. However, the carbon ratio naphthalene/alkylnaphthalene (7.3 at 450°C, 4.6 at 500 and 550°C) does not correspond with the benzene/toluene evolution (11.5, 8.9, 7.3) suggesting the co-presence of other route to obtain the alkylnaphthalenes, more relevant at intermediate temperatures.

We suggest the Diels-Alder reaction between a benzofuran molecule and a propylene one, the last compound being obtained by benzofuran cracking. This Diels-Alder reaction has not been previously proposed in the literature, and the relevance in the benzofuran cracking is conditioned to the propylene that could be obtained from benzofuran inverse Diels-Alder reaction and subsequent hydrolysis of furan [22]. Experimentally, the presence of propylene, at least in low amounts, is corroborated since indenenes (cyclic compounds obtained by the polymerization and cyclizations of alkenes) are detected in gas phase (0.6, 0.7 and 2.8% at 450, 500 and 550°C respectively).

According to the experimental results, the reaction pathway proposed for the benzofuran cracking is summarized in **Scheme 2**. Considering this scheme, benzofuran mainly produces benzene by decarbonylation, obtaining alkylbenzene if this decarbonylation only includes the formation of a CO molecule, and not the lack of the other carbon. The presence of small amounts of naphthalenes suggests a partial cracking, involving reactive intermediates, such as furan or propylene, required to obtain these compounds. This fraction is significantly less

relevant than the non-detected carbon, suggesting a relevant amount of coke produced during the reaction.



Scheme 2: Suggested mechanistic reaction of pure benzofuran cracking over ZSM-5 being furan and propylene *in situ* obtained by the benzofuran cracking

The highest percentage of undetected compounds (52 %), assumed as a mixture of coke and light organic molecules such as CO, CO₂ that are not detected by GC-FID, is obtained at the lowest temperature, with a significant decrease to 36% at 550°C. According to the main mechanism proposed to obtain benzene, almost 10 % of this percentage is justified by decarbonylation reactions, with around 25 % of unknown product, assumed as solids.

In order to obtain more information about the solid deposits produced on the catalytic surface, temperature programmed oxidation (TPO) analyses of the spent catalysts were carried out. The TPO spectra, compared in **Figure 2**, demonstrate a clear decrease in the total amount

of solid deposits as the reaction temperature increases, from 3816 $\mu\text{mol/g}$ at 450°C to 1246 $\mu\text{mol/g}$ at 450°C, in terms of CO_2 released during coke combustion.

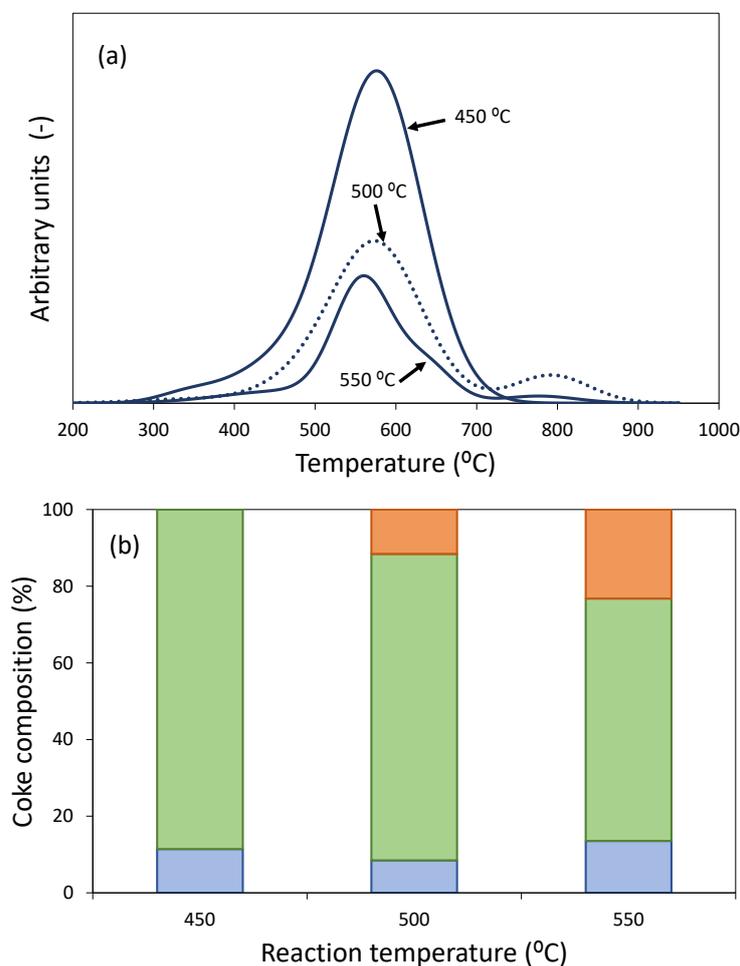


Figure 2: a) TPO spectra of spent catalyst after benzofuran cracking at different temperatures; b) relative weight of oxygenated (blue), low-density (green) and high-density (blue) graphitic coke.

These results suggest that a minimum temperature is required to avoid benzofuran self-condensation reactions. The deconvolution of these spectra suggests the presence of up to five different deposits, with maximums releasing temperatures at 345, 460, 570, 635 and 785 °C. According to the literature, oxygenated deposits decompose at temperatures below 500 °C (the two first peaks identified in the analyses), whereas higher temperatures

correspond to graphitic coke [22], the ratio H/C decreasing as the oxidation temperature increases [35].

The relative analysis (Fig. 2b) has been done looping the peaks in three families: oxygenated coke (<500°C), low-density coke (500-650°C) and high-density coke (>700°C). Partially hydrogenated graphitic coke (low-density one) is the majority type of deposit in all the cases, observing a decreasing trend from 89 to 63 % as the temperature increases from 450 to 550 °C, in favour of the appearance of a more graphitic coke (lower H/C ratio). This type of deposits is not observed in the spent catalyst after reaction at 450 °C, whereas it represents more than 23 % at 550°C. Oxygenated coke accounts for ca. 12 % at both extreme temperatures, with a minimum of 6 % at the intermediate one. According to these results, oxygenated deposits are obtained at all the temperatures, with a fast rate at low temperatures, 500°C being the optimum one to maximize the rate to produce graphitic coke from these deposits. The overall amount of these deposits decreases with the temperature, (from 436 to 170 mol/g of CO₂) with a positive effect in the catalytic stability. In any case, the deactivation is very relevant at these conditions, with a decrease in benzofuran conversion from 100 to 10 % in less than two hours-on-stream.

