Heterogeneous Catalytic Oligomerization of Ethylene

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A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

University of Washington
2017

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Program Authorized to Offer Degree:
School of Environmental and Forest Sciences

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Abstract

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Throughout this work, we report results for the oligomerization of ethylene over Ni-Hβ in a packed bed reactor. We performed a parameterized study over temperature (30ºC-190ºC), pressure (8.5-25.6 bar), and weighted hourly space velocity (2.0-5.5 hr^{-1}). We observed that the ethylene conversion increased with reaction pressure due primarily to the slower velocities at higher pressures. Increasing the temperature of the reactor led to the formation of larger oligomers and coke, but its effect on the conversion was small. The space velocity played an important role on ethylene conversion and product selectivity, with higher conversions observed at lower space velocities and higher selectivities to butene at higher space velocities. We also conducted a long experiment to determine the activity of the Ni-Hβ catalyst over 72 hours-on-stream at 19.0 bar partial pressure of ethylene, 120ºC, and 3.1 hr^{-1} WHSV. We observed that catalyst deactivation occurred only during the startup period largely due to coke formation. Despite this initial

deactivation, negligible coke formation occurred after 8 hours time-on-stream, as the conversion remained steady at 47% for the duration of the experiment.

We also carried out oligomerization of ethylene using Ni-Hβ in a laboratory-scale packed bed reactor for the synthesis of liquid hydrocarbons. We evaluated the effect of several process variables (temperature, pressure, weighted hourly space velocity, and nickel loading) on the liquid hydrocarbon/coke yield, ethylene conversion, and oligomeric product selectivity. Increases in pressure resulted in higher ethylene conversion, corresponding to a liquid yield of 12.4 wt.% with 5.7 wt.% coke. As the pressure increased, the selectivity towards octenes doubled alongside a decrease in butenes, which suggested that higher pressures promoted butene dimerization. Under the conditions studied, a minimum temperature of 120ºC was required to produce liquid hydrocarbons. The liquid yield increased with temperature, with 17 wt.% observed at 190ºC. Higher reaction temperatures led to the formation of odd-numbered oligomers primarily due to acid-catalyzed cracking reactions. In the range of space velocities tested, a moderate WHSV of 2.0 hr^{-1} resulted in a local maximum of 10.6 wt.% of liquid hydrocarbon yield. A moderate nickel loading of 3.4 wt.% also resulted in the highest liquid yield out of the three loadings tested (10.6 wt.%). The variation in nickel loading revealed the importance of having a synergistic balance of nickel and acid sites on the catalyst to maximize ethylene conversion and maintain high liquid hydrocarbon yield.

Lastly, we used supercritical ethylene as both a solvent and as a reactant for ethylene oligomerization over two silica-alumina type catalysts: Ni-Hβ and Ni-Al-SBA-15. Specifically, the effect of pressure and temperature on the overall conversion and product selectivity were evaluated in the range from 0 to 65 bar and 30 to 120ºC. At subcritical conditions, the ethylene conversion reached a plateau of around 50%. By increasing the pressure past the critical point of ethylene, the conversion drastically increased to 71%. The increased conversion can be attributed to the solubility of certain oligomers, namely butene, in supercritical ethylene that promotes desorption from catalytic active site before further oligomerization. We also tested a mesoporous catalyst, Ni-Al-SBA-15 and observed conversion trends analogous to that of Ni-Hβ. At supercritical conditions, ethylene oligomerization over Ni-Al-SBA-15 was more selective towards the butene product, with nearly 74 wt.% butenes observed. The catalyst activity increased with temperature from 30ºC to 120ºC. The experiment conducted at 30ºC showed very little activity and ethylene conversion, however it effectively heavy molecular weight species from the catalyst. This condition, albeit being not effective for ethylene oligomerization, could be implemented as an *in-situ* technique to regenerate the catalyst during process operation.

Acknowledgements

This has been a surreal journey so far. To this day, I am still in shock as to how many pieces had to fall into place for me to be where I am now, a few steps away from holding a doctorate degree. The Ph.D. was not an easy task, and the voyage throughout would have not been possible without the kindness and assistance of my advisor, my committee, and all the colleagues that I have had the fortune of working with throughout the past five years.

First and foremost, I am incredibly grateful to have had the opportunity to meet and work with Professor Fernando Resende. I had first met him serendipitously as a senior in college at a national conference in Minneapolis where I was wandering around with an empty stomach and a resume stashed in my backpack. It was at a Tsinghua University reception (with free food) where I had bumped into Professor Resende, where, to be honest, both of us did not belong. Nevertheless, I was pleasantly surprised by his enthusiasm for alternative energy, as that was my primary motivation for studying chemical engineering at the University of California, Irvine. But what caught my attention was how kind he was, and I was floored when I received an email from him when I returned to Irvine, encouraging me to apply to the University of Washington.

Since the days I was accepted and chose to attend the University of Washington, I knew that I had made the right decision. I had always been told that selecting the right advisor was critical, and Professor Resende was a great fit for me. Throughout the Ph.D., I have had the luxury of obtaining valuable experience in starting up a laboratory, guiding my own research project in bifunctional catalysis for my M.S. thesis, and gaining the skills and confidence to work on a multimillion dollar grant with the USDA. Without his guidance, mentorship, and support throughout the years, none of this would have been possible. He challenged me to be a better scientist and to be confident in my abilities. I will not forget the number of revisions that he read

through for my publications and thesis chapters, all of which have helped me progress in my understanding of the topic. In addition, his feedback and questions would also help me think critically about the topic at hand, and this constant feedback loop allowed me to generate several intriguing ideas throughout my time here. I am glad to have been one of his first students in the laboratory, and I will look back with fondness with what we accomplished since we first started.

I would also like to thank Professor Renata Bura, Professor Anthony Dichiara, Professor Richard Gustafson, and Professor Jim Pfaendtner for their support and guidance throughout the arduous process of the degree. Their questions and feedback throughout my many committee meetings, examinations, and our individual meetings helped me obtain new perspectives on my work that I would not have thought of. I am especially grateful for their availability and mentorship during difficult times throughout the last five years. I also want to thank Professor Luiz Anjos and Dr. Fernando Camargo for their time and their expertise in the laboratory. Both were former visiting scholars that worked in the laboratory alongside the graduate students, and were both instrumental to my development as a scientist.

I am also especially fortunate to have worked with so many wonderful colleagues here at the University of Washington. Guanqun Luo and I joined the laboratory together at the same time, and she and I both experienced the difficult, yet exciting start-up phase of the laboratory. Her insight and experience with the analytical devices in the laboratory was invaluable, and I can wholeheartedly say that I would not be as learned as I am now with gas-chromatography if it were not for her knowledge (and patience). I am thankful for her great advice to me during some difficult times. I am also glad to have met Kayla, who was also there with me and Guanqun when the laboratory first started. Kayla was a great colleague in Bloedel, as her energy and her excitement for research was contagious. What I learned the most from her, and something that I will take into my professional career, was to maintain balance in my work and in my life. Striving for that balance has been a key component for me to maintain a level head throughout my Ph.D.

There have been numerous undergraduate researchers that have come and gone in the laboratory, and I am incredibly thankful for their help. A few that come to mind are Devin Chandler and Gabriel Seufitelli. Both Devin and Gabriel were former undergraduate researchers that worked with me in the laboratory and helped with running experiments and analyzing samples. Devin came from the Mechanical Engineering department and Gabriel was a summer undergraduate student visiting from Brazil. They were both great to work with and a pleasure to be around. I am especially thankful for Devin's handiness in the Mechanical Engineering machine shop. Both students are now graduate students in the lab, and I am excited to see them progress as researchers as they advance forward in graduate school to also obtain their doctorates.

I also want to thank the researchers at the Nikolla Lab at Wayne State University for their collaboration with our group on several interesting catalysis projects. Learning more about catalysis from Professor Eranda Nikolla and Dr. Asha Mudiyanselage helped me tremendously during my M.S. thesis as well as the work I did for my dissertation. Their willingness and enthusiasm to work with our group on several projects helped open my eyes to the power of collaboration, despite being in different time zones. I am glad that we got to work together, as it was a great learning experience for me as a growing professional.

Last, but not least, I am grateful to have my family with me throughout my degree. My parents, Elise Tseng and Peter Jan, have had to make numerous sacrifices throughout the years to allow for me to have the opportunities that I have now. I am beyond blessed to have both as my parents, as I would not be where I am now without their love and support throughout my life. They have always been supportive of my decisions, and for that I am truly thankful for having the freedom and opportunity to receive a doctorate in the United States. Mom and Dad, thank you for always being there for me by my side. The same can be said for my sister, Chelsea Jan, who has grown and matured so much ever since I started college. Thank you for giving me great advice during some of my tough times during school. I am excited to see the great accomplishments that I know you will achieve.

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Chapter 1: Introduction and Literature Review

Ethylene as a chemical reactant

Ethylene is one of the most important organic chemicals, with a worldwide capacity of nearly 140 million tons per year[1]. The traditional processes used to produce ethylene gas have been derived mostly from the petrochemical industry through steam cracking of saturated hydrocarbons[2]. Greener, alternative processes, however, have been theorized and executed by utilizing natural gas, coal, and biomass as feedstocks for ethylene production. Bioethanol, for example, can be produced through a sequential scheme of enzymatic hydrolysis of lignocellulosic biomass with a downstream fermentation process on the hydrolyzed sugars. The ethanol produced from this stage can then be incorporated into gasoline mixtures or further dehydrated into water and ethylene over a conventional alumina catalyst.

As a raw material, ethylene is incorporated into a wide array of synthesis procedures for a versatile range of valuable chemical intermediates and products. Several key industrial reactions of ethylene include polymerization, oxidation, halogenation, alkylation, and oligomerization[1–3]. Linear-alpha olefins and various plastics (low and high density polyethylene) are highly applicable in many industries, and are produced through oligomerization and polymerization pathways, respectively. Linear alpha-olefins are widely applicable for the synthesis of many industrial and consumer products, with examples such as detergents, lubricants, surfactants, among others. As indicated by the broad scale of products produced, ethylene oligomerization is clearly an important reaction for many sectors and industries.

Homogeneous Catalysts for Ethylene Oligomerization

Ethylene oligomerization is a common process, implemented at a commercial scale primarily using homogeneous catalysis. Research on alkene oligomerization previously conducted by Chevron and Shell led to the development of several commercial processes, namely the Shell Higher Olefin Process (SHOP) that implements a nickel-phosphine complex[4–6].

The common homogeneous catalysts used for ethylene oligomerization are typically organometallic complexes consisting of transition metal heteroatoms (Ni, Co, Fe, to name a few) with side ligands, along with an alkylated aluminum cocatalyst participating in the reaction[1,2]. These catalysts have shown high activity for ethylene oligomerization. However, despite the high activity, the implementation of homogeneous processes has multiple technical and economic issues. The first major issue of these processes is that these reactions are typically conducted in continuous stirred tank reactors (CSTR) and batch systems, where the catalyst is in the same phase as the solvent in the reactor. Once the reaction is complete, the catalyst must be recovered and/or regenerated for continued usage. However, the separation of the catalyst from the aforementioned solvent and the products is a cumbersome task that necessitates advanced separation processes to achieve adequate recovery of the catalyst[3,7,8]. In addition, homogeneous catalysts are also maligned for low catalytic activity in the presence of trace impurities in the reactant feed[3]. Lastly, homogeneous catalysis and the processes that utilize them have also been criticized for not abiding to green chemistry principles due to the heavy use of organic solvents. This importance is particularly emphasized for newer companies aiming to establish alternative energy processes, as the cost and recovery of homogeneous catalysts is also a major capital expense. As such, it is evident that greener processes must be studied and designed to facilitate ethylene oligomerization processes. Heterogeneous catalysts may serve as an alternative solution.

Heterogeneous Catalysts for Ethylene Oligomerization

Heterogeneous catalytic processes are desirable for ethylene oligomerization at both an industrial and academic standpoint. Apart from slurry batch fed systems, packed bed reactors are two phase, gas-solid systems that are solvent-free. Though the current literature is limited in scope, the most promising catalysts that have been studied consist of nickel supported on inorganic porous materials, such as silica-alumina materials that consist of microporous and macroporous zeolites[2]. Heterogeneous ethylene oligomerization processes face several technical challenges. The first major challenge is determining the proper catalysts and operating conditions for efficient, selective oligomerization. Parameters such as pore size, acidity, available surface area, and active metal loading will play a role in selecting the correct catalyst, whereas the temperature, pressure, and reactant-to-catalyst ratio (hereafter referred to as the weighted hourly space velocity, WHSV) must be optimized for the catalyst and products desired. The second challenge is the issue of product selectivity, as these processes typically produce a wide product distribution. For oligomerization/polymerization processes, the resulting products can follow a Schulz-Flory distribution ($C4 > C6 > C8 > \ldots > C_{2n}$) or a Poisson distribution[2,9]. This spectrum of products can be problematic to overcome if a specific dimer or trimer is desired. However, this wide distribution of hydrocarbon products may be desirable for certain processes, such as for liquid fuel production.

The most studied heterogeneous catalysts for ethylene oligomerization consist of nickel supported on silica-alumina systems, namely zeolites such as Zeolite Y[10,11] and β[3], amorphous SiO_2-Al_2O_3[12–15], SBA-15[1,16], and Al-MCM-41(labeled as Ni-MCM-41)[2,17–19]. According to their pore sizes, these materials are classified as mesoporous pore structures that have pore diameters in the range of 2-50 nm (with the exception Y zeolites). Microporous Ni-Y and Ni-MCM-22 zeolite catalysts have pore sizes up to 2 nm, and previous studies have shown that these catalysts suffer rapid deactivation due to heavy, branched oligomers that form on the strong Brønsted acid sites that remain trapped in the micropores[3,18,20]. Mesoporous materials with larger pore sizes can eliminate this steric constraint and improve diffusion rates for larger oligomeric compounds. As a result of this increased pore size, mesoporous catalysts with nickel have been shown to be far more active for ethylene oligomerization than microporous materials. Of these materials, Zeolite β is the least studied. Zeolite β is a unique material as it consists of an ordered mesoporous structure with microporous subchannels[3]. Martinez et al. demonstrated the effectiveness of Ni-β in a packed bed reactor for facilitating ethylene oligomerization reactions with a number of different Ni loadings up to 5 wt.% using both incipient wetness impregnation and ion-exchange techniques. Their work showed that Ni-Hβ catalysts were active for ethylene oligomerization in a heterogeneous, packed bed system and that an increase in the nickel loading played a critical role in tailoring the product distribution from light to heavy liquid oligomers up to diesel-range hydrocarbons[3]. However, the number of literature citations regarding packed bed, flow systems for ethylene oligomerization, in general, is scarce.

The activity and long-term behavior of heterogeneous catalysts is dependent on how the catalyst can resist the accumulation of carbonaceous deposits, otherwise known as coke, which lower the catalyst activity. High-temperature regeneration processes are generally used to burn off the coke deposit from the catalyst[21]. However, these regeneration cycles may be problematic for the overall lifetimes of the catalysts, as finely dispersed metal particles tend to sinter into bulkier agglomerates at higher temperatures[22].

Ethylene Oligomerization

Ethylene oligomerization, as discussed previously, is a viable chemical reaction to form linear alpha olefins. To better transition from homogeneous catalytic systems to heterogeneous catalysts, parameters of the overall reaction must be characterized and studied. Specifically, the operating parameters, spanning from the reaction temperature to the reaction pressure, must be examined for their effect on the reaction. Other pertinent parameters useful for reactor design include the weighted hourly space velocity, which dictates the ratio of the reactant ethylene mass flow rate with the amount of catalyst used. Moreover, specific features pertaining to the design of the catalyst must also be studied, as the catalyst is the primary vehicle for the reaction. Parameters such as the pore size, acid site concentration, and active metal concentration must be accounted for on their overall effect on ethylene oligomerization. This section will be focused on discussing the effects of the parameters on ethylene oligomerization over the span of articles published in this research area.

Effect of Pore Size

For ethylene oligomerization reactions, the pore size has been shown to be one of the most important characteristics. In general, the catalyst pore size plays a tremendous role in catalytic reactions that occur over heterogeneous catalysts. For heterogeneous catalysts, the modes of transport are dictated by the ease of diffusion of the reactant molecules to the actives sites of the catalyst. The steps involved in carrying out a chemical reaction in the presence of a heterogeneous catalyst are outlined as follows[23]:

1. Diffusion of the reactant from the bulk stream to the gas-solid interface
2. Diffusion of the reactant through the interior pores of the catalyst
3. Adsorption of the reactant species to the chemical active site
4. Reaction of the adsorbed reactant with other adsorbents into products
5. Desorption of the products from the active site
6. Diffusion of the product from the active site through the interior pores of the catalyst
7. Diffusion of the product from the catalyst surface into the bulk stream

In steps 1, 2, 6, and 7, diffusion is the primary mode of transport that facilitates the delivery of the reactant to the catalyst, thus initiating the reaction. The pore size, therefore, is one of the major factors to consider for the design of a catalyst, as the pore size acts analogously as a “gatekeeper” for the reactant molecules before any chemical reaction can occur.

The differentiation between materials and their pore sizes can be delineated into two prevalent categories: microporous and mesoporous materials. Microporous materials have pore sizes on the span of less than 2 nm in diameter[24]. Some zeolites, such as ZSM-5, can be categorized as microporous materials. Industrial applications can take advantage of the unique and narrow pore size to force isomerization reactions, for example, of o- and m-xylene to the more valuable p-xylene isomer[25].

However, in the case of ethylene oligomerization, the activity of the catalyst improves drastically as the pore sizes increase, as shown in Figure 1.1. Lallemand et al synthesized Ni-MCM-22, a zeolite consisting of micropores, and observed rapid deactivation and negligible catalyst activity due to pore blocking and heavy oligomeric accumulation[18].

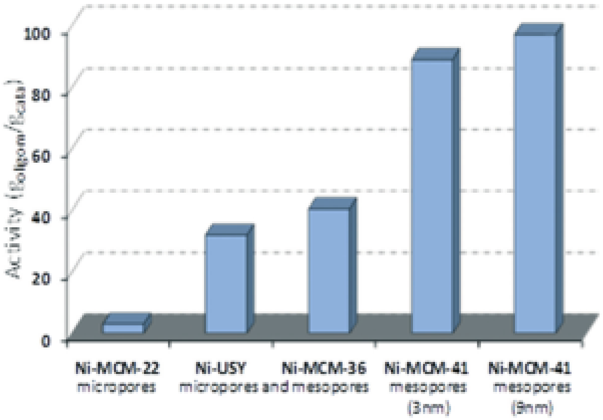

Figure 1.1. Activity as a function of pore size, observed through several microporous and mesoporous materials[2]

The catalyst activity significantly increased for Ni-USY and Ni-MCM-36 materials, both of which are composed of a combination of micropores and mesopores. The reasoning behind this was due to the presence of the mesopores[11,18]. Having mesopores in the framework of the catalyst allowed for allowed for the diffusion of larger oligomers. The authors theorized that the larger oligomers that accumulated in the microporous material could diffuse more efficiently through mesoporous material, thus allowing for higher overall catalyst activity and turnover. Accordingly, a purely mesoporous material, Ni-MCM-41, performed the best, having the highest activity[26]. It should be noted that all the materials were tested in a semi-batch reactor with a heptane solvent.

Effect of Acid Site Concentration

The role of the acid sites in nickel-based silica alumina catalysts for ethylene oligomerization has been a highly contested topic. While it is understood throughout the research that nickel sites are imperative for ethylene oligomerization, the role of the acid sites is still unclear. Several authors claim that the acid sites are necessary for ethylene oligomerization. The activity of the nickel exchanged silica-alumina was found to be proportional to the acid strength of the surface[10,27,28]. Lapidus et al. suggested that, for silica-alumina materials prepared by ionic exchange of Ni^{2+}, that catalytic activity is also dependent on the number of acid sites as a function of the aluminum content[29]. They found that the combinatorial effect of having both nickel and acid sites to be beneficial for facilitating ethylene oligomerization reactions. Another author, Sohn, conducted ethylene oligomerization with sulfated nickel catalysts and found a correlation between catalyst activity and acid strength with NiO and $NiSO_4$ supported on different substrates, such as TiO_2, ZrO_2, and the predominant SiO_2-Al_2O_3 seen in most of the literature[30–33]. Davydov and coworkers suggested that the role of the proton was used to facilitate a nickel reduction reaction of divalent nickel to monovalent nickel (Ni^{2+} to Ni^{+}). From the results, the authors suggested that the Ni^{+} species is the active form of the catalyst due to this reduction. Ng and Creaser also suggested that the Ni^{+} and H^{+} coupling played a major role in carrying out oligomerization. The variety of the interpretation of the results suggests that the role of the acid site is still an area of high interest for this process.

However, the influence of having too high of a concentration of acid sites on a support was found to be detrimental for the oligomerization reaction and the resulting catalyst activity. For Ni-based zeolites, a very high density of acid sites may be detrimental to the activity by promoting the formation of long chain oligomers, responsible for pore blocking and catalyst deactivation sources[11,18]. In the case of Ni-containing mesoporous materials, Hulea et al. found that the amount of oligomers strongly increased when the acidic site concentration decreased from 0.72 to 0.3 mmol/g[26]. In addition, a very low acidity is detrimental for the catalytic activity. A high acid/nickel ion site ratio results in rapid surface deactivation of Ni-containing materials due to acid-catalyzed reactions, which are responsible for the formation of strong adsorbed long-chain oligomers[18,26]. Consequently, only a carefully selected acid site density has a beneficial influence on the stability of Ni-based catalysts and implicitly on the oligomerization activity.

Effect of Nickel Loading

The catalytic activity of nickel was found to be critical for carrying out ethylene oligomerization reactions for several substrates. For nickel loadings of 5 wt.% and 10 wt.% for NiO/SiO_2-Al_2O_3 catalysts, the ethylene conversion was found to be at 30.4% and 23.8% respectively at 275ºC[29]. The same authors also tested Ni-Y catalysts at similar loadings and observed that the conversion followed a similar trend, with 39.2% conversion at 4.7 wt.% and 29.4% conversion at 8.1 wt.% nickel loading[34]. Nicolaides et al observed that the ethylene conversion increased steadily until a nickel loading of 1.5 wt.%, after which a sharp decrease in ethylene conversion was observed[35]. The research group concluded that this result was due to higher activity per nickel site at lower nickel loadings compared to higher nickel loadings, which resulted in lower activity at higher nickel loadings. This behavior was also consistent with the work we performed in Chapter 2, where we found that higher nickel loadings led to high ethylene conversion and high oligomerization activity, with heavy oligomers up to C16 observed in the liquid hydrocarbon product. In contrast, higher nickel loadings up to 5 wt.% had a marked lighter product and the conversion was lower, which is consistent with the results discussed earlier.

To better understand the rationale behind this behavior, Heveling et al. attributed the lower activity at higher nickel loadings to a selective growth reaction that was dictated by Schulz-Flory statistics[13]. The authors determined that the high nickel content positively affected the growth factor, α. Thus, high nickel loadings were better theorized to be better attributed to the formation of diesel-range olefins. However, despite this high activity, the overall deactivation and lower conversion of the catalyst was generally attributed to the growth of long oligomers that prevented further reaction. As such, having too high of a nickel loading, while theoretically useful for growing larger oligomers, is restricted by having too low of a conversion and catalyst activity.

The localized state of the nickel species on catalyst support was found to play a major role in the oligomerization of ethylene. To further investigate this, several studies were conducted using ionic-exchange and impregnation synthesis methods to introduce nickel onto a catalytic substrate. Several authors observed that ionic-exchanging the nickel to the substrate resulted in higher catalytic activity, with 2 wt.% being a local maximum. After 2 wt.% of nickel, the activity sharply drops off. The authors of this study rationalized that the reason behind this is due to the nickel ions more than 2 wt.% are most likely present on the material as solid NiO species[9]. NiO is inactive for ethylene oligomerization and are detrimental to the reaction due to partial blocking of the catalyst pores. This behavior was verified using temperature-programmed reduction (TPR), with the results indicating that, above a certain threshold, nickel only appears as NiO. The reasoning behind a preliminary ion exchange is due to the charge imbalances presented in the material because of framework aluminum. The presence of silicon in the framework (4^+ charge) neutralizes the charges of the surrounding oxygen atoms. If the aluminum (3^+ charge) replaces the silicon, an unbalanced negative charge is created in the silica-alumina framework. This negative charge can only be compensated with an accompanying cation, such as ionic forms of nickel and acidic protons. Therefore, the aluminum content is responsible for the number of cations the material can theoretically be ion-exchanged with.

Martinez et al. observed that the activity of Ni–Beta catalyst increased with an increase in the Ni loading up to 2.7 wt.%[3]. The activity plateaued at nickel loadings past 2.7 wt.% until a constant conversion of 85% was achieved at 5 wt%[3]. This result was corroborated by Heveling et al., as they observed that a Ni-exchanged silica–alumina with 0.73 wt.% nickel had noticeably higher conversion and catalyst activity compared to a catalyst with a higher nickel loading (3.84 wt.%)[12]. The major findings from these articles indicates that a lower weight percentage is effective for ethylene oligomerization. However, the difficulty with these catalytic systems is understanding the specific nature of the active nickel species on the catalyst. Though the authors did not specify the characteristics of the active nickel species, the results indicate that lower nickel loadings ion-exchanged with the material was far more active for ethylene oligomerization[2]. This behavior is portrayed in Figure 1.2.

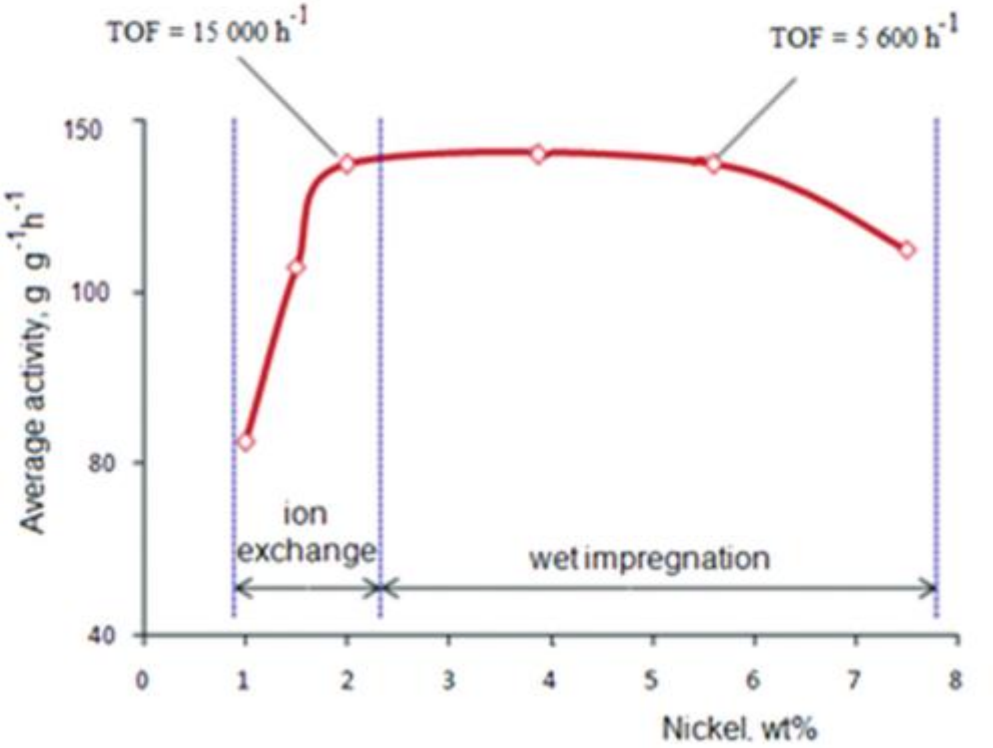

Figure 1.2. Oligomerization activity as a function of nickel loading[9]

Effect of Temperature

The temperature of the reaction plays a critical role in determining the overall stability of a catalyst as the reaction progresses. In turn, the stability of the catalyst will also impact the reaction pathways as well as the types of products generated. For ethylene oligomerization, the reaction temperature has been observed to have a multitude of effects on the reaction. For slurry semi-batch systems, researchers have observed that the reaction rate tends to decrease with an increase in the reaction temperature[2,26]. This behavior has been attributed to a decrease in ethylene solubility in the heptane solvent commonly used as the reaction medium for these systems. However, this decrease in the reaction rate was not due to the catalyst not being active for reaction, but more so attributed to the heat and mass transfer limitations of the reactor configuration. In contrast, these mass transfer limitations are removed in fixed bed reactors as there is no longer a solvent that the ethylene needs to be dissolved into.

To further investigate the implementation of nickel oligomerization catalysts in fixed bed reactors, several authors conducted low temperature studies over a fixed bed reactor over a variety of silica-alumina substrates. Ng and Creaser ran ethylene oligomerization with Ni-HY catalyst in the range of 50ºC to 70ºC in a packed bed reactor. They observed that butenes were the most favorable and selective product at lower reaction temperatures[10]. With a slight uptick in the reaction temperature to 70ºC, they observed that the selectivity towards hexenes increased, suggesting that a small increase in temperature was enough to further facilitate oligomerization of butene with ethylene to form hexenes. In conjunction to this behavior, the activity of the catalyst was also found to increase in this narrow range, from 6.04 mmol $g^{-1}h^{-1}$ to 13.19 mmol $g^{-1}h^{-1}$ at 50ºC and 70ºC, respectively. Heveling et al. also tested Ni-HY and Ni-SiO_2-Al_2O_3 catalysts over a range of temperatures spanning 40-360ºC[12,20]. They observed two distinct temperature regimes that had high conversion and activity near 120ºC and at temperatures above 300ºC. This volcano-type of curves for activity were also observed by Hulea et al with Ni-Y and Ni-MCM-41 in batch systems, with maxima for conversion and activity at 50ºC and 150ºC, respectively[11,26].

As such, some researchers performed further studies that examined the effect of higher reaction temperatures on ethylene oligomerization[12]. The product distribution for a number of systems were observed to shift with temperature. At low temperatures, the major oligomerization product observed for most systems was primarily butene. However, as the reaction temperature increased, the product distribution shifted to that of a Schulz-Flory distribution, with C4>C6>C8>C10>…> C(2n). The effect of high temperature indicated that there a bimodal or potentially polymodal distribution of activity. The rationale that the authors provided behind this behavior is that the nickel species at higher temperatures become far more unstable and tended to facilitate other secondary reactions. These reactions could include, especially in the presence of materials with acid sites, secondary oligomerization, cracking, alkylation, disproportionation, and isomerization reactions which would result in the formation of saturated and unsaturated hydrocarbons[2].

Effect of Pressure

Ethylene oligomerization is a chemical reaction that is strongly dependent on the reaction pressure. For chemical reactor systems involving semi-batch processing, the ethylene pressure plays a great role in determining its solubility in the solvent containing the catalyst. This, however, is an inherent diffusional limitation of these three-phase system, as the rate of ethylene oligomerization is strongly dependent on the selected solvent as well as the solubility of ethylene in that given solvent. As expected, the rate of reaction increased proportionally with ethylene pressure for semi-batch systems using Ni-MCM-41 catalysts[26]. The literature detailing the role of pressure in flow systems, however, is limited. The impact of pressure on Ni-HY catalysts was evaluated by Ng and Creaser. They observed that the activity of the catalyst increased with pressure, though the rationale behind this behavior was unclear. Reaction kinetics dictate that, for gas-phase reactions, the rate of reaction should increase as the partial pressure of the gaseous reactant (ethylene) increases. In addition, the number of ethylene molecules increases as the pressure increases, which would allow for higher degrees of collision with the catalytic active sites. As such, the reaction pressure for flow system is beneficial for both higher ethylene conversion and catalyst activity.

Supercritical Fluids

A fluid past its critical pressure and temperature exists as a superposition of a liquid and a gas, having properties representative to both phases[36]. Supercritical fluids (SCFs), such as supercritical (SC) CO_2, have been used as green solvents for extractions and mediums for reactions. SCFs are very useful mediums for reactions due to the drastic changes in many properties, such as high solubilities and molecular diffusivities, which are characteristic of liquids and gases, respectively[37]. The major benefit of SCFs is the ability to overcome potential interphase transport limitations that would normally play a greater role in a discrete gas or liquid phase[38].

The improved solubility observed in SCFs has important applications for chemical reactions. Compounds that are usually insoluble in a fluid at regular, ambient conditions can become readily soluble under supercritical conditions. For instance, low reactions rates are expected when reactants are only sparingly soluble in, for example, a gas, which readily occurs in homogeneous catalysis. In a SCF, however, accelerated reaction rates can be achieved due to the drastic improvement in reactant solubility. The enhanced solubility of supercritical fluids has been theorized to be effective for not only improving reaction rates, but also for potentially reducing carbon deposition on heterogeneous catalysts[39]. By suppressing the formation of these carbonaceous deposits, higher catalyst lifetimes can theoretically be achieved.

A noticeable decrease in carbon accumulation on heterogeneous catalysts has been observed in SCFs. The work of Tiltscher et al. highlighted the application of SCFs as a reaction medium for 1-hexene isomerization. Gas-phase 1-hexene isomerization was tested over macroporous α-Al_2O_3 catalysts and it was observed that the formation of cis/trans 2-hexene was not influenced by temperature at pressures below the critical point[40]. Catalyst deactivation was typically observed to occur due to the accumulation of nonvolatile hexene oligomers in the pores and active sites of the catalyst. The reaction mechanism, however, changes abruptly at pressures above the critical pressure with very little coke deposition occurring. This, in turn, can be used a tool to prevent catalyst deactivation[40]. Subramaniam and coworkers extended the work on 1-hexene isomerization by performing the same reaction over a microporous Pt/ γ-Al_2O_3[41]. They noted that the activity of the catalyst was lower at subcritical conditions, whereas the activity was sustained above the critical pressure. The authors attributed this behavior to the solvating properties of the dense SCFs that mitigated the formation and deposition of hexene oligomers in the catalyst pores[41,42]. Hassan et al. observed that, during naphthalene hydrogenation, the coke deposition was 38% lower at supercritical conditions on NiMo/Al_2O_3 catalysts[39]. The effect of pressure had a pronounced effect on the overall conversion of naphthalene, with nearly 100% conversion at 60 bar and at 300ºC. In addition, supercritical ethylene has been shown be a suitable solvent for the dissolution of naphthalene at low temperatures and higher pressures. Diepen and Scheffer analyzed the dissolution of naphthalene with supercritical ethylene at 12, 25, and 35ºC at pressures above 110 atm[43]. They observed that the temperature plays a tremendous role in the solubility of the naphthalene, and that lower temperatures at constant pressure could have higher impact on the solubility.

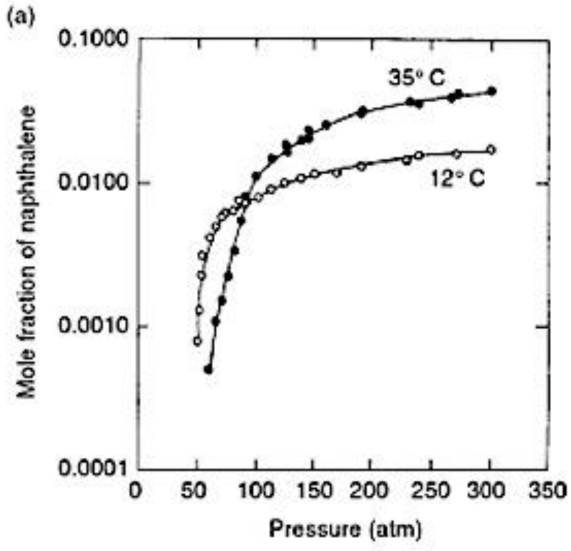

Figure 1.3. Solvation behavior of naphthalene in ethylene at supercritical conditions[36]

The application of supercritical reaction conditions for coke mitigation or for chemical reaction for ethylene oligomerization has not been previously studied. Figure 1.3 shows two isotherms for the solubility of naphthalene, considered as a precursor molecule for coke, in ethylene at sub- and supercritical conditions. The critical temperature and pressure of ethylene is at 9.5ºC and 50.4 bar, respectively. In Figure 1.3, the mole fraction of naphthalene dissolved increases sharply as the ethylene partial pressure increases above the critical point for both isotherms. This is an indication that, above the critical point of ethylene, the solubility of naphthalene was orders of magnitude higher than at subcritical conditions. There also appears to be a strong dependence on the temperature, as SC ethylene at 12°C had drastically higher naphthalene than compared to SC ethylene at 35°C.

Direction of the Thesis

The overall objective of the thesis is to produce liquid hydrocarbons via catalytic oligomerization reactions of ethylene over heterogeneous catalysts. The effects of pertinent processing parameters, such as temperature, pressure, space velocity, and nickel concentration, are controlled and detailed throughout the work. The role of supercritical ethylene for ethylene oligomerization was also evaluated for its potential as both a solvent and a chemical reactant. Ethylene oligomerization over heterogeneous catalysts is an area of research still in its infancy, and this work aims to provide key insights on this burgeoning area of research.

Objective 1: Ethylene oligomerization over Ni-Hβ heterogeneous catalysts

The first research objective was to evaluate the role of Ni-Hβ catalysts on ethylene oligomerization over a range of operating conditions. The pertinent parameters we tested were the temperature, pressure, weight hourly space velocity (WHSV) on the catalyst support. The parameterized study focused primarily on the role of these process variable on the conversion, product distribution, and product yields.

Objective 2: Liquid hydrocarbon production via ethylene oligomerization over Ni-Hβ

The second research objective of the thesis focused primarily on the production of liquid hydrocarbons over Ni-Hβ in a laboratory scale reactor. We conducted laboratory experiments with Ni-Hβ and evaluated the role of nickel loading, pressure, temperature, and WHSV on the yields of liquid hydrocarbon and coke, ethylene conversion, and selectivity towards the suite of oligomeric products.

Objective 3: Oligomerization of supercritical ethylene over silica-alumina catalysts

The third objective is focused on the influence of supercritical conditions for catalytic ethylene oligomerization over silica-alumina catalysts, namely Ni-Hβ and Ni-Al-SBA-15. This work looked primarily at the role of supercritical ethylene as a solvent as well as a chemical reactant. The effects of subcritical and supercritical conditions were evaluated and discussed in terms of their effects on the overall ethylene conversion and product selectivity. The impact of these conditions on reaction pathways is also discussed.

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Chapter 2: Ethylene Oligomerization over Ni-Hβ Heterogeneous Catalysts

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Abstract

We report results for the oligomerization of ethylene over Ni-Hβ in a packed bed reactor. We performed a parameterized study over temperature (30ºC-190ºC), pressure (8.5-25.6 bar), and weighted hourly space velocity (2.0-5.5 hr^{-1}). The ethylene conversion increased with reaction pressure due to the slower velocities at higher pressures. Overall, higher temperatures led to the formation of larger oligomers and coke, but its effect on the conversion was small. The space velocity played an important role on ethylene conversion and product selectivity, with higher conversions observed at lower space velocities and higher selectivities to butene at higher space velocities. We verified the activity of the Ni-Hβ catalyst activity over 78 hours-on-stream at 19.0 bar partial pressure of ethylene, 120ºC, and 3.1 hr^{-1} WHSV. Catalyst deactivation takes place only during the startup period largely due to coke formation. However, negligible coke formation occurred after 8 hours time-on-stream, as the conversion remained steady at 47% for the duration of the experiment.

Introduction

Ethylene is the simplest alkene observed in nature. This simple organic chemical is also a vital reactant for several chemical reactions directed towards the formation of valuable products. Most of the ethylene available today is produced by cracking heavier hydrocarbons extracted from crude oil in the petroleum industry[1,2]. Renewable routes for ethylene production have been theorized. Bioethanol derived from renewable resources, such as biomass, can be a starting point for ethylene production, through a dehydration reaction to produce ethylene and water, with oligomerization of the produced ethylene to form the desired olefins.

Ethylene oligomerization forms higher-order olefins that can be further upgraded to produce a myriad of commercial products, such as acids, detergents, plasticizers, oil additives, and transportation fuels[1,3,4]. This process has been performed commercially, typically in liquid-phase with a homogeneous catalyst in an organic solvent. Organometallic catalysts consisting of a heteroatom (Ni, Co, Cr, Fe) adjoined with alkylated ligands have demonstrated high activity and high selectivity towards targeted olefins[3]. Despite these advantages, the general drawbacks associated with using homogeneous catalysts include low catalyst reusability, high sensitivity to impurities in the reactant stream, as well as the poor separation of the catalysts from the product stream[1,5]. In addition, homogeneous-phase reactions suffer from high solvent usage and are not considered environmentally-friendly processes.

Due to the challenges and environmental drawbacks associated with using homogeneous catalysts, expanding research into developing heterogeneous processes for ethylene oligomerization has been of considerable academic and industrial interest. Much of the work pertaining to heterogeneous ethylene oligomerization has employed three-phase slurry reactors that operate in semi-batch mode[4–9]. In this mode, the solid catalyst is suspended in a solvent, such as heptane, contained in a sealed vessel, and ethylene pressurizes the reactor. The pressure increases ethylene solubility in the solvent to allow for increased catalyst activity. Other types of reactor configurations, such as a packed bed reactor, can be used to promote gas-solid interactions without the need for organic solvents. In the latter mode, product separation is much more convenient as the phases of the catalyst and the products are dissimilar in nature. In this work, we carried out oligomerization of ethylene in a packed bed reactor.

The activity of metal-loaded inorganic substrates consisting of silica-alumina has been studied previously for ethylene oligomerization, with nickel metal on silica-alumina frameworks showing the most promise. The silica-alumina substrates must be doped with active metals to promote catalytic activity for ethylene oligomerization. Several major parameters of these solid materials, namely the pore size and the silicon to aluminum ratio, had profound effects on the extent of the reaction[2,6,8,10–12]. The pore size was found to have a proportional relationship with catalyst activity, with higher pore sizes resulting in higher oligomerization activity. When microporous materials, such as Ni-MCM-22 and nickel-loaded zeolites, were used, only small amounts of oligomers were detected[6,10]. Mesoporous materials, such as Ni-MCM-41, demonstrated markedly high catalyst activity[8,13,14]. Catalyst deactivation was observed to occur at a faster rate with microporous materials due to the narrower pore sizes sterically hindering the diffusion of the oligomeric products. It was theorized that the large mesopores of the material more readily facilitated the diffusion of heavier oligomeric products, thereby preventing product accumulation and allowing prolonged oligomerization activity. In addition, the silicon to aluminum ratio was found to play a significant role in the overall activity of the catalyst. The presence of silicon in the framework (4^+ charge) neutralizes the charges of the surrounding oxygen atoms. If the aluminum (3^+ charge) replaces the silicon, an unbalanced negative charge is created in the silica-alumina framework. This negative charge can only be compensated with an accompanying cation, such as ionic forms of nickel and acidic protons. Martinez and coworkers observed that the relationship between acidic protons and nickel has a profound effect not only on the textural properties of the material, but also on the resulting oligomerization products and activity of the catalyst. For Ni-Hβ catalysts, an increase in the nickel loading resulted in a decrease of the available surface area for reaction along with a decrease in the concentration of Brønsted acid sites. Having both nickel and acidic protons throughout the catalyst, however, was found to be critical, as nickel was theorized to be solely responsible for initial activation of ethylene and primary oligomerization whereas acidic protons were necessary for carrying out secondary isomerization, oligomerization, and cracking reactions[3].

The current literature detailing the effects of process parameters for ethylene oligomerization over Ni-Hβ catalyst is limited to one published study, and further insight onto the performance of this catalyst would be beneficial for understanding its potential. In this work, the roles of several process parameters, namely pressure, temperature, and weighted hourly space velocity (WHSV) will be discussed using Ni-Hβ in a continuous packed bed reactor. To the best of our knowledge, this is the first systematic study of the effect of these operating parameters with Ni-Hβ. In addition, the activity of the catalyst over three days on stream is presented to evaluate its deactivation.

Experimental Methods

Catalyst Synthesis

We purchased the commercial beta zeolite from Zeolyst (CP814E, SiO_2/Al_2O_3=25, ammonium form) and used it as is without prior treatment. To introduce nickel on the support, we slowly dripped a 0.34M solution of nickel nitrate (Sigma Aldrich) onto the zeolite powder for over 5 hours at room temperature to achieve a liquid-to-solid ratio of 5 cm^3/g. This slow exchange resulted in a dark grey slurry labeled as Ni-NH_4-β. After five hours of mixing, we washed the resulting dark grey slurry and vacuum filtered it to obtain a grey paste. We then dried the paste overnight at 110ºC for 12 hours, which resulted in a pale green powder. Immediately after drying, we calcined the powder at 550ºC for 5 hours in an air oven to remove ammonia from any residual ammonium sites, which produced a light grey powder labeled as the Ni-Hβ catalyst. We then crushed the catalyst using a mortar and pestle and used it as is without any further treatment.

Catalyst Characterization

To determine the nickel loading in the material, we used ICP-OES (inductively coupled plasma-optical emission spectroscopy) using EPA protocol 200.7, where we digested the solid material with nitric acid and hydrochloric acid. However, this protocol is unable to accurately measure the silicon and aluminum content, and we assume that the supplier provided SiO_2/Al_2O_3 ratio of 25 is correct.

To determine the nanocrystalline structure of the catalyst, we imaged the materials using transmission electron microscopy (TEM). We sonicated the catalyst powder in ethanol to create a fine dispersion, and then dripped the solution onto a 250 μm copper grid. We then loaded the copper grid into the microscope using a single-tilt holder into the sample compartment of a Tecnai G2 F20 Supertwin TEM. We collected the diffraction profiles of the materials using a Bruker D8 Discover with a high-power rotating Cu anode x-ray source. We also collected scanning electron microscopy (SEM) images with a FEI Sirion XL30 microscope after sputter coating the samples with silver paint to mitigate distortion and image hot spots due to electron charging.

Catalytic Reactor

Ethylene oligomerization experiments were performed in a continuous flow fixed-bed reactor. The reactor was constructed with 1” OD Schedule 80 SS316 tubing. Prior to each experiment, the reactor was loaded with approximately 8 grams of fresh catalyst in-between two beds of quartz wool. The reactor was pressure-tested and leak checked prior to every experiment. After pressure testing, the catalyst was pretreated at 300ºC in N_2 at 200 mL/min for 16 hours under atmospheric pressure. This pretreatment step was intended to purge any air or moisture from the system, as moisture has been previously observed to severely hinder the catalyst performance. A downstream GC-FID-TCD Shimadzu GC-2014 with a HP-PLOT-Q column (0.53mm x 30m x 40µm) was used to monitor the gas composition online from the reactor prior to testing. After pretreatment, the temperature of the reactor was brought down to the desired reaction temperature and nitrogen gas was used to pressurize the system. The pressure was controlled and maintained by using an Equilibar dome-loaded backpressure regulator. After stabilizing the set point temperature and pressures, the ethylene flow (350.94 mL/min) started, mixing along with the nitrogen (314.28 mL/min) to initiate the reactions in the catalytic bed. A heated transfer line downstream of the reactor was kept at 120ºC to prevent product condensation and product gases were measured periodically through on-line GC/TCD. The coke yield was determined gravimetrically by measuring the weight of the reactor contents before and after the reaction. Calibration curves for ethylene, propylene, and 1-butene were constructed using gas standards, whereas calibration curves for the higher olefins (1-hexene, 1-octene, 1-decene, 1-dodecene) were made by liquid injection of solutions of varying concentration. Mass balances excluding the unreacted ethylene for all reported experiments were closed above 90%. The reproducibility of the reactor was verified by replicating three experiments at reaction conditions, T: 120ºC, WHSV: 3.1

hr^{-}1, P_{C2H4}: 19 bar. Error bars are reported for subsequent experiments using these standard deviations.

Selectivity, S_i, and the conversion, X, have been defined as follows:

$$S_i\ (wt.\%) = \frac{mass\ of\ compound\ i}{mass\ of\ all\ measured\ compounds} \times 100$$

$$X\ (mol.\%\ of\ inlet\ ethylene) = \frac{molar\ flow\ rate\ of\ ethylene\ consumed}{molar\ feed\ rate\ of\ ethylene} \times 100$$

$$Coke\ yield = \frac{final\ mass\ of\ catalyst\ bed - initial\ mass\ of\ catalyst\ bed}{mass\ feed\ rate\ of\ ethylene * time} \times\ 100$$

In reporting the selectivities, we group the hydrocarbons by the number of carbon atoms in the molecule (C4, C5, C6, etc.), which were determined based on their retention time from the calibrations conducted previously.

Results and Discussion

Catalyst Characterization

The X-ray diffractograms for ammonium-β and Ni-Hβ is shown in Figure 2.1. The large peak at 22º 2θ is characteristic of silica-containing species and is identical for both forms of the catalyst. Three distinct diffraction peaks, as noted by Martinez and coworkers, at 37.2º, 43.3º, and 62.9º 2θ represent the (111), (200), and (220) plane Miller indices of face-centered cubic NiO crystallites, respectively, and appear only on the Ni-Hβ diffractogram[3].

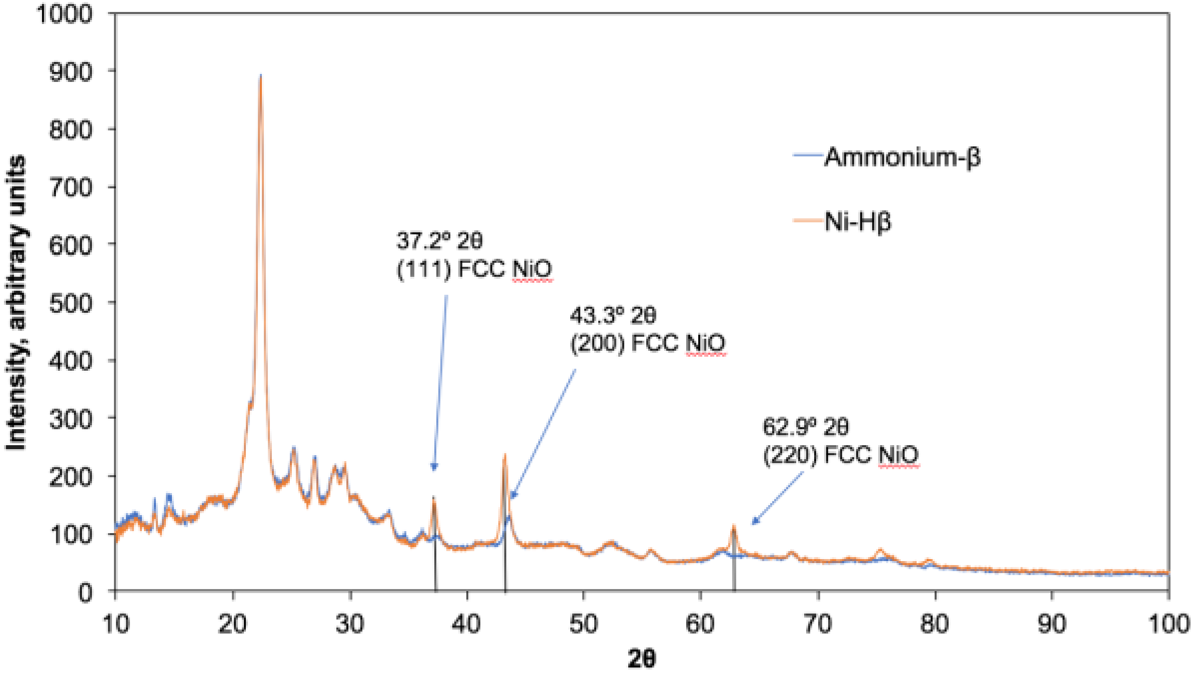

Figure 2.1. Diffraction profile of the parent β zeolite before and after nickel impregnation

The presence of these crystallites is apparent in the transmission electron microscopy image in Figure 2.2. The darker spots on the TEM image represent the NiO clusters on the external surface of the material. The loading of nickel was found to influence their appearance in x-ray diffraction for Ni-Hβ materials. It has been reported that NiO clusters appear at nickel loadings above 1.8-3.8 wt.%[3]. The nickel content of the material used in the present work was measured to be 3.4 wt.% through ICP-OES, and is near the point where NiO clusters are expected to be observed, in accordance to the literature. Exchange sites that were occupied by the

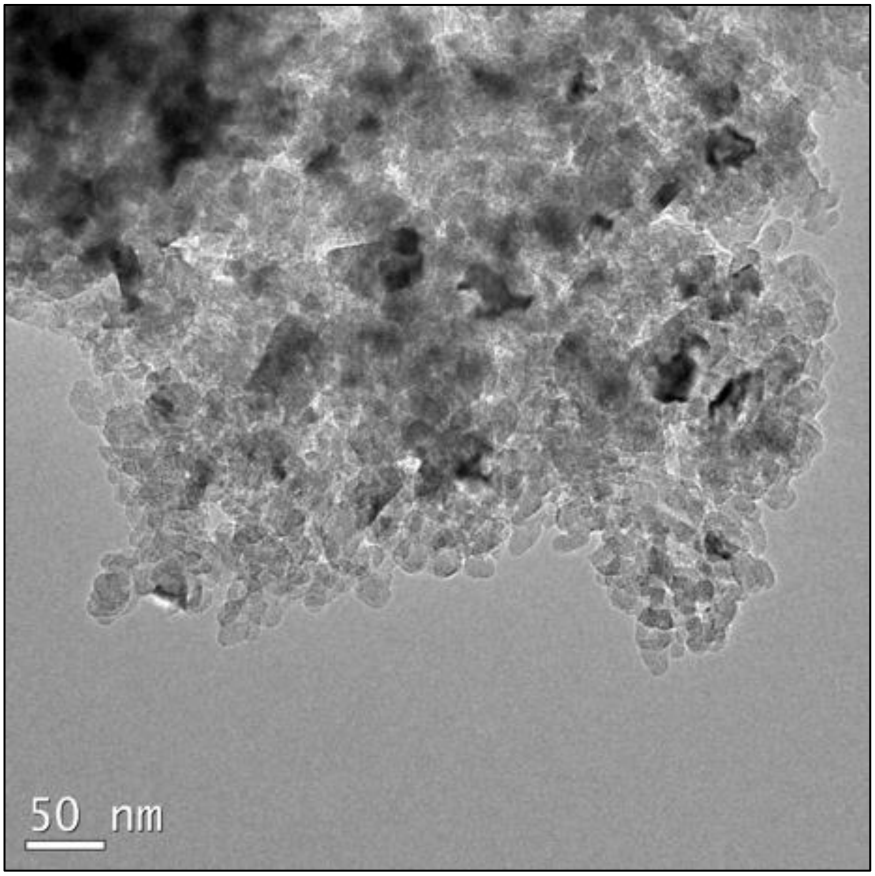

Figure 2.2. TEM Image of Ni-Hβ

ammonium in the parent material can either be occupied with divalent nickel ions or residual protons resulting from the removal of ammonia from unchanged ammonium. It is possible that nickel has saturated the exchange positions inside the pores, leading to additional nickel deposited on the exterior[3].

We were unable to conduct nitrogen physisorption experiments for analysis of the Ni-Hβ catalyst. However, as noted by Martinez et al., the textural and physical properties of the parent material do not appear to change drastically upon impregnation of the nickel metal[3]. In addition, the authors observed that these same textural properties, namely the surface area and the pore diameter/volume, were largely unaffected throughout the course of the reaction. This result indicates that the catalyst has robust material properties and can maintain its structural and textural form during process operation[3]. Images of the catalyst were also collected at the microscale using scanning electron microscopy, as shown in Figure 2.3. The granules of Ni-Hβ appear to be uniform throughout the image, suggesting that the catalyst is unaffected by the incorporation of nickel.

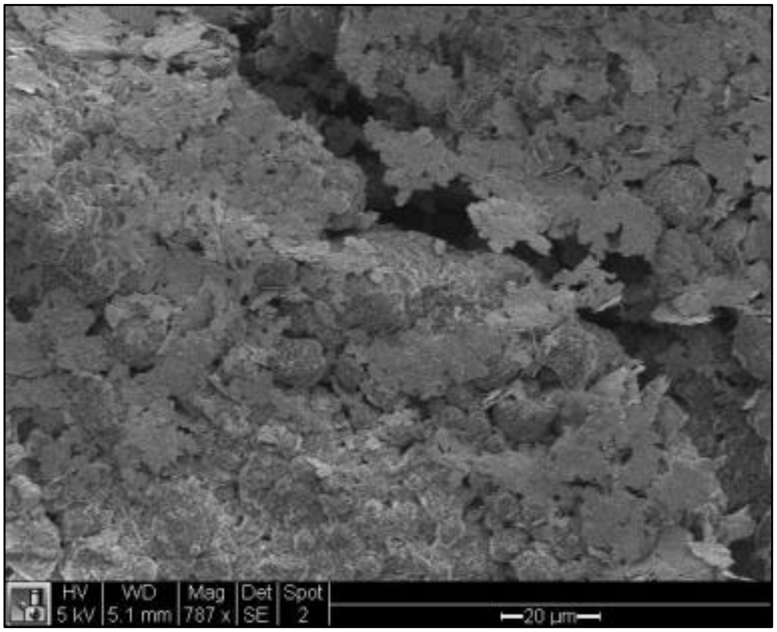

Figure 2.3. Scanning electron microