Study of the catalytic reactions of ethylene oligomerization in subcritical and supercritical media over a NiBEA catalyst

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Abstract

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We report a study of the catalytic reactions of ethylene oligomerization over nickel impregnated in aluminum silicate using subcritical and supercritical media. We found the BET surface area decreases with increasing nickel loading, indicating the deposition of NiO particles in the catalyst surface. We compared the performance of the NiBEA catalyst with the protonated form of the commercial support used during the preparation and showed that, although the protonated form promotes the oligomerization of ethylene, the corresponding oligomers do not desorb from the catalyst surface. Conversely, the introduction of nickel in the catalyst facilitates the desorption of the oligomers. Additionally, we used FTIR and GC-MS/FID to characterize the adsorbed and desorbed oligomers, and develop reaction pathways for the ethylene oligomerization over the NiBEA catalyst. We found that both adsorbed and desorbed oligomers are aliphatic, and the non-desorbed products constitute the coke. Additionally, we found that pressure and temperature both increase the oligomerization and desorption rates of adsorbed oligomers. Under

supercritical conditions, the amount of coke formed on the catalyst and the desorbed products molecular weight both increase, relative to subcritical conditions. However, the supercritical conditions also promote the dissolution of the coke from the catalyst surface. We provided visual evidence of (1) the formation of coke in the catalyst surface, and (2) the coke dissolution phenomena under supercritical conditions. Finally, we determined that the coke molecules at supercritical conditions are aliphatic cyclic molecules with a high degree of branching.

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1 Introduction

Ethylene (C_2H_4) is the simplest alkene and one of the most important chemicals from an industrial point of view. Currently, most of the ethylene is produced from the cracking of naphtha, and the production exceeds 140 million tons per year with a 3.5 % increase forecast for the next 5 years.[1], [2] However, ethylene can also be produced from renewable resources.[1] In fact, the dehydration of bioethanol, produced from biomass, leads to the production of bio-ethylene, which has the same molecular structure and chemical properties of the ethylene produced through the petrochemical route. Today, bio-ethylene accounts for 0.3% of the total ethylene market, with countries such as Brazil and India leading the global bio-ethylene production.[1] Therefore, there is still a potential market for the development of an environmentally friendly ethylene. Most of the ethylene produced today is used as a feedstock in polymerization reactions; however, it can also be used in oxidation, halogenation, alkylation, hydration, and oligomerization, for the production of a vast range of chemicals.[4]–[6] Ethylene oligomerization has an important role in the production of linear alpha-olefins, which are feedstocks in the production of fuels, lubricants, and surfactants. Additionally, higher alpha-olefins can also undergo oligomerization. Therefore, the oligomerization of bio-ethylene would constitute a renewable route for the production of fuels and chemicals from biomass.

The oligomerization of alpha-olefins is a catalytic process which can be performed in homogenous or heterogeneous media.[4]–[7] Two examples of commercial homogenous oligomerization processes are the Dimersol (IFP) and SHOP (Shell), which use nickel-based homogenous catalysts to convert propene and butene into hexene and heptene, and ethylene into oligomers in the C_4-C_{20} range, respectively.[4]–[6] However, the difficulty in recycling the catalyst, pricey equipment required to perform the separation of the catalyst from the effluent, and the disposal of non-environmentally friendly chemicals[4]–[7] led to the development of heterogeneous catalysts for the oligomerization of alpha-olefins.[8]–[10] The use of heterogeneous catalysts provides a way to overcome some of the problems involved in the homogeneous catalysis. Examples of heterogeneous catalysts used in oligomerization reactions are acidic catalysts and nickel supported in inorganic structures.

The introduction of nickel in inorganic structures can be achieved using techniques such as ion-exchange, impregnation, and coprecipitation.[6] There is a major interest in the development of nickel exchanged in inorganic structures as heterogeneous catalysts since it is believed that ethylene only undergoes oligomerization over acidic catalyst at very high temperatures and yields low conversions leading to the formation of strongly adsorbed species in the catalyst. Many studies focused on the development of nickel supported in inorganic structures for the ethylene oligomerization.[8]–[10] These studies tested different nickel exchanged in inorganic supports such as AlMCM-41, amorphous silica-aluminum, and Y zeolite. They studied the effects of temperature, pressure, and weight hourly space velocity (WHSV) on the heterogeneous ethylene oligomerization under subcritical conditions. F.T.T Ng *et al* proposed a reaction mechanism based on the role of the nickel and acid sites on the dimerization of ethylene over nickel exchanged Y zeolite. V. Hulea *et al* proposed a reaction pathway for the oligomerization of ethylene over a Ni-MSA catalyst, accounting for desorbed oligomers formed via oligomerization and isomerization reactions. Furthermore, other studies used FTIR [11]–[13] to postulate reaction mechanisms to describe the heterogeneous oligomerization reactions over acidic catalysts at very low temperatures; however, they only accounted for adsorbed species, and no information about the desorbed products was reported. Therefore, in this work, we propose to characterize the species formed on the catalyst surface and liquid product during the heterogeneous ethylene oligomerization over a NiBEA catalyst. We used FTIR to measure the coke formed in the catalyst, and collected the liquid products of the reaction. We proposed reaction pathways based on adsorbed and desorbed oligomers involved in oligomerization, isomerization and cracking reactions. To the best of our knowledge, this is the first work to develop reaction pathways for the ethylene oligomerization over a nickel exchanged in a catalyst with a BEA (Beta) topology.

In addition to the characterization of adsorbed and desorbed products and development of the reaction pathways to describe the overall ethylene oligomerization process over the NiBEA catalyst, we propose the development of the catalytic study under subcritical and supercritical media. For nickel supported in microporous inorganic structures, coke formation, and therefore loss of activity, is an issue.[8] One way to overcome this problem is the introduction of mesoporosity in the catalyst. One special support which can minimize this problem is the BEA (or Beta) zeolite. The introduction of nickel in the BEA zeolite has been proved to oligomerize ethylene at mild conditions, which is believed to hardly proceed via acidic catalysts due to the formation of unstable carbocation intermediates. Also, the NiBEA catalyst showed an increased lifecycle compared to other inorganic catalysts, because it prevents the formation of strongly adsorbed branched molecules in the acid sites, which block the microporous mouth; therefore, minimizing the formation of coke in the catalyst.[7] Nevertheless, the formation of coke is still a challenge, and oxidation treatment to eliminate the coke from the catalyst has been shown to affect the catalyst structure, thus, lowering its performance.[27] On the other hand, reactions in supercritical media were postulated as an alternative that promotes dissolution of the coke from the catalyst surface; therefore, prolonging the catalysts lifetime.[16]

Usually, coke is characterized as polycyclic aromatic molecules.[14] It has been reported previously that there is an increase of naphthalene solubility in supercritical ethylene relative to subcritical ethylene.[15] However, for reactions carried out at temperatures below 200 ^{o}C, coke is formed primarily from condensation and rearrangement steps, therefore, depending on the nature of the reaction.[26] Nevertheless, it is still believed that supercritical fluid can dissolve coke. Supercritical media has already been used to study the oligomerization of ethylene over HZSM-5 in supercritical n-pentane, and it was reported that the catalyst lifetime was improved by the removal of heavier compounds from the catalyst.[16] However, the present paper differs from the work already reported in the literature since (1) the catalyst used is exchanged with nickel and have a BEA topology, which is different than the HZSM-5, and (2) the reactions reported in the present paper are performed in supercritical ethylene, without the presence of another solvent. Additionally, Fan Li *et al* suggested the solvent effect of the supercritical ethylene based on the increase of aromatic compounds in the product stream. In the present paper, we show visual evidence of the coke formation on the catalyst surface, and coke dissolution, under supercritical conditions.

In summary, we propose a catalytic study of the ethylene oligomerization over a NiBEA catalyst under subcritical and supercritical ethylene conditions by combining the information of adsorbed and desorbed oligomers. Furthermore, we postulated reaction pathways based on the data obtained for adsorbed and desorbed products under the conditions studied. Finally, we compared the effects of the supercritical ethylene conditions on the ethylene oligomerization relative to subcritical conditions, including visual evidence of the coke dissolution phenomena under supercritical conditions.

2 Experimental Method

2.1 Material

We purchased ammonium exchanged zeolite with a BEA structure, abbreviated as NH_4BEA, with a SiO_2/Al_3O_2 = 25 from Zeolyst International. We obtained the protonated form, abbreviated as HBEA, after calcination of the NH_4BEA form at 550 ^oC for 5 hours in the presence of air. We produced the nickel exchanged zeolite, abbreviated as NiBEA, by ion exchange of the NH_4BEA form with a 0.51 M solution of $Ni(NO_3)_2$ purchased from Sigma-Aldrich. We added the $Ni(NO_3)_2$ solution dropwise for 1 hour to the NH_4BEA powder, producing a slurry which was stirred for 5 hours using a Teflon stir bar. Then, we filtered the slurry under vacuum, following with washing in deionized water. After the filtration, we dried the solid at 100 ^oC overnight. After drying, a material similar to a clay was obtained, which was ground. Finally, we calcined the powder at 550 ^oC for 5 hours to remove the remaining ammonium and activate the catalyst.

2.2 Catalyst Characterization

ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy) analysis was performed using EPA protocol 200.7, in which the catalyst samples were digested with nitric acid and hydrochloric acid, to calculate the wt% of nickel in the catalyst. We collected IR spectra in an FT-IR Prestige-21 spectrometer (Shimadzu) with a DLATGS detector attached to a DRIFT cell (Harrick Sci.) and an HVC chamber (Harrick Sci.) mounted with a ZnSe window. The use of an environmental chamber allowed *in-situ* analysis of the HBEA and NiBEA catalysts. For the catalyst characterization, we collected spectra using a resolution of 16 cm^{-1}, however, in situations for which identification of peaks was compromised, a 4 cm^{-1} resolution was used. We used an average of 100 spectra to obtain the final spectrum. Before each characterization experiment, we mixed the catalysts with KBr (> 99 % FT-IR grade Sigma-Aldrich) with a 5 % dilution. Therefore, for each experiment, we diluted 5 mg of catalyst with 95 mg of KBr. We used a nitrogen (>99%

Praxair) line attached to the HVC chamber to pre-treat the catalysts before the measurement of the spectrum. The pre-treatment consisted in heating up the catalyst at a heating rate of 200 ^oC/hour up to 500 ^oC, then maintaining the temperature for 1 hour. The goal of this treatment was to remove adsorbed water and impurities from the surface of the catalyst. After the *in-situ* pre-treatment, we reduced the temperature to 30 ^oC and collected the spectrum of the activated catalyst. We normalized the spectra of the activated catalyst according to the procedure described elsewhere.[17] However, in this work, we used the framework vibrational mode in the range of 2400-2000 cm^{-1} to normalize the spectra (as opposed to 1800-1200 cm^{-1} used in [17]). Therefore, the absorbance in that region was the same for all samples. Finally, N_2 adsorption was performed using a Micromeritics TriStar II. Prior to each experiment, we dried the samples overnight (for spent catalysts), then we degassed the samples for 24 hours at 150 ^oC.

2.3 Ethylene Oligomerization Experiments

We carried out the oligomerization of ethylene using the HVC chamber (Harrick Sci.) mounted in a Praying Mantis DRIFT (Harrick Sci.). We used a manifold to feed C_2H_4 (99.5% Praxair), and N_2 (>99% Praxair) into the reactor. We collected the liquid products of the reaction using an impinger, which was placed in a dry ice bath at -20 ^oC, and was attached to the outlet stream of the HVC chamber. We used a heating tape to avoid condensation of the products inside of the line connecting the HVC chamber and the impinger. We filled the impinger with 10 ml of dichloromethane (DCM), which was used as the solvent, since it is a standard for MS analysis. We analyzed the liquid collected after the reaction using a GC (QP-2010 Ultra Shimadzu) equipped with a capillary column (Shimadzu) with a length of 30 m and an inner diameter of 0.25 mm, and an MS and FID detectors, which were used for identification and quantification of the liquid products, respectively. We used the results from the MS to compare the differences in composition between the products which remained adsorbed in the catalyst and the products which were desorbed after the reaction. We used the FID data to calculate the oligomers selectivity for the conditions studied in the current paper, according to Equation 1:

$$S(\%) = 100 \times \frac{m_i}{\sum_j^n m_j} \tag{1}$$

where $S(\%)$ is the product selectivity in percentage, m_i is the mass of the oligomers, n is the total number of products, and j is the index relative to each one of the products. Since a complex mixture of oligomers was produced, with multiple isomers containing the same number of carbons, the isomers were grouped together. Therefore, we calculated the selectivity in terms of products with number of carbons ranging from C_3 to C_{10+}, in which C_{10+} consists in the oligomers with more than 10 carbons.

We divided the experimental work into two components. The first consists in the investigation of the catalytic reactions of ethylene oligomerization under subcritical and supercritical conditions, referred as *Effects of Reaction Conditions and Parameters*. The second part consisted in the study of the effects of supercritical conditions on the ethylene oligomerization, referred as *Analysis of the Effects of Supercritical Fluid Conditions*. The results for each individual component are presented separately.

2.4 Effects of Reaction Conditions and Parameters

First, we performed a temperature screening (1) to determine at which temperature the formation of coke starts, and (2) to determine the effect of the nickel exchange in the designed catalyst. For all the experiments presented in this section, we diluted the catalyst with KBr using a 5% dilution (5 mg of catalyst with 95 mg of KBr). Prior to each experiment, we pre-treated the fresh catalyst by increasing the temperature from 30 to 300 ^oC with a heating rate of 4 $^oC/min$, under 100 ml/min of nitrogen. We maintained the temperature at 300 ^{o}C for 1 hour, then we reduced it to 30 ^{o}C. We performed the reactions by ramping the temperature from 30 to 300 ^{o}C, at ambient pressure 0 bar (gauge), with a heating rate of 4 ^{o}C/min, using an ethylene flow rate of 15 ml/min (STD), yielding a WHSV of 226.8 h^{-1}. We collected spectra with resolution of 4 cm^{-1} over the experiment. We observed that the ethylene peaks originated from the gas phase overlapped with the peaks of the oligomers formed in the catalyst. We prevented this problem by subtracting the ethylene spectra from the final spectra. Therefore, an additional experiment was conducted with pure KBr to collect the spectra of the ethylene in the gas phase using the same conditions as the original experiment. The background subtraction resolved the peaks assigned to the oligomers produced during the reaction.

Moreover, we conducted studies to compare the effects of temperature and pressure on the ethylene oligomerization over the NiBEA catalyst. We used three temperatures (30^{o}C, 100^{o}C, 200^{o}C) and pressures (6.9 bar, 34.5 bar, and 62 bar). We pressurized the system using an ethylene flow rate of 300 ml/min to minimize chemical reactions during the pressurization process. Once the system was at the reaction pressure, we increased the temperature to the setpoint using a heating rate of 20 ^{o}C/min. Finally, after the system was under the desired conditions, we initiated the flow of ethylene into the reactor at 15 ml/min for 100 min (TOS = 100 min). The calculated WHSV for these experiments was 226.8 h^{-1}. The spectra of ethylene gas phase at higher pressures increased significantly, and for this reason, we were not able to perform the subtraction of the ethylene gas phase spectra, which was overlapping with the oligomers spectra. Therefore, for this set of experiments, the spectra of the reacted catalyst were collected only after the reaction, with the objective to identify the nature of the oligomers formed for each condition studied.

2.5 Analysis of the Effects of Supercritical Fluid Conditions (SCFC)

We used supercritical ethylene to study the effects of the SCFC in the solubilization of the coke species adsorbed in the catalyst. To observe and characterize the coke formation phenomena, we used pure catalyst (without KBr) in the HVC chamber. Therefore, we increased the catalyst loading from 5 mg to 55 mg. We used the same pressurization and heating procedures described in section *2.4*. However, we increased the ethylene flow rate to 600 ml/min during the pressurization process to avoid reactions over the larger mass of catalyst. For the oligomerization reaction, we increased the ethylene flow rate from 15 to 165 ml/min. The other variables were the same as in the experiment described in section 2.4. The calculated WHSV for this set of experiments was 226.8 h^{-1}.

The experiments at SCFC were divided into two sections. The first section consisted in the study of the conditions listed in Table 1. Since the ethylene critical temperature and pressure are 9.4 ^{o}C and 51.2 bar, respectively, the experiments were designed to compare the effects of the subcritical, supercritical, and dense supercritical media on the ethylene oligomerization over the NiBEA catalyst. We collected pictures of the catalyst surface every 20 minutes during the *Dense Supercritical* experiment to show the coke formation and dissolution phenomena. In the second section, we performed the *Dense Supercritical* experiment using a TOS = 50 min, to collect the material formed at the surface of the catalyst.

Table 1: Conditions used to compare the effect of subcritical and supercritical conditions on the ethylene oligomerization over the NiBEA catalyst

Conditions	Temperature (^{o}C)	Pressure (bar)
Subcritical	100	34.5
Supercritical	100	57
Dense Supercritical	200	57

2.6 Statistical Analysis

We performed a triplicate of the experiment conducted at 30 ^oC and 34.5 bar for the set of experiments described at section 2.4. We used this triplicate to calculate the standard deviation of the CH_2/CH_3 ratio of the oligomers remaining on the catalyst surface after the reaction. Also, we performed a duplicate of the dense supercritical condition presented in section 2.5 to calculate the standard deviation of the product selectivity for the oligomers collected in the impinger. We used this standard deviation for the experiments described in section 2.4.

3 Results and Discussion

3.1 Catalyst Characterization

The ICP analysis of the NiBEA catalysts shows a nickel loading of 1, 1.5, 2.5, 4.1, and 6 %wt. We used the catalyst with a nickel loading of 4.1 wt% to perform the reaction experiments. As shown in Figure 1.A, after the impregnation of the NH_4BEA with the $Ni(NO_3)_2$ solution, the nickel loading increased with the concentration of the solution, indicating the deposition of nickel particles on the catalyst; however, the relationship is not linear. Also, the BET surface area calculated from the N_2 adsorption experiments decreases with increasing $Ni(NO_3)_2$ concentration. It is known that the introduction of nickel in the zeolite framework is dictated by ion exchange for nickel loading below 2 wt%. On the other hand, for nickel loading greater than 2 wt%, wet impregnation takes place; therefore, leading to the formation of NiO clusters at the catalyst surface, which blocks the catalyst pore structure.[4] Figure 1.B shows the spectrum of the HBEA and NiBEA zeolite measured at 30 °C after the pre-treatment.

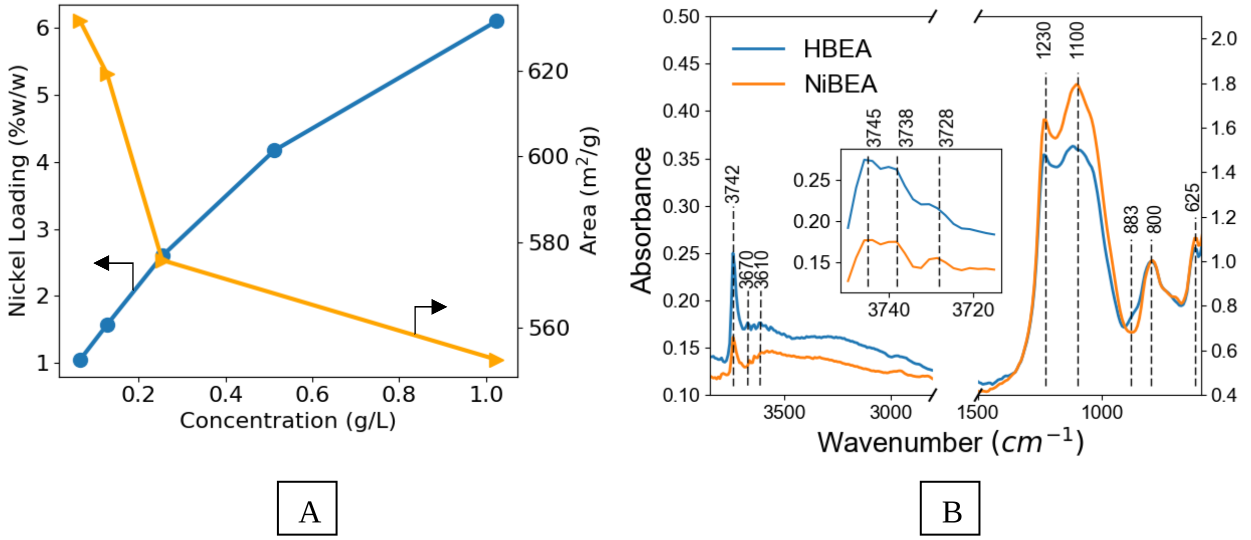

Figure 1: (A) Nickel loading and BET surface area as a function of the $Ni(NO_3)_2$ solution. (B) FT-IR spectra of H-BEA (blue) and NiBEA (orange) after pre-treatment and outgassing. Spectra were collected at 30 °C and a 16 cm^{-1} resolution. The inset shows the OH stretching region for both catalysts collected at a resolution of 4 cm^{-1}.

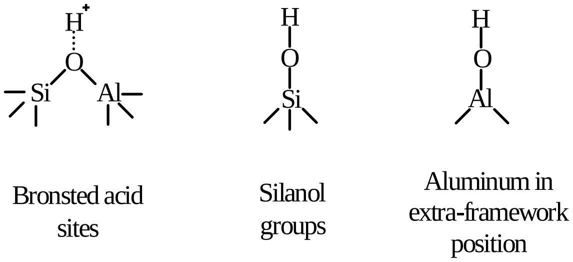

Figure 2: Representation of hydroxyl groups in the BEA structure. Adapted from [3].

The region between 4000 and 3000 cm^{-1} is assigned to the *v*(OH) of the BEA zeolites and the assignment of these peaks has been vastly reported in the literature.[11]–[13], [17]–[20] Both spectra have an apparent peak at 3742 cm^{-1}, which is assigned to the *v*(OH) of silanol groups. However, higher resolution results (4 cm^{-1}, inset in Figure 1.B) actually show three peaks near this wavenumber. The peak at 3745 cm^{-1} is assigned to the *v*(OH) of the silanol groups at the external surface of the catalyst. On the other hand, the peaks at 3738 and 3728 cm^{-1} are assigned to silanol groups inside the pore structures. Furthermore, the peaks at 3670 and 3610 cm^{-1} are assigned to hydroxyl groups connected to aluminum in extra-framework positions and bridging hydroxyl groups, respectively. The bridging hydroxyl groups are characterized as strong Bronsted sites, which have been reported as the active site in oligomerization reactions over acidic heterogeneous catalysts.[11]–[13] Figure 2 shows the atomic representations of the hydroxyl groups in the environments mentioned.

Furthermore, additional peaks are present in the fingerprint region (ranging from 1500 to 600 cm^{-1}). This region is important in the characterization of ion-exchanged zeolites since it shows the stretching and bending modes of the tetrahedral (T = Si or Al) atoms.[17], [21], [22] The peaks at 1230 and 1100 cm^{-1} are assigned to the intertetrahedral T-O asymmetrical vibrational mode of the BEA support. On the other hand, the peak at 800 cm^{-1} with a shoulder at 735 cm^{-1} is assigned to intertetrahedral symmetric T-O stretching mode. The peak with low intensity at 883 cm^{-1} is assigned to the vibrational mode of either Si-O or Al-O bonds.[17]

The HBEA and NiBEA share most of the features assigned in the spectra presented in Figure 1.B. However, the peaks assigned to the *v*(OH) are less intense for the NiBEA compared to the HBEA, with complete disappearance of the peaks at 3670 and 3610 cm^{-1}, indicating substantial nickel exchange in the Bronsted sites. The hydroxyl groups connected to the framework aluminum have a strong acidic character; therefore, it is expected that nickel will exchange these sites more easily than the silanol groups, which have less acidic character. However, despite the weak acidic character of the silanol groups, the intensity of the peak at 3742 cm^{-1} also decreased after nickel exchange, with an additional decrease of the ratio of silanol groups outside/inside of the BEA structure. This suggests that nickel exchange is favored on the outside of the pores, and is an indication of NiO clusters formed at the outer surfaces of the BEA structure. Therefore, not only the strong acid sites were substituted by nickel ions, but the formation of NiO clusters perturbed the weak acid sites. Furthermore, the peak at 883 cm^{-1} also decreased after nickel exchange. The same trend was reported previously for the ion exchange of Cs in the hydrogen form of a commercial BEA zeolite.[17] The reduction in the intensity indicates that nickel ions exchanged sites in environments containing aluminum or silicon.

3.2 Effect of Reaction Conditions and Parameters

3.2.1 Nature of Adsorbed Oligomers

Figure 3 shows the IR spectra of the HBEA and NiBEA (4.1 %wt nickel loading) catalyst collected over the course of the ethylene oligomerization, at atmospheric pressure, varying the temperature from 30 to 300 °C. The color bar in Figure 3 displays the temperature gradient for each spectrum. Peaks at the wavenumber region shown indicate the oligomers which are formed at the surface of the catalyst. As mentioned at the Experimental Section 2.4, the WHSV used for these experiments is very high; therefore, it is expected that the conversion of ethylene at the surface of the catalyst will be very low. Thus, the concentration of oligomers at the bulk phase is negligible with respect to the total concentration of ethylene. Therefore, we assume that the peaks of the oligomers in the present spectra are not related to species in the gas phase, but primarily to species adsorbed in the catalyst. The series of spectra presented in Figure 3 show that both catalysts are active for the ethylene oligomerization. The peaks at 2956 and 2926 cm^{-1} are assigned to the

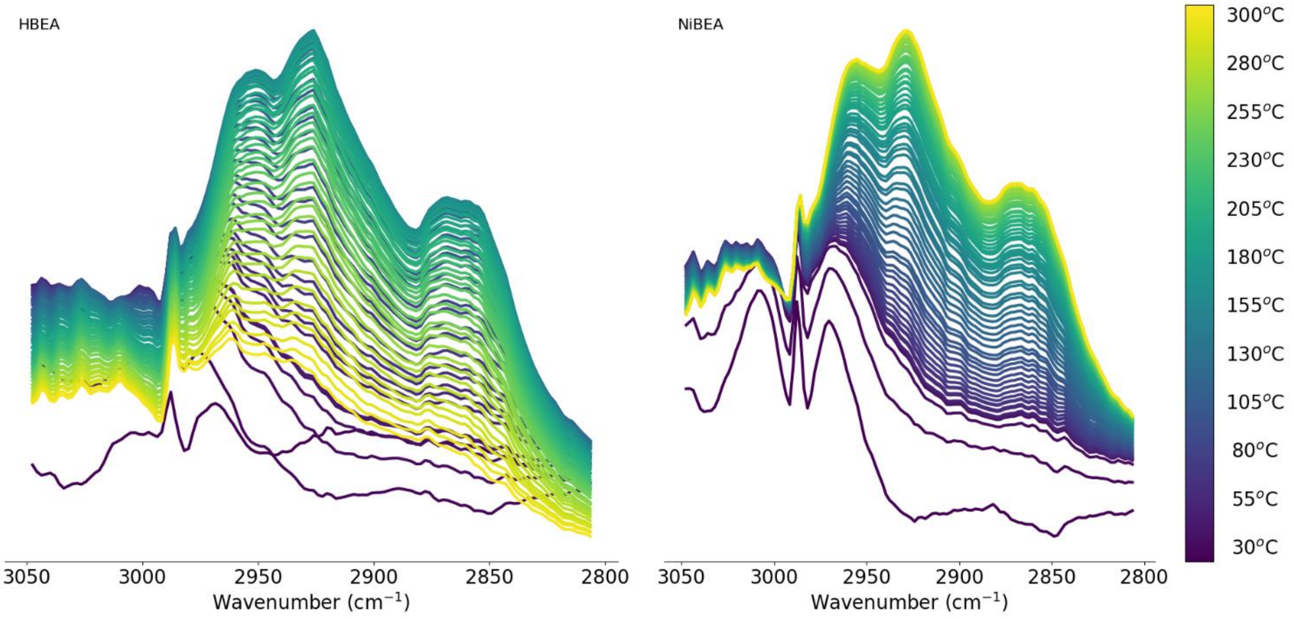

Figure 3: FTIR spectra of the HBEA (series of spectra on the left) and NiBEA (series of spectra on the right) catalysts showing the *v*(CH) region. Spectra were collected at resolution 4 cm^{-1}.

$v_{asym}(CH_3)$ and $v_{asym}(CH_2)$, respectively. Also, a peak at 2863 cm^{-1} is observed. This peak arises from the overlapping of two other peaks at 2853 and 2869 cm^{-1}, which are assigned to the $v_{sym}(CH_3)$ and $v_{sym}(CH_2)$, respectively.[11]–[13], [19], [23] Furthermore, the spectra of the outgassed NiBEA and HBEA show the absence of peaks above 3000 cm^{-1} indicating that the oligomers formed at the surface of the catalyst are not aromatic. This indication is consistent with the literature for the oligomerization of 1-hexene over HZSM-5.[23]

3.2.2 Effect of the Nickel

In Figure 3 the two catalysts show opposite behavior with respect to the production of oligomers at the surface of the catalyst with increasing temperature. It can be observed in Figure 4 that both catalysts show an increase in the CH_2/CH_3 ratio with increasing temperature below 150 °C. However, when the temperature is increased over 150 °C, the CH_2/CH_3 decreases for the

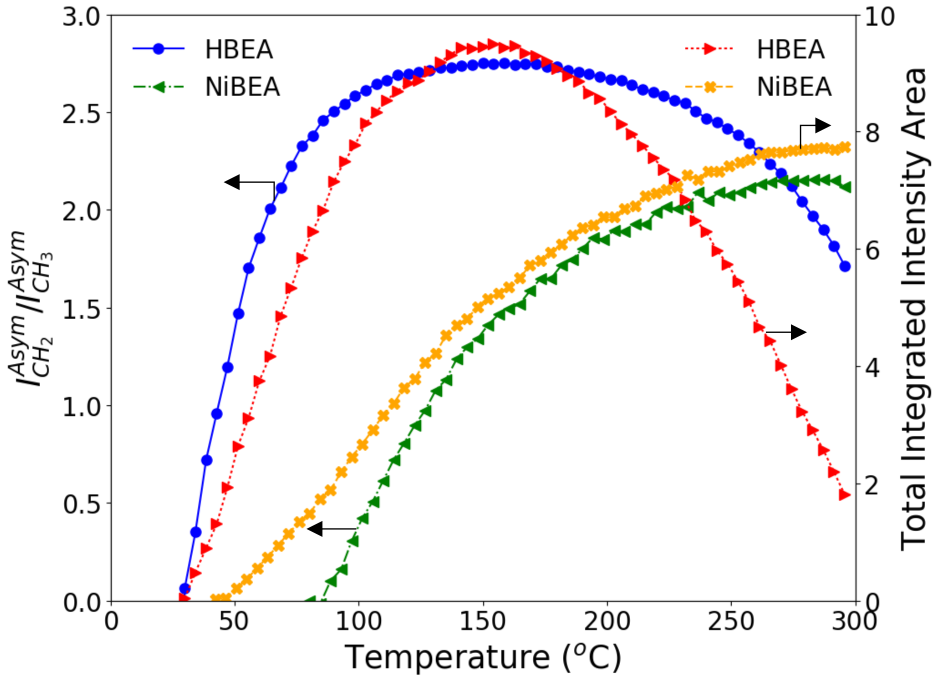

Figure 4: Calculated CH_2/CH_3 ratio and the total peak area from 2800-3000 cm^{-1} for the spectra presented in Figure 3.

HBEA. On the other hand, for the NiBEA, the CH_2/CH_3 ratio keeps increasing, indicating that the oligomerization continues beyond 150 ^oC.

Furthermore, Figure 4 shows that the total integrated intensity area of oligomers formed over the HBEA decreases when the temperature increases from 150 to 300 ^oC. In fact, there is a maximum at 150 ^oC for the HBEA catalyst. Conversely, for the NiBEA catalyst, the integrated intensity area keeps increasing with increasing temperature. This observation suggests that the HBEA catalyst, which has only acidic sites, starts to perform cracking of the oligomers which are adsorbed in the catalyst. Therefore, above 150 ^oC, the cracking reactions promoted by the acidic groups become prevalent over oligomerization reaction. On the other hand, the NiBEA catalyst is able to maintain the oligomerization, reducing the cracking of the oligomers. It is important to point out that there can still be some cracking of oligomers for the NiBEA catalyst, but the oligomerization prevails in the entire range studied. Furthermore, for temperatures greater than 150 ^oC the amount of oligomers on the NiBEA continues to increase despite the decrease of oligomers in the HBEA. This strongly suggests that coke is formed on nickel sites, in addition to being formed on acid sites.

The acidity of the catalyst is an important variable during the oligomerization of ethylene since the size of the molecules is strongly affected by this variable. Indeed, acid sites are known to form strongly adsorbed species; therefore, limiting the desorption of oligomers from the catalysts surface.[4], [8] It is important to highlight, however, that the analysis of products at the surface of the catalyst does not provide all necessary information for understanding of the

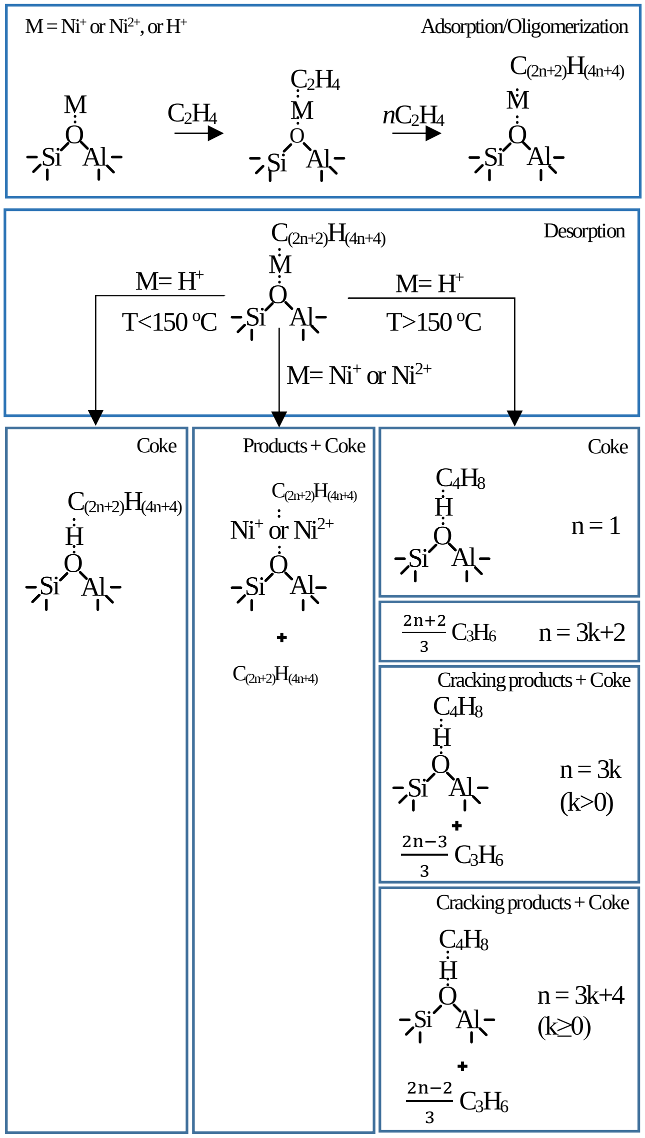

Figure 5: Reaction pathway for the adsorption, reaction and desorption of the ethylene molecules over the HBEA and NiBEA catalyst during the oligomerization of ethylene, varying the temperature from 30 to 300 °C, at atmospheric pressure.

reactions, since these molecules have to desorb once they oligomerize. In fact, the analysis of the liquid product collected for both catalysts supports that the NiBEA and HBEA behave very differently with respect to the desorption of the products.

The GC-MS spectra of the liquid product collected in the impinger, for the oligomerization over the NiBEA catalyst, shows mostly 1-butene followed by *cis*- and *trans*- butene, in addition to

1-hexene and 2-pentene-3-methyl. On the other hand, the reaction performed over the HBEA catalyst does not present any liquid products. The absence of products suggests that the cracking reactions lead to the formation of propane or propene, which could not be collected in the impinger due to the very low boiling point. Moreover, after the conclusion of the reaction, some oligomers remained on the catalyst, as indicated in Figure 3. Summarizing, these results indicate that (1) both NiBEA and HBEA catalysts are able to promote the oligomerization of ethylene, (2) coke and liquid products formed during the oligomerization of ethylene over the NiBEA catalyst are aliphatic, therefore, characterizing the coke as products which did not desorb from the catalyst surface, and (3) the NiBEA catalyst favors the desorption of products from the surface of the catalyst, compared to the HBEA catalyst, and reduces cracking reactions. The results presented support the reaction pathway for the ethylene oligomerization at atmospheric pressure shown in Figure 5.

3.2.3 Effect of the Pressure and Temperature on the Overall Ethylene Oligomerization Over the NiBEA (4.1 %wt) Catalyst

Figure 6 shows the ratio of CH_2/CH_3, calculated using IR spectra, for the oligomers adsorbed in the catalyst after the oligomerization of ethylene for a total reaction time of 100 minutes, as function of pressure and temperature. The number of carbons of the oligomers adsorbed increases with increasing ethylene partial pressure for all the conditions analyzed, except for the experiment carried out at 200 ^{o}C and 34.5 bar. Also, Figure 7.A shows the product selectivity for the product collected in the impinger for each reaction condition. As the pressure increases, the selectivity shifts to the formation of high molecular weight compounds. In fact, the increase of ethylene oligomerization rates with increasing ethylene partial pressure has been reported in the literature for different silica-alumina catalyst, using both slurry and fixed-bed reactors.[8]–[10], [24], [25].

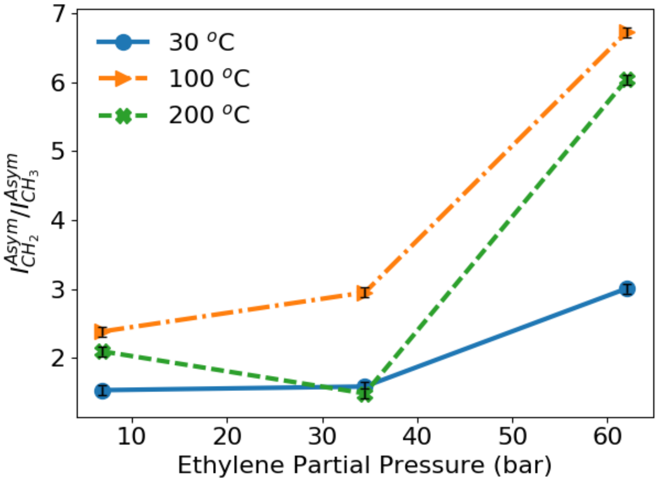

Figure 6: Integrated intensity ratio of the CH_2 and CH_3 vibration modes of the oligomers adsorbed in the catalyst formed during the oligomerization of ethylene over NiBEA.

Furthermore, Figure 6 shows that the ratio of CH_2/CH_3 is greater for all the experiments conducted at 100 °C, compared to 30 and 200 °C. On the other hand, the analysis of the liquid collected in the impinger shows that the molecular weight of the liquid products increases with increasing temperature. Therefore, a significant portion of the heavy products formed during the reaction at 100 °C remained adsorbed on the catalyst. Conversely, for the experiments conducted at 200 °C, even though the FTIR data shows lower molecular weight compounds adsorbed in the catalyst, the analysis of the liquid collected in the impinger shows a greater selectivity for high molecular weight compounds. This is an indication that the desorption of the oligomers is affected by the temperature. Both the oligomerization and desorption rates increase with increasing

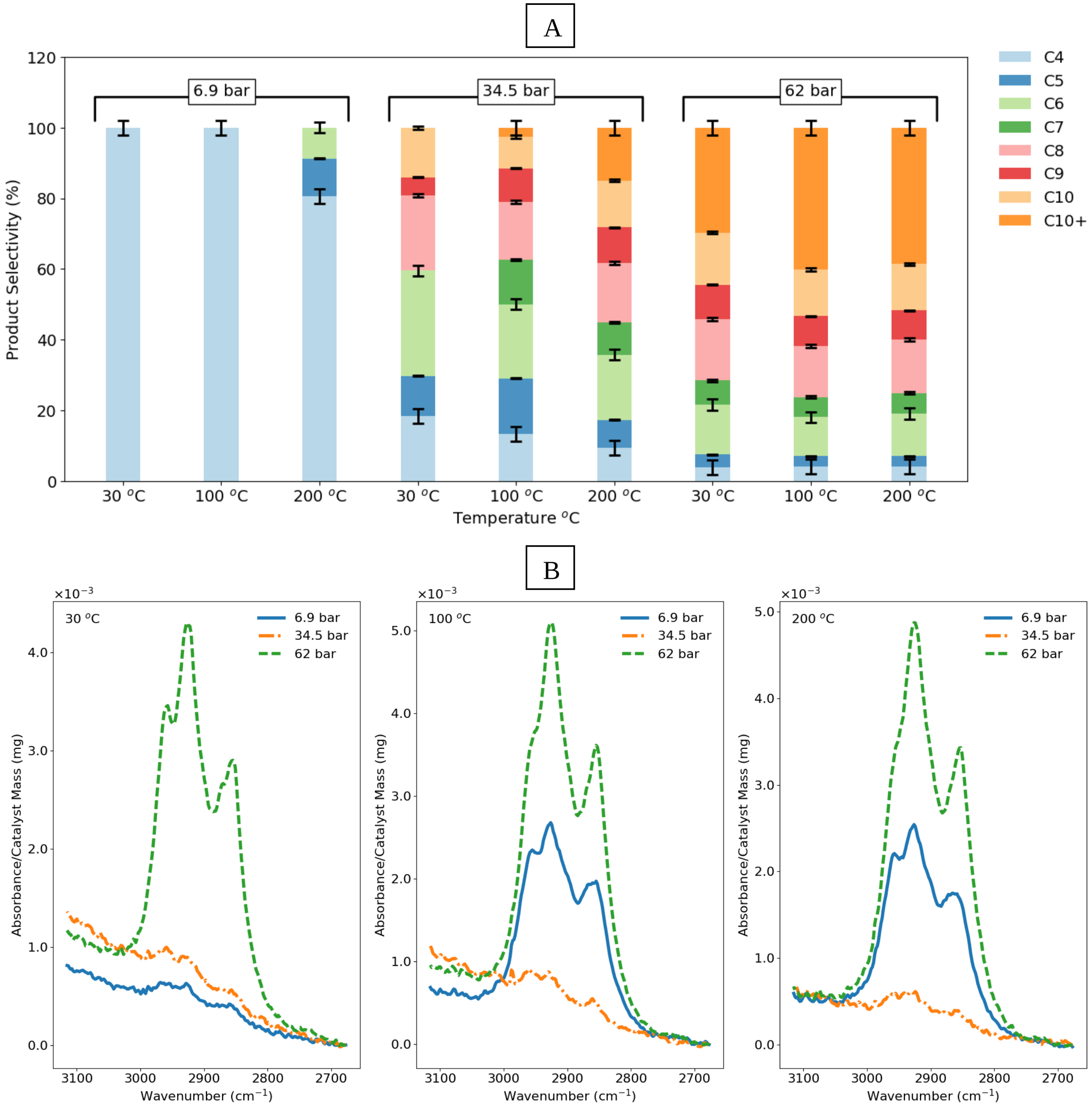

Figure 7: (A) Product selectivity for each of the conditions studied in section 3.2.3. Heavy products are classified as C_{10+}. Spectra of the catalyst outgassed at the temperature of the reaction after the oligomerization of ethylene.

temperature. In other words, the CH_2/CH_3 ratios shown in Figure 6 are affected by the relative contribution of the desorption and reaction steps. It is possible that a change in temperature from

100 ^{o}C to 200 ^{o}C increases the desorption rates to a higher extent than it increases the oligomerization rates, leading to a reduction in CH_2/CH_3 ratio.

3.2.4 Effect of the Pressure and Temperature on Coke Formation

Figure 7.B shows the spectra of the catalyst outgassed after the reaction, showing the CH stretching region. As already mentioned, the nature of the coke remaining in the catalyst after the reaction is aliphatic. For the experiment carried out at 30^{o}C and 6.9 bar, little coke is formed on the catalyst. This can be explained by low kinetic rates at this condition. In contrast, for the reactions performed at 100 and 200 ^{o}C (at 6.9 bar) the peaks associated with the oligomers adsorbed in the catalyst are much more intense, indicating that there are more oligomers adsorbed. Moreover, the experiments at 100 and 200 ^{o}C reveal that the reaction conducted at 34.5 bar formed less coke compared to the other two pressures. This result suggests that even though the reaction rate increased due to the increase of the ethylene partial pressure, the oligomers formed in the catalyst desorbed and diffused to the gas phase.

3.2.5 Effect of the Pressure and Temperature on Liquid Products Composition

For the series of experiments at 30 ^{o}C, only 1-butene was formed at 6.9 bar in the liquid product. This indicates that 1-butene is the first compound formed during the oligomerization of ethylene over the NiBEA catalyst. In fact, we showed previously that the experiments conducted at ambient pressure led to the formation of mostly 1-butene. As the temperature increases, *cis*/*trans*-butene are formed beside to 1-butene. Indeed, 1-butene has already been postulated as the starting product of the ethylene oligomerization, and the isomerization of 1-butene to form *cis*/*trans* -butene has been shown to occur at elevated temperatures.[4] In addition, at 34.5 bar, it is possible to observe the formation of dimers, trimers and tetramers comprising both alpha olefins and its respective isomers. Additionally, compounds formed via cracking reactions are present among the liquid product. The GC-MS analysis of the liquid product collected for the reactions performed above 6.9 bar shows 3-ethyl-1-pentene, 2,3-dimethyl-1-pentene, and 3-ethyl-3-heptene. This suggests that, cracking reactions follow the same pathway, therefore, leading to the formation of similar oligomers. Nevertheless, it is important to highlight that, even though the cracking products are similar, the selectivity of the products formed from cracking reactions changes with temperature and pressure, as shown in Figure 7.A. One interesting observation is the presence of alpha-olefins (1-olefin) only up to C_8. This might be an indication that (1) the products with more than 8 carbons are formed from the cracking of heavy molecular weight coke molecules, (2) they are formed from secondary oligomerization reactions between oligomers produced from the primary oligomerization of ethylene, or (3) C_{10} and C_{10}+ products are formed from the reaction of ethylene with C_8 products formed from the isomerization of C_8 alpha-olefins. Based on the products observed, we hypothesize that route (3) is the predominant one.

3.2.6 Effect of the Subcritical and Supercritical Ethylene Media

Supercritical ethylene has a major effect in the oligomerization kinetics, as it can be observed in Figure 6 that the CH_2/CH_3 ratio of the species in the catalyst is greater for all experiments conducted at the supercritical conditions (62 bar) compared to subcritical conditions (6.9 and 34.5 bar) at the same temperature. Also, it can be observed in Figure 7.B that the supercritical experiments formed more coke on the catalyst compared to the experiments in subcritical ethylene. It is important to point out that the increase of pressure from subcritical to supercritical increases the oligomerization rates, therefore, increasing the coke formation rate at the catalyst surface. Therefore, the increase of the desorption constant in the supercritical region is not enough to compensate the increase of the oligomerization rate. The combined FTIR and product selectivity data (Figures 6, 7.A, and 7.B) provide important information about the catalytic oligomerization of ethylene over the NiBEA catalyst. However, they do not provide detailed information about the chemical nature of the adsorbed products, i.e., the degree of branching of the molecules, or if the molecules are linear or cyclic, since a complex mixture of hydrocarbons is formed over the course of the reaction. The analysis of the GC-MS data for liquid product collected at supercritical ethylene phase shows heavy molecular weight oligomers in a greater concentration than what is observed in the subcritical experiments. This can be an indication of dissolution of the coke from the catalyst surface by the supercritical ethylene. The nature of the desorbed oligomers under supercritical conditions is similar to the desorbed products obtained in the experiments below the critical point. In fact, the molecules are paraffins with a low degree of branching, and most of the compounds present one methyl or ethyl groups. However, the number of carbons increase, with some molecules having up to 20 carbons. The presence of longer molecules is an indication that the desorption of heavier hydrocarbons is favored at supercritical conditions.

The data presented for the previous set of experiments shows that both pressure and temperature increase the rate of the oligomerization. Also, it is possible that the supercritical fluid acts as a solvent for the coke formed over the course of the reaction. The supercritical region is, among the conditions studied in this work, the preferable one for the oligomerization of ethylene over the NiBEA catalyst, since it presents a distribution of products shifted to heavier molecular

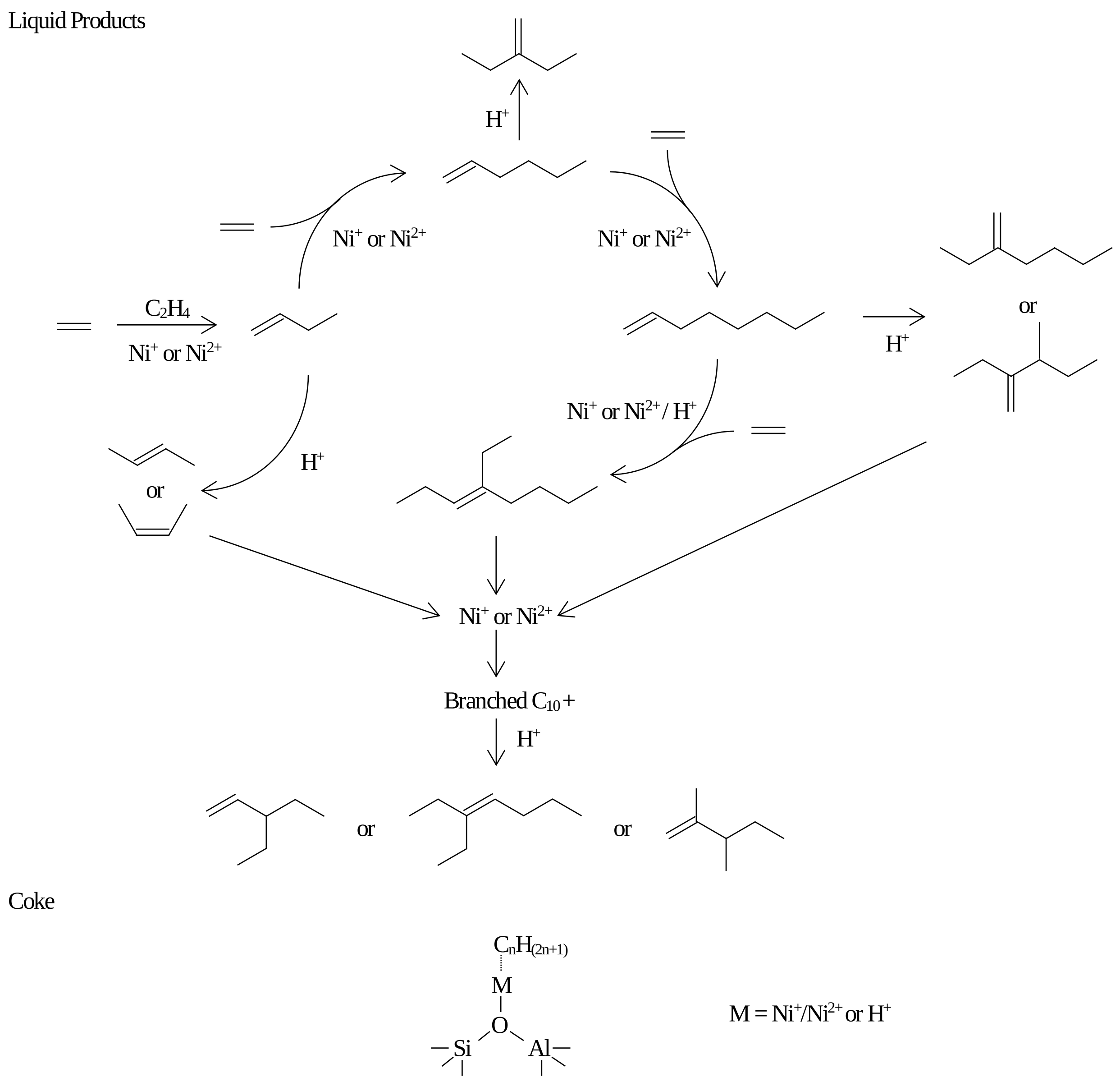

Figure 8: Reaction pathway showing the major compounds produced via the oligomerization, isomerization and cracking reactions over the NiBEA catalyst, and the nature of the coke. All compounds presented in this scheme were detected in the GC/MS analysis of the liquid collected in the impinger after the reaction period. Ni^+ or Ni^{2+} are involved in the oligomerization reactions, and H^+ are involved in isomerization, and cracking reactions. In cases in which oligomerization and isomerization reactions are involved, both Ni^+ or Ni^{2+} and H^+ sites are represented.

weight compounds; therefore, indicating that (1) the catalyst is very active for the oligomerization of ethylene at these conditions, and (2) the desorption of coke is enhanced at supercritical conditions. However, despite the presence of heavier molecular weight compounds in the impinger, the FTIR combined with the MS and FID data are not able to provide evidence of the dissolution of the coke at supercritical conditions. Thus, additional experiments are required to validate the hypothesis that the supercritical fluid can extract coke. Figure 8 shows the proposed reaction pathway, for the ethylene oligomerization at a temperature range of 30 to 200 ^{o}C, and a pressure range of 6.9 to 62 bar, based on the liquid products collected and identified after the reaction.

3.3 Analysis of the Effects of Supercritical Fluid Conditions

Table 2 compares the product selectivity of one subcritical and the two supercritical conditions from Table 1. The selectivity for C_3-C_5 decreases as the reaction conditions change from subcritical to supercritical, and it further decreases with the change from supercritical to dense supercritical. On the other hand, the selectivity for heavy molecular weight hydrocarbons (products ranging from C_9 to C_{10+}) increases, with a greater selectivity for heavier molecular weight compounds at the dense supercritical condition.

The shift of the product selectivity to heavier molecular weight compounds when the conditions change from subcritical to supercritical was already discussed in the previous section (3.2.6). However, in the set of experiments discussed here, the system operates at an ethylene flow rate of 165 ml/min, as opposed to 15 ml/min for the experiments described in section 3.2. Therefore, it is expected for the mass transfer convection rate of the products in the supercritical ethylene to increase, thus, removing more heavy compounds adsorbed on the catalyst. Also, the decrease in the selectivity of C_3 and C_5 indicates that the cracking of C_6 and C_{10} is minimized at supercritical conditions. Instead, the cracking reactions affect large molecular weight compounds to a greater extent, with an increase in the selectivity of C_9. The formation of heavier compounds followed by the desorption from the catalyst surface at supercritical conditions is evident in Table 2. In summary, the experiment at dense supercritical fluid conditions provides strong evidence of (1) enhancement of the kinetics of oligomerization under SCFC, and (2) dissolution of the coke formed in the NiBEA catalyst by the supercritical ethylene. Figure 9 presents a set of pictures of the pressurization and reaction processes. The picture of the fresh catalyst is displayed for comparison.

Table 2: Product selectivity (%) of the compounds collected in the liquid product for the experiments reported in this section and listed in Table 1.

Oligomerization Conditions		Product Selectivity (%)								
Pressure (bar)	Temperature (°C)	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{10}+
34.5[a]	100	13.8	49.7	2.3	19.8	2	5.8	0.8	4.5	1.3
58.6[b]	100	7.7	37.5	2	30.2	2.7	5.6	1.8	5.4	7.1
58.6[c]	200	0	33.3	0.7	27.9	1.6	9.2	2.3	7.2	17.8
Standard deviation (%)		0.9	2.1	0.1	1.5	0.3	0.5	0.1	0.4	2.1

a: Subcritical condition
b: Supercritical condition
c: Dense supercritical conditions.

Initially, it is possible to observe a change in the catalyst surface color from white (Figure 9.A - Before Pre-treatment) to beige, after the pre-treatment (Figure 9.A – After Pre-treatment). The change in color is most likely related to the thermal treatment of the catalyst. Also, when the system is pressurized to the set point, no change in the catalyst surface color can be observed (Figure 9.A - 57 bar, 200 °C). As mentioned in the Experimental Procedure 2.5, a flow rate of 600 ml/min of pure ethylene was used to pressurize the reactor. Therefore, if any chemical reaction occurred during this process, its extent was not high enough to change the catalyst color.

However, once the pressure and temperature reached the set point (Figure 9.A - 57 bar, 200 ^{o}C), the flow rate of ethylene was reduced to 165 ml/min to initiate the reaction. Figure 9.B shows the pictures of the catalyst surface in different time intervals over the course of the reaction. When the flow rate is reduced, the catalyst becomes more active for the oligomerization and its surface starts to become dark. After 20 minutes, the catalyst surface is completely dark. The dark aspect of the catalyst is an indication of coke formation. As discussed previously in section 3.2, the coke studied in this work is constituted of aliphatic molecules.[14] After 60 minutes of TOS, the catalyst surface color starts to become clear (Frame B - 60 min) and after the total reaction time (Frame B - 100 min) the catalyst surface resembles the catalyst before the reaction (Figure 9.A - 57 bar, 200 ^{o}C). This variation in color shows that, in fact, the supercritical ethylene dissolved the coke formed at the surface of the catalyst bed. To the best of our knowledge, this work is the first to provide visual evidence of the dissolution of the coke formed during chemical reactions over heterogeneous catalysts under supercritical conditions, and although the enhanced solvating effect

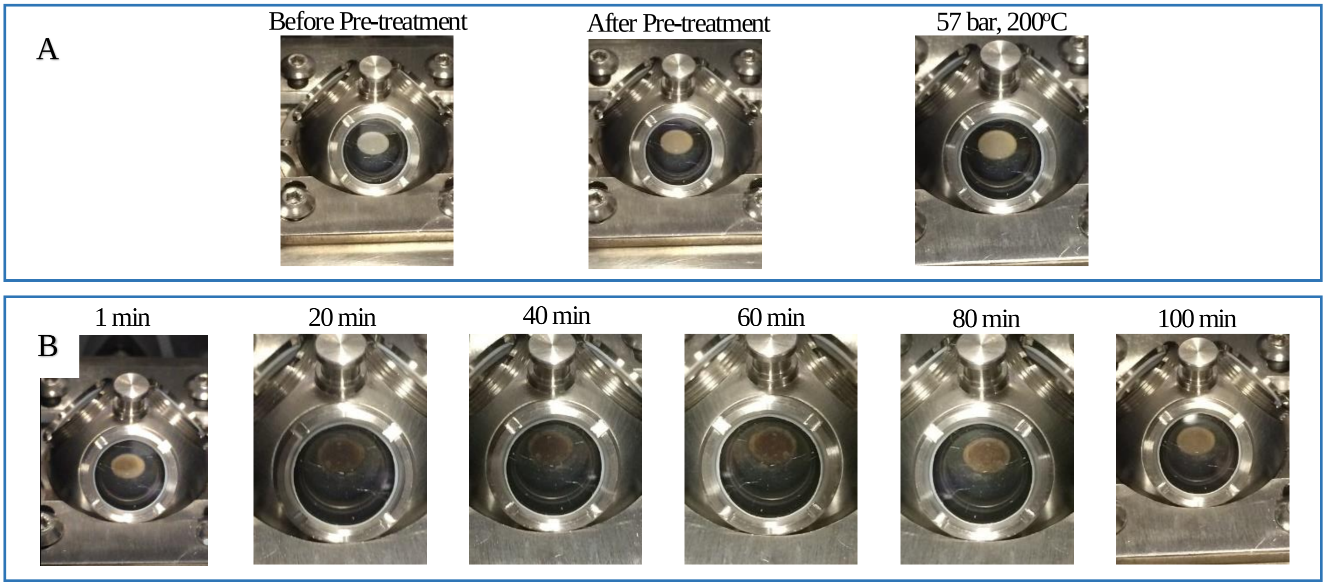

Figure 9: Pictures of the catalyst before the reaction (Before Pre-treatment), after the pre-treatment, after reach the reaction conditions (57 bar, 200 ^{o}C), and the catalyst in different time intervals over the course of the reaction (1, 20, 40, 60, 80, 100 minutes).

of the supercritical ethylene has already been reported in the literature, to the best of our knowledge this is the first work to show the phenomena *in-situ* during the reaction.

Nevertheless, one question remains: What causes the products to stay adsorbed in the catalyst? We previously showed that both the coke and the desorbed products are aliphatic, and no information about the degree of branching or cyclic nature of the coke was attained in the previous sections. The second experiment (described in the Experimental Procedure 2.5) was used to answer this question. Instead of using a TOS of 100 minutes, we performed the experiment for a shorter time to collect the coke material from the reactor and perform the characterization. Since the experiment at dense supercritical condition produced more coke compared to the other two experiments, we repeated this experiment, however, using a TOS equal to 50 minutes.

The main objective of this step was to collect the coked catalyst and obtain information about the chemical composition of the desorbed molecules. We observed that the dark material which was adsorbed at 57 bar desorbed at the end of the experiment, after depressurization. In addition, a layer of liquid (some visible droplets) was formed on the inner surface of the window (Figure

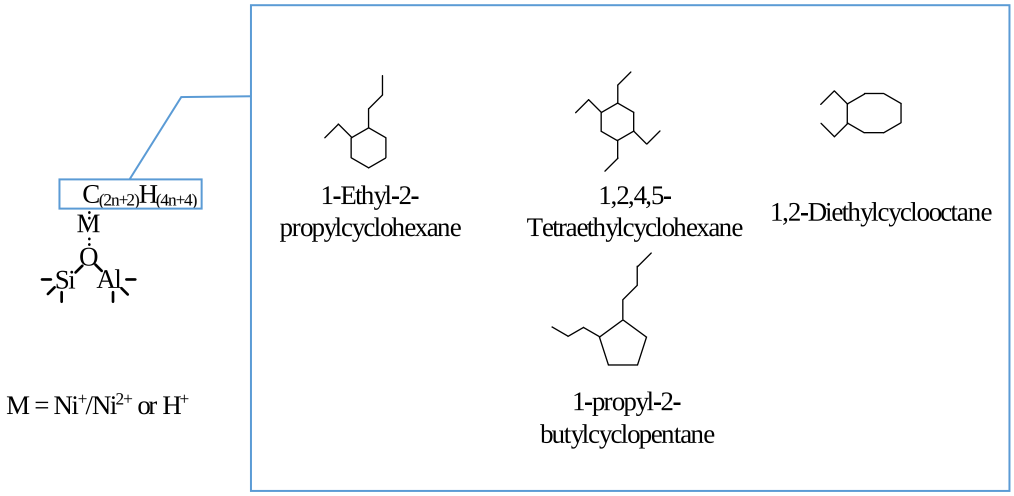

Figure 10: Composition of the coke based on the liquid collected after depressurizing the reactor for the reaction carried out at 57 bar, 200 °C, and a total TOS of 50 minutes.

not shown for the sake of brevity). We collected this liquid and analyzed it using the GC-MS. The analysis of the liquid shows that it is formed mostly by cyclic aliphatic hydrocarbons. It is likely that the reduction of the pressure in the system led these molecules, which were forming a network at the surface of the catalyst, to desorb. The observation of cyclic molecules in the coke supports the idea that, even though both coke and desorbed products are aliphatic, the cyclic nature of the coke may be the reason for it to remain adsorbed in the catalyst, under supercritical conditions. Furthermore, for the experiment performed at supercritical ethylene for 100 min, the GC-MS analysis of the liquid collected in the impinger shows peaks assigned to cyclic molecules with a high degree of branching. We hypothesize that the liquid formed at the inner surface of the window is the coke, which desorbed from the catalyst surface after the pressure was reduced. Furthermore, the formation of coke on the catalyst surface was not observed for the experiment conducted at 57 bar and 100 ^{o}C, and the experiment conducted at subcritical conditions did not present any of these compounds in the liquid products. These observations combined support the conclusion that (1) the reaction kinetics is enhanced, and (2) the coke is dissolved at supercritical conditions. In summary, we characterized the coke as highly branched cyclic molecules. Figure 10 shows some of the molecules present in GC/MS spectra of the liquid collected at the inner surface of the chamber window. These molecules are characterized as the coke produced during the ethylene oligomerization over the NiBEA catalyst at supercritical conditions.

4 Conclusion

We reported in this paper a study of the catalytic reactions of ethylene oligomerization over a nickel supported in aluminum silicate catalyst with a BEA topology under subcritical and supercritical conditions. The N_2 adsorption shows a reduction of the catalyst BET surface area with increasing $Ni(NO_3)_2$ concentration, which indicates the deposition of NiO in the catalyst surface. The oligomerization experiments conducted with the NiBEA catalyst (4.1 wt% nickel loading) show that the protonated form of the commercial support is able to oligomerize ethylene, however, producing exclusively adsorbed products. On the other hand, the catalyst exchanged with nickel maintains the ethylene oligomerization, leading to the formation of desorbed products. On the other hand, the catalyst with only acidic sites forms strongly adsorbed species leading to coke formation and promotes the cracking of the products (likely propene) for temperatures higher than 150 ^{o}C. In addition, the nature of the coke is aliphatic. Screening experiments show that the increase of pressure and temperature increase both the oligomerization rates and the desorption of oligomers from the catalyst surface. However, the increase in the reaction kinetics at supercritical conditions is greater than the increase of the desorption constant, leading to the deposition of additional coke at the catalyst surface. However, the supercritical ethylene promotes the dissolution of the coke hydrocarbons from the catalyst surface. We were able to obtain visual confirmation of the phenomena *in-situ* and identification of the coke as cyclic molecules using GC-MS/FID. Finally, we postulated reaction pathways based on the results obtained.

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Future Plans

The present paper elucidates the catalytic reactions involved in the ethylene oligomerization over the NiBEA catalyst. However, there is still a variety of catalysts with promising properties that can be tested for the ethylene oligomerization. For example, zeolites with different topologies can be used. Additionally, carbon nanotubes (CNT) have interesting properties, such as high flexibility and thermal conductivity, which would favor the oligomerization in a packed-bed reactor. Furthermore, the easy to control the CNT pore diameter would favor the shift of the product selectivity towards specific chemicals of industrial interest. Moreover, chromium and molybdenum, which are used in the ethylene oligomerization over homogeneous catalysts, can be good candidates as a replacement of nickel for the ethylene oligomerization over heterogeneous catalysts.

Although many studies reported the effects of pressure, temperature, and weight hourly space velocity on the ethylene oligomerization over heterogeneous catalysts, there is still a lack of studies about the kinetics of the ethylene oligomerization over heterogeneous catalysts. Only a few studies successfully reported the kinetics of the ethylene oligomerization, although comprising a limited range of catalysts. Therefore, ethylene oligomerization over heterogeneous catalysts still requires a deeper understanding of the reaction kinetics, including other catalysts such as nickel-exchanged in BEA.

Expanding to other areas, the change of the feedstock is another important field available for research. Propene and butene have been shown to require lower reaction conditions to undergo oligomerization. Therefore, these compounds would be good alternatives to produce higher alpha-olefins, therefore, expanding the product range of the reaction. Nevertheless, more studies using propene and butene have been reported in the literature, relative to the use of ethylene as a feedstock. Nevertheless, the combination of these feedstocks (which requires lower energy to undergo oligomerization) with a novel catalyst, such as CNT, would be a promising process to replace the technology currently used for the production of olefins.