The TPO data can be explained by three synergic reasons: i) adsorption processes, being less relevant as the temperature increases; ii) the prevalence of condensation reactions at low temperatures, promoting the coke formation by oligomerization, previously corroborated in the literature [23]; and, iii) the promotion of benzofuran cracking at high temperatures, producing light compounds, less relevant coke precursors. Despite the positive effect of increasing temperature, the optimum conditions must be determined balancing the coke production with the selectivity losses observed once alkenes are produced, with a huge amount of new compounds that reduce the production of target compounds.

Despite GC-MS or TPO does not allow the individual identification of these heavy compounds, these results are congruent with previous coke production studies during catalytic pyrolysis of model compounds relevant to pyrolysis bio-oil over ZSM-5 [35], in which authors conclude that coke precursors are a complex family of PAHs (mainly anthracenes and phenanthrenes) and their derivatives obtaining by the co-presence of a huge amount of uncontrolled reactions, involving oligomerization, dehydrogenation, cyclization, alkylation, rearrangement and condensation, all of them with a common point of being promoted by acid sites.

Two main conclusions can be obtained from the preliminary studies: the key role of the reaction temperature and that the olefins formed during BZF cracking play a prominent role on the reaction pathways. Assuming that the oligomerization capacity decreases with the alkylation grade, the effect of co-feeding an alkylating reactant must be more deeply analysed. Thus, temperature and propylene co-feeding effects are deeply analysed in the following section, from the selectivity and stability point of view.

3.2. Benzofuran and propylene Diels-Alder reaction: influence of reaction temperature in the product distribution

Considering the anticipated positive effect of co-feeding an alkene, this study was carried out with a propylene/benzofuran 3/1 ratio. As introduced before, propylene is chosen as alkylation reactant according to the optimum results obtained in the literature for other Diels Alder reactions [17, 21, 28]. The influence of the temperature was studied in the range from 300 to 550°C. This range is selected based in the Guedes *et al.* results, after reviewing the temperature employed in 150 papers about biomass pyrolysis [26]. A blank experiment co-feeding propylene and benzofuran discards the reaction in absence of catalyst, with less than 1 % of BZF conversion in this temperature range. The expected synergetic effect of co-feeding propylene and tuning the temperature would define optimum conditions for the reaction

softer than the previous one observed in absence of propylene, when the reaction requires a minimum of 500°C to minimize the benzofuran self-condensation. Total benzofuran conversion is observed at initial times, despite the conditions. The reaction temperature plays a key role in the initial products' distribution, as it is shown in **Figure 3**. When reaction is carried out at temperatures lower than 400°C, coke and alkenes are the main product obtained, with more total yields higher than 80 % in both cases. A clear decreasing trend in these undesired products is observed from 300 to 500°C, this temperature being the minimum of coke observed (14.9 %). At higher temperature, the selectivity of carbon losses (corresponding to coke, CO and CO₂) increases again, suggesting a relevant role of decarbonylation reactions, producing CO_x, or the co-presence of two different coke precursors, favoured by opposite conditions.

At low temperatures, coke is highly likely due to the benzofuran Diels-Alder self-condensation as well as the alkene oligomerizations. The relevance of this side reaction decreases with the temperature, as it is confirmed by the increasing amount of alkenes at temperatures over 400°C as well as the appearance of cross Diels-Alder products, reducing the relative relevance of the carbon deposits production. Minimum temperatures of 400°C are needed to obtain benzenes and naphthalenes with selectivities higher than 10 %.

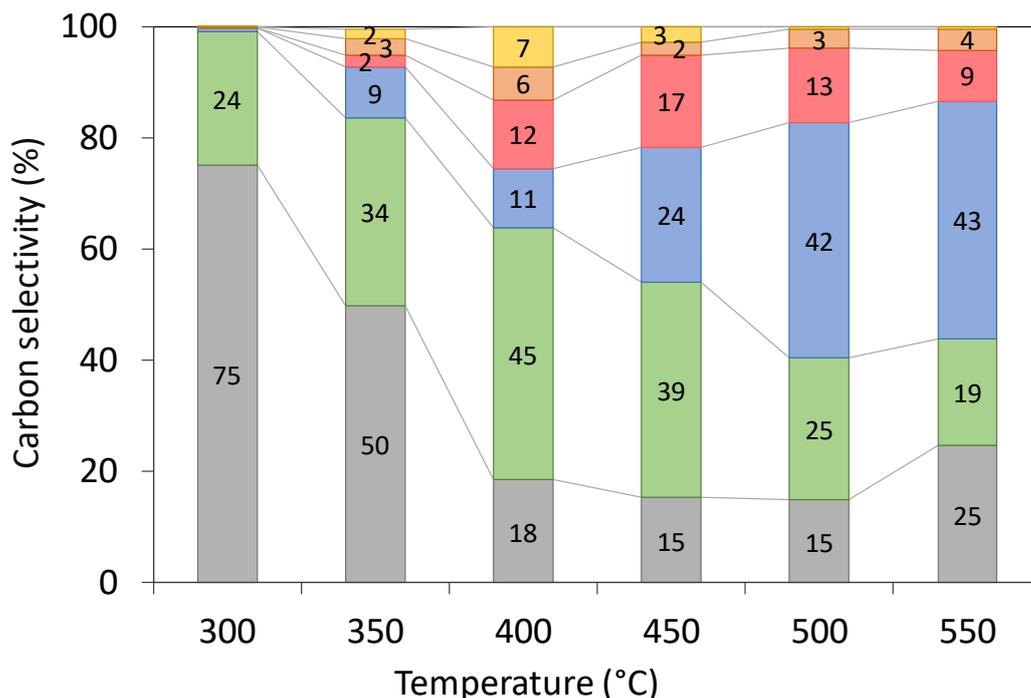


Figure 3: Selectivity distribution as function on reaction temperature at constant 3:1 P:BZF ratio. Symbols: (■) furans, (■) indenenes, (■) naphthalenes, (■) benzenes, (■) alkenes and (■) CO, CO₂ and coke.

Concerning the benzenes, their selectivity increases with the temperature, reaching maxima higher than 40 % at 500 and 550°C. On the other hand, naphthalenes selectivities reach a maximum of 17 % at 450°C. The decrease in the selectivity of this family of compounds at higher temperatures, as well as the increase of “non-defined carbonaceous compounds” obtained at these conditions, is congruent with subsequent condensations involving naphthalenes, obtaining graphitic coke. It must be pointed out that the 25 % of carbon losses observed at 550°C does not directly correspond to the coke production, since it also considers the CO and CO₂ that is obtained by decarbonylation reactions, these reactions being also favoured by the temperature. According to this result, an increase in the catalytic stability is suggested, with less amount of coke produced as the temperature increases. These results are in good agreement with previous analyses of Diels-Alder reaction of furan al propylene [17].

The analysis by lumped chemicals is described in **Figure 4**, observing clear trends in all the cases. All the results plotted correspond to initial reaction times. Results concerning benzenes and naphthalenes at temperatures below 350 and 400°C, respectively, are not considered because the total selectivity is too low to guarantee a good accuracy in the individual analysis. At low temperatures, polyalkylbenzenes and alkyl-naphthalenes are the most relevant compounds among monocyclic and bicyclic aromatics (28% at 350°C, 46% at 400°C, respectively). In all the cases, the polyalkyl-derivates selectivities decrease with the temperature (for example, dialkyl-naphthalenes decrease from 34% at 400°C to 16% at 550°C), suggesting an increasing relevance of cracking when increasing the temperature, obtaining benzene as the main product (44% selectivity at 550°C). As to alkenes, butenes are the main compounds obtained at low temperatures (69% at 300°C), with a clear decreasing trend, obtaining ethylene as the main alkene at higher temperatures (68% at 550°C). This result is explained by the co-existence of two factors: the increasing cyclizing trend of heavy alkenes and their cracking, being both aspects favoured by the temperature and with a common consequence of increasing the relative weight of light fractions [36-38].

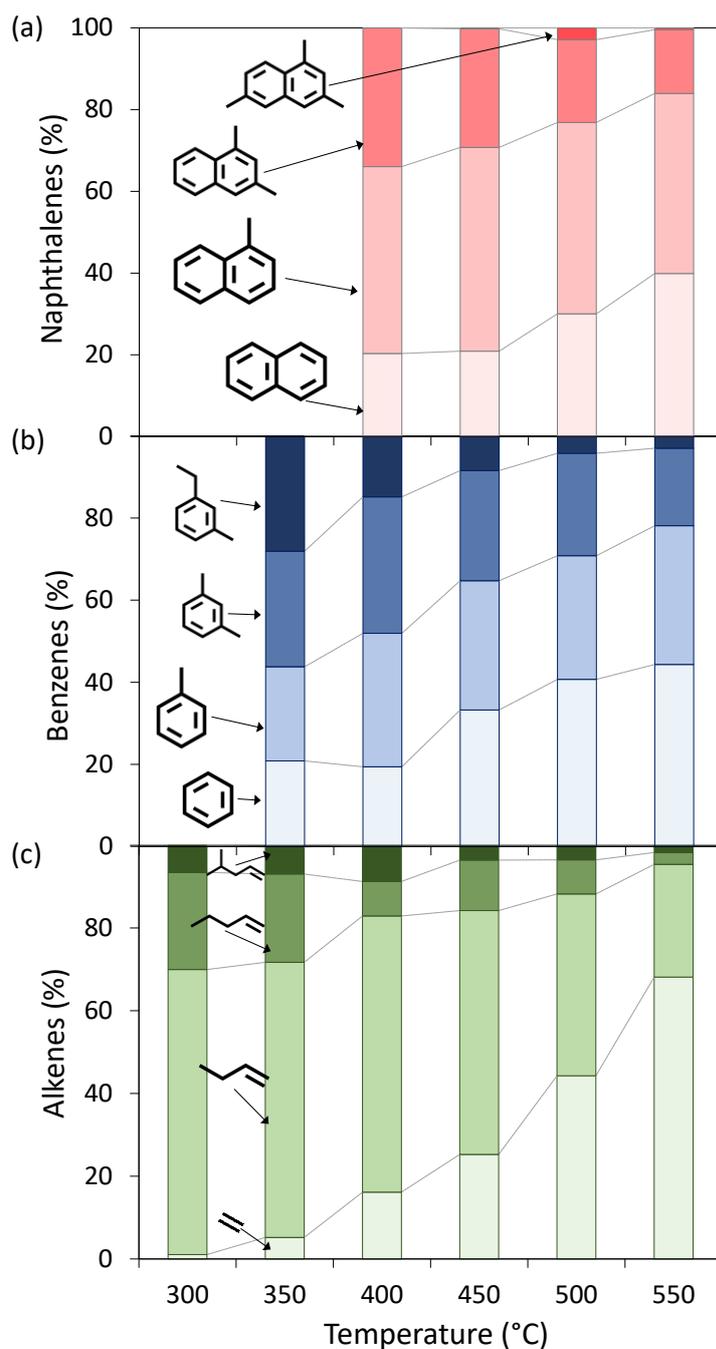


Figure 4: Selectivity distribution as function of the temperature. Results corresponding to (a) naphthalenes, (b) benzenes and (c) alkenes

The alkyl derivatives selectivity and productivity increase as the temperature decreases (81% and 80% selectivity of alkyl benzenes and alkyl naphthalenes at 400 °C; values corresponding to productivities of 0.70 and 0.83 mmol C/h, respectively). These results suggest that the stability

of these adducts is also conditioned by disproportionation equilibrium, these reactions being favoured by high temperatures.

According to these results, the temperature of 500°C seems to be the optimum one, with a total selectivity of 59 % of aromatic compounds (including benzenes, naphthalenes and indenenes). These results are in good agreement with previous studies using this catalyst, concluding that 500°C is the optimum temperature for Diels-Alder reactions, despite the reactant used [23, 26].

3.3. Benzofuran and propylene Diels-Alder reaction: influence of temperature in the stability

According to the previous results [17, 39], there is a strong influence of reaction temperature on the deactivation kinetics, a deep study of the evolution of reactant conversions as function of the time on stream being required. Six different temperatures have been analysed, from 300 to 550°C, with constant increments of 50°C. Lowest temperatures are discarded because only the benzofuran oligomerization takes places, whereas the maximum temperature is limited by the zeolite preparation procedure. These experiments were carried out with a constant P/BZF ratio of 3/1 and 240 mg of ZSM-5, values corresponding to WHSV of 0.70 and 0.66 h⁻¹ to propylene and benzofuran, respectively. A blank experiment at 500°C was carried out, discarding any conversion in absence of catalyst.

Since benzofuran is the limiting reactant, full conversion is reached at low TOS despite the temperature tested, as shown in **Figure 5**. Due the high reactivity of the furanic compounds, this 100 % is reached almost at all the conditions tested in the literature when using ZSM-5 [27,40,41]. A clear influence of the reaction temperature in the stability is observed, with an exponential increase of TOS required to reduce this conversion to 60 %. Thus, this decrease occurs after (see Fig. 5b) converting less than 0.2 grams of benzofuran per gram of catalyst

(g_{BZF}/g_{cat}) at temperatures below 400°C (<0.3 h of TOS), whereas this value is more than 26 times higher when working at 550°C (4.7 g_{BZF}/g_{cat} , 7.2 h of TOS).

At temperatures below 450°C, the decrease in the benzofuran conversion is observed since the first point, whereas there is an initial flat step at 100 % when working at the highest temperatures. The continuous production of coke during these flat periods (15% and 25 % at 500 and 550°C), without observing any significant evolution of the gas phase composition (42-46 % of benzenes, 8-15 % of naphthalenes, 3 % indenenes), suggests that the catalytic amount used is in excess for these conditions. Thus, deactivation would be continuously produced by the coke deposition but it is only observed by the decrease in the conversion when the number of free active sites is a limiting factor. Once the conversion starts decreasing, the progress with the temperature follows a linear trend.

This increase in the stability is congruent with the decrease in the coke deposition rate observed by the TPO analysis of the spent catalyst. As it is observed in Figure 5b, the deposition rate is more than nine times lower at 550°C than at 300°C (from 990 to 110 mol/g·h). TPO spectra were deconvoluted in the three main contributions detected in the previous experiments, with maximums at 460, 560 and 630 °C, the relative weight of each peak being shown in Fig. 5c. As in previous experiments, the low-density graphitic coke is the main type of deposit obtained, with relative weight from 65 to 72 %. Considering the slight differences, the relevance of this type of solid in the stability is discarded. On the other hand, the oxygenated coke is quite significant at the lowest reaction temperatures, being close to 30 % of the total solids, whereas the high-density graphitic coke appears with significant amount at 500 and 550°C (20 %). According to these results, the stability increases when this last type of coke increases, requiring also oxygenated coke to be minimized. These conditions correspond with the maximum productivity of benzenes, the most interesting family of compounds.

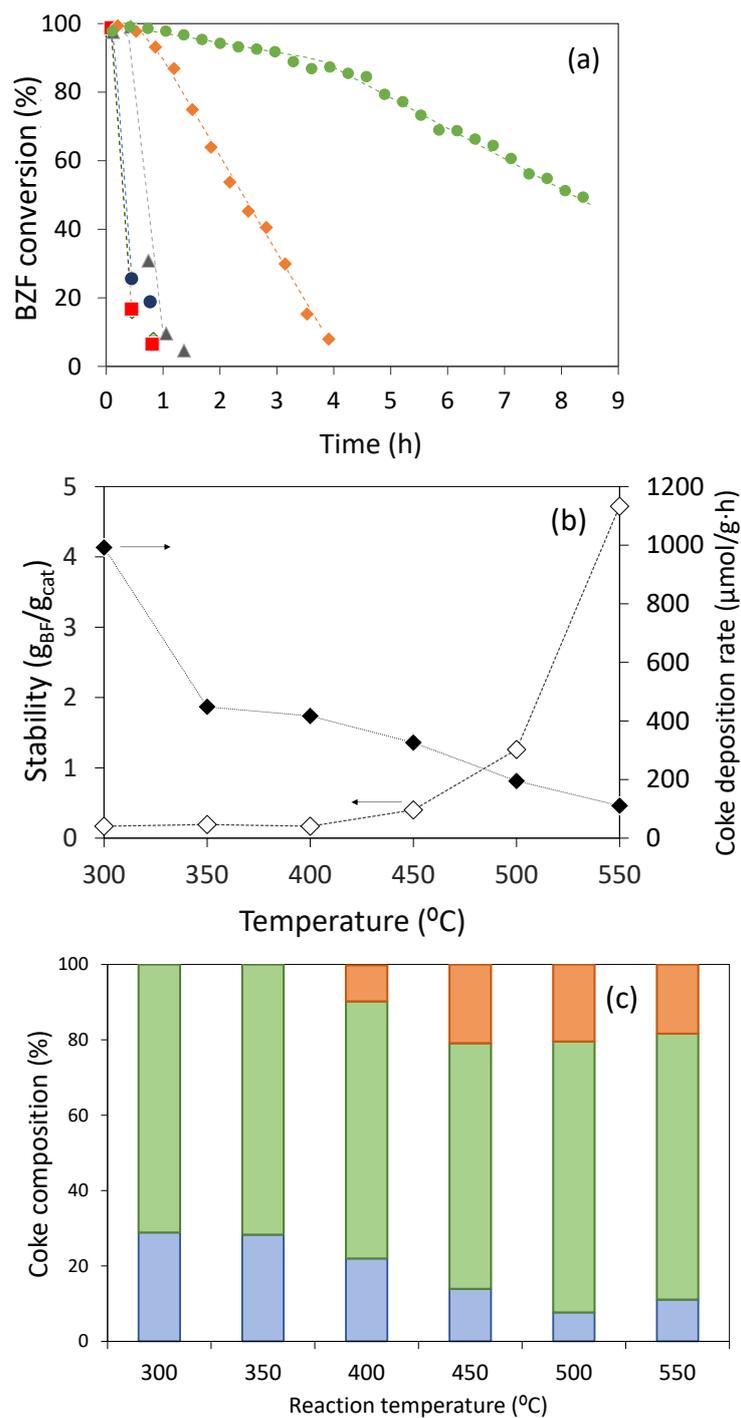


Figure 5: (a) Evolution of the benzofuran conversion in the P/BZF (3/1) reaction. Results correspond to (◆) 300°C, (●) 350°C, (■) 400°C, (▲) 450°C, (◆) 500°C, (●) 550°C; (b) Reaction stability in terms of BZF per gram of catalyst needed to decrease conversion from 100 to 60% (◆) and coke deposition rate (◆); (c) relative weight of oxygenated (blue), low-density (green) and high-density (orange) graphitic coke

In order to quantitatively compare the deactivation behaviour of the catalysts, and considering that the evolution of the conversion with the time-on-stream is almost linear after the end of the full conversion period, the slope of these lines was considered (k_{app}). This approach means to consider a zero-th order deactivation kinetics, according to the Szepe-Levenspiel theory. Despite the lack of deep deactivation studies for this type of reactions, similar trends have been observed in Diels-Alder reaction between alkylfurans and alkenes over acid zeolites, and the zero-order deactivation model is congruent with the constant deactivation rates suggested in previous papers [27,39-41].

At high temperatures, a clear decreasing trend in k_{app} is obtained (**Figure 6**), in good agreement with the stability increase observed in the experiments. Experiment with at 550°C deserves special attention since the conversion seems to follow two different trends: a soft decrease during the first 4 h, and a more pronounced one at longer TOS. Only the second one was considered for the deactivation analysis, suggesting that the first one corresponds to the progressive pore blockage produced by isolated molecules. According to this hypothesis, only the second part would correspond to the coke formation, once the adsorption is so relevant than the oligomerizations between molecules is faster and produces the real deactivation due to coke deposition. If this parameter is plotted vs. the temperature, it is observed that it is not dependent at lower temperatures (conditions of fast deactivation), whereas it presents an exponential decrease for temperatures higher than 400 K.

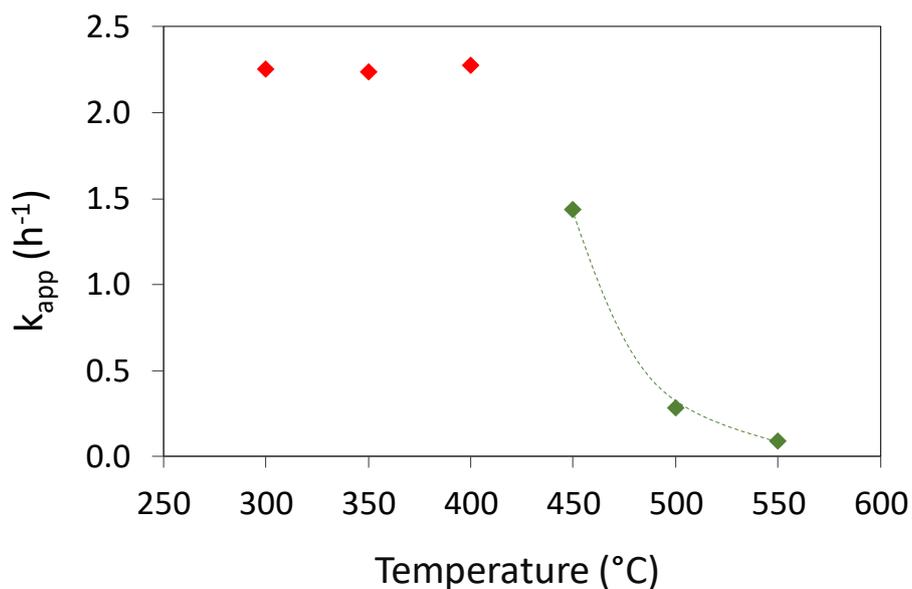


Figure 6: Apparent deactivation rate constant as function of the reaction temperature considering a zero-order kinetic model

3.4. Benzofuran and propylene Diels-Alder reaction: influence of reactants ratio in selectivity and stability

The next set of experiments were performed at 500°C, in order to balance the catalyst activity and the stability. Different P/BZF ratios, from 0/1 to 24/1, are studied at this temperature, with the aim to analyse the influence in the product distribution as well as in the catalytic activity, since it is expected that alkylations reduce the oligomerization activity, having a more controlled products' mixture, focused on benzenes and naphthalenes families and reducing the coke deposits. The selectivity distribution obtained at initial TOS plotted in **Figure 7**.

The total selectivity to benzenes and naphthalenes slightly varies in the range of 55-60 %, despite the conditions used, observing a continuous decrease of naphthalenes as the propylene excess increases. As expected, a relevant selectivity corresponds to alkenes, increasing when the propylene excess rises from 3/1 to 12/1 (from 25 to 37 %). The different behaviour of the 24/1 ratio is explained by the cyclization capacity of these alkenes and the

different equilibriums between cracking and oligomerizations between these compounds. This is corroborated by the lack of evolution observed when the alkene group is disaggregated studied, shown in **Figure 8**, with similar results despite the excess of propylene used (42-46 % of ethylene; 44-50 % of butenes; 5-8 % of pentenes and less than 2 % of heavier alkenes).

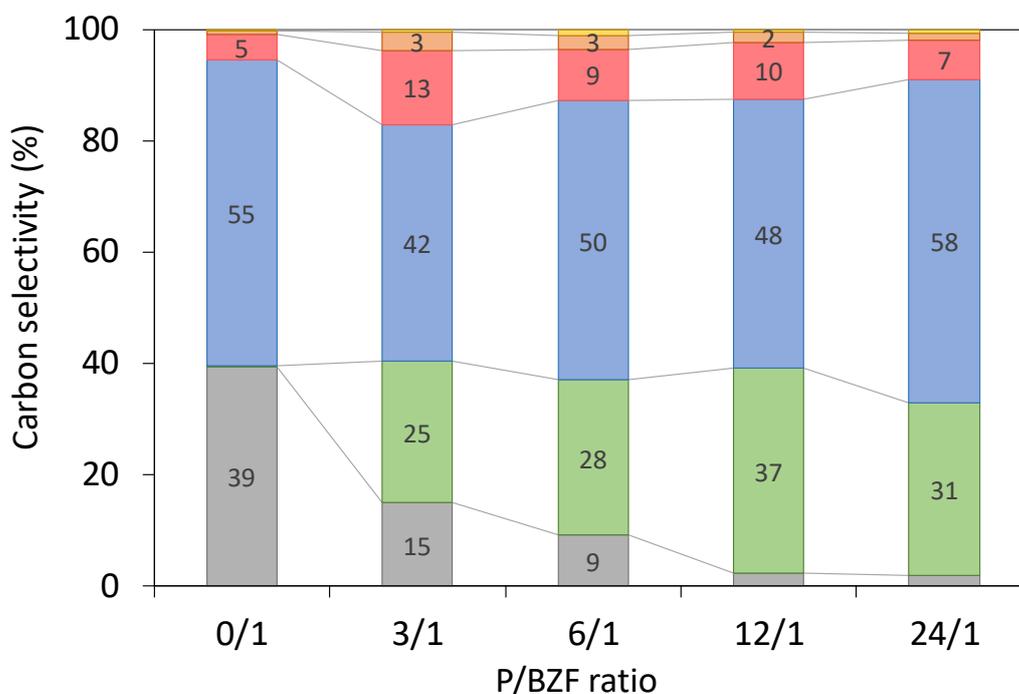


Figure 7: Initial products distribution obtained in the propylene/benzofuran Diels-Alder reaction at 500°C as function of the P/BZF ratio in terms of carbon selectivity. Symbols: (■) furans, (■) indenenes, (■) naphthalenes, (■) benzenes, (■) alkenes and (■) CO₂ and coke.

On the other hand, a continuous increase in the alkylation ratio is detected in the families of benzenes and naphthalenes, observing a decrease of benzene (from 89 to 20 %, with 0/1 to 24/1, respectively) and naphthalene (from 73 to 24 %, in the same range analysed). Despite the low selectivities of trialkylnaphthalenes and trialkylbenzenes, the increase in alkyl and dialkyl derivatives is clearly observed, with maximums of 41 % of toluene and 32 % of dialkylbenzene among the monocyclic aromatics, and 44 % of alkylnaphthalene and 32 % dialkylnaphthalene in the naphthalenes (all these data considered at 24/1 ratio). These results

correspond to relative increases of 192 % and 564 % in the alkylation grade of benzenes and naphthalenes families, respectively, when comparing to the cracking of pure benzofuran.

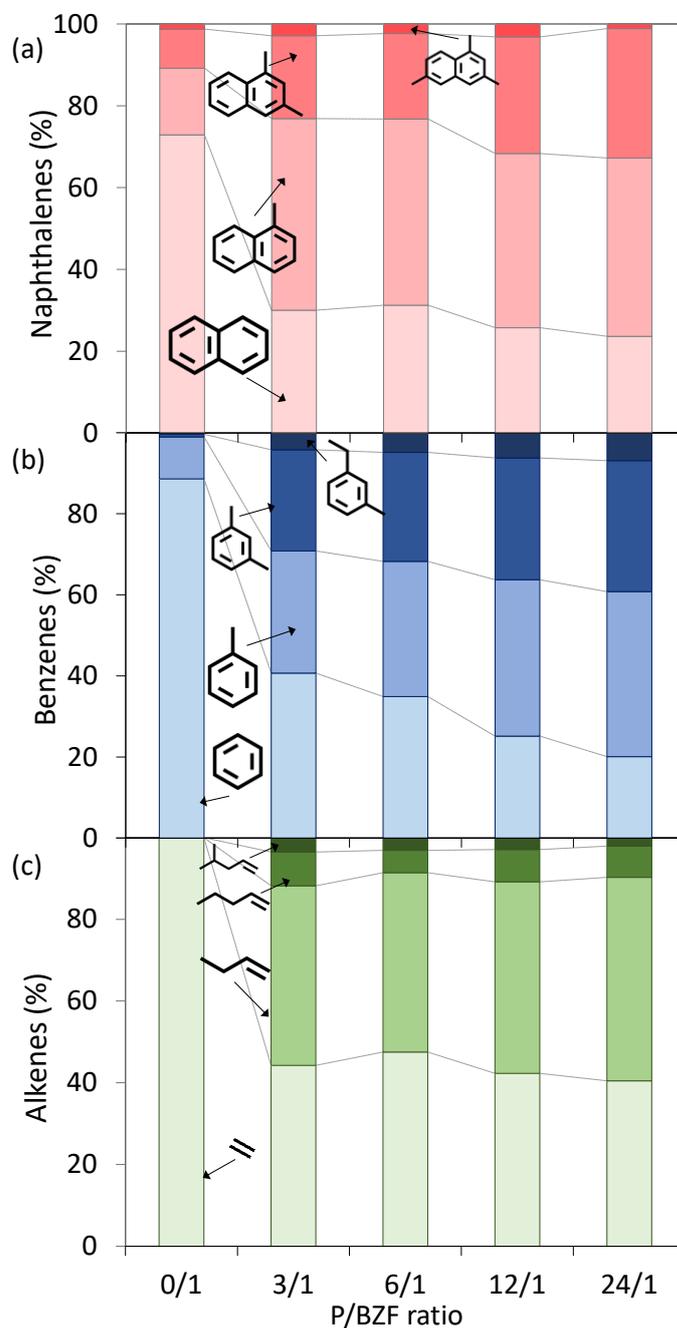


Figure 8: Selectivities distribution lumped by chemical similarity. Results corresponding to: (a) benzenes; (b) naphthalenes; (c) alkenes

The study at different P/BZF ratio also allows checking the route proposed for the direct alkylnaphthalene production by the Diels-Alder reaction between benzofuran and propylene. The molar yield of methylnaphthalene obtained at initial times is plotted in **Figure 9**. A clear positive effect of propylene in the methylnaphthalene productivity is observed, which could be justified by two concomitant reasons: a higher toluene production and the proposed route of direct Diels-Alder reaction between benzofuran (diene) and propylene (dienophile). In order to check the relevance of this specific route, the relative ratios alkylnaphthalene/naphthalene and toluene/benzene are simultaneously analysed in Fig. 9b. It is observed how the toluene/ratio keeps almost constant independently of the propylene amount (1.5 ± 0.1), whereas there is a clear increase in the alkylation ratio of naphthalenes (form 0.1 to 1.7). This lack of correlation suggests that propylene can be reacting directly with the benzofuran, without requiring the previous step involving the toluene.

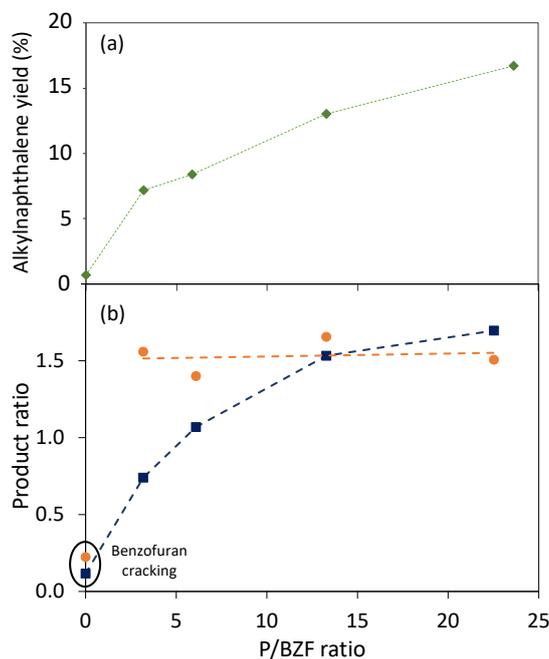


Figure 9: (a) Evolution of the methylnaphthalene molar yield and; (b) (●) alkylnaphthalene/naphthalene ratio and (■) toluene/benzene ratios as function of the propylene/benzofuran ratio

As discussed before, once the propylene is introduced the products distribution is altered, affecting also to the coke. Thus, it is expected to positive affect to the catalytic activity, as it is studied analysing the evolution of conversions as function of the time on stream, **Figure 10**.

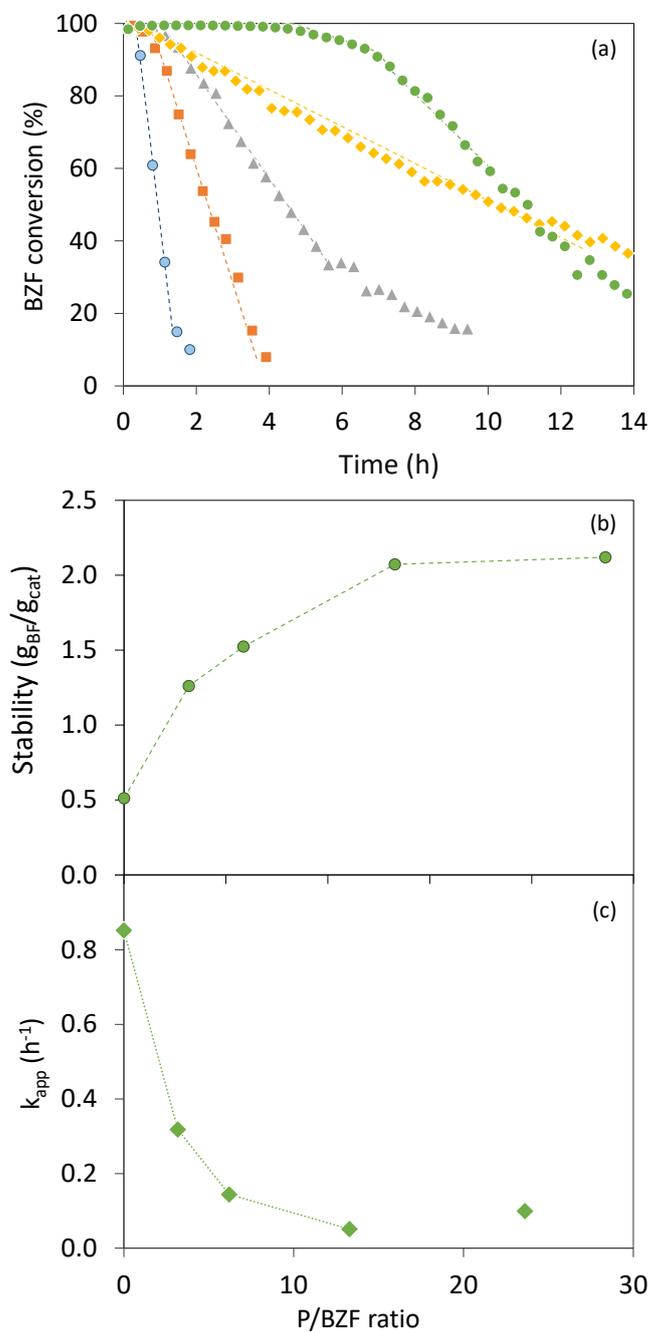


Figure 10: (a) Evolution of the benzofuran conversion with the TOS at 500°C as function of the

P/BZF ratio: (●) 0/1, (■) 3/1, (▲) 6/1, (◆) 12/1, (●) 24/1. (b) Reaction stability and;

(c) Apparent deactivation kinetic rate

The expected improvement in the catalytic stability is clearly observed. Thus, comparing working with 12/1 and 0/1, an increment higher than 320 % in benzofuran transformed before reducing the conversion from 100 to 60 % is obtained (from 0.5 to 2.1 $\text{g}_{\text{BZF}}/\text{g}_{\text{cat.}}$). According to the TPO results, this improvement is also observed in the coke deposition rate, decreasing from 910 to 110 $\mu\text{mol}/\text{g}\cdot\text{h}$, from 0/1 and 12/1 ratios, respectively. Higher propylene excesses have not any relevant effect, neither in the stability nor the coke deposition rate, considering that reaction conditions are saturated at this ratio, suggesting the previously mentioned initial stage in which the active sites blockage is slower, due to the individual deposition of different compounds before their oligomerizations. Concerning the type of coke produced, no significant differences are observed, obtaining a similar distribution with almost all the ratios, marked by the prevalence of low-density graphitic coke. There is only a relevant increase in the high-density graphitic coke when working at 24/1 ratio (more than 30 %). This result corroborates that this coke is mainly produced by the alkenes oligomerization, without playing a relevant role in the catalytic deactivation. Applying the kinetic study, these results correspond to a clear exponential decrease in the k_{app} , with values 21 times lower at 12/1 than at 0/1 (0.04 and 0.85 h^{-1} , respectively). The goodness of this approach is observed in **Figure 10a**, where experimental points are compared with the fitted values (broken lines).

According to these results, propylene is known as a notorious alkylation compound, with a relevant improvement in the catalytic stability. This result is in good agreement with previous data reported for the propylene-furan reactions [22]. This approach also indicates that deactivation by coke is promoted by the condensation of, mainly, less alkylated aromatic compounds (benzofuran and naphthalene).

3.5. Catalytic reusability

Once the optimum conditions considering the equilibrium stability vs. selectivity have been defined (500°C), the reusability of this material was evaluated using a P/BZF ratio of 3.

Assuming that the coke deposition has been strongly decreased but not totally prevented, a thermal treatment (12 h, 400°C in air flow) between cycles was included with the aim of clean the surface by coke oxidation. The evolution of propylene and benzofuran conversion is shown in **Figure 11**. According to experimental results, this treatment is completely inefficient to recover the zeolite, with constant 20 % of benzofuran conversion in the second cycle (the stable conversion due to surface reaction) and a significant decrease in the propylene conversion (from 70 to 55 %).

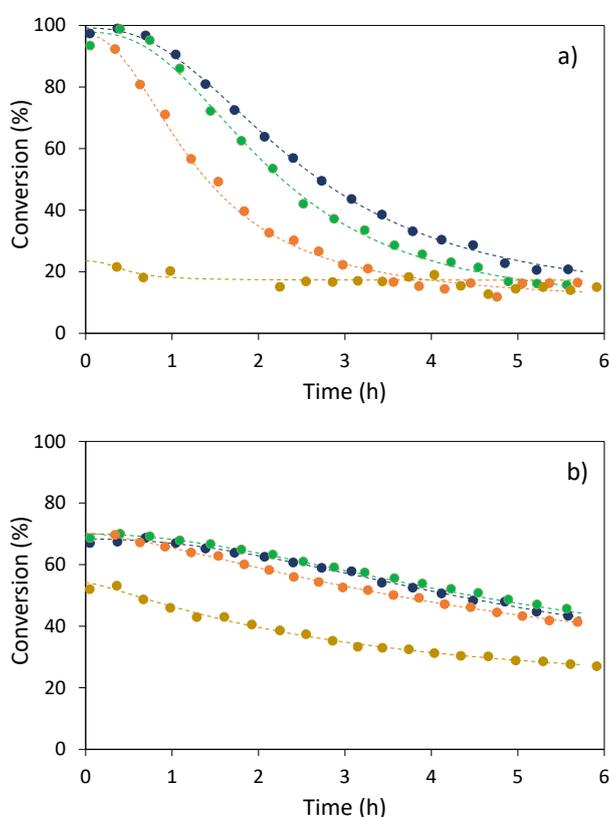


Figure 11: Evolution of a) benzofuran and b) propylene conversion after different cycles at 500°C with a P/BZF ratio of 3. Data correspond to: (●) first cycle; (●) second cycle after a thermal treatment at 400°C; and (●) second and (●) third cycles after thermal treatments at 550°C

The influence of calcination temperature was analysed with an extra reusability test with at more severe conditions (550°C). This temperature was chosen since it is the maximum

temperature reached during the preparation procedure and higher temperatures could compromise the catalytic structure. Experimental results are also included in Figure 11, showing three consecutive cycles. With the three cycles, a total benzofuran conversion is reached at initial times, observing a soft deactivation with the time, with final stable conversions around 20-23 %. Main effect is related to the deactivation kinetic, observing a slight increase on its rate from 0.23 h^{-1} to 0.36 h^{-1} , values corresponding to the first and third cycles, respectively. Concerning the propylene, no significant differences were observed during these three cycles, with starting conversions of 70 % and soft decreases to values close to 40 % after 6 h time-on-stream. The products distribution follows the same trend in the three experiments, with differences lower than 2 % between cycles (data deeply analysed in previous sections).

According to these results, the heat treatment is efficient to recover the initial activity of this material, both in terms of conversion and selectivities. The temperature of the heat treatment plays a key role, requiring an equilibrium between the coke oxidation temperature observed by the TPO analyses and the material stability.

4. Conclusions

This work provides a deep study of benzofuran behaviour as a common intermediate of biomass catalytic pyrolysis. The evolution of reaction products, as well as coke precursors, as function of the temperature and the co-feeding of an alkene allow determining the optimum condition to minimize the ZSM-5 deactivation caused by these solid deposits. The stability increases at the highest studied temperatures. Low temperatures promote the formation of oxygenated coke and alkenes (up to 99%), whereas high temperatures lead to the formation of aromatics (up to 60%), also promoting the formation of polyaromatic coke. Consequently, due to a compromise between selectivity and stability, 500°C is defined as the optimum condition.

Co-feeding alkenes is demonstrated as an interesting alternative to minimize the catalyst deactivation caused by BZF. The presence of alkylated aromatics hinders further oligomerizations, minimizing the formation of polyaromatic coke. A relevant role of the Diels-Alder reaction between benzofuran and propylene yielding methylnaphthalene (without the intermediate formation of toluene) is also suggested. This new route also explains the increase in the stability, since benzofuran (very reactive) follows an alternative reaction pathway not leading to coke formation. Thus, reactions performed with a high propylene excess lead to a reduction of 96 % of coke deposits with an increase of life period of the catalyst higher than 420 %.

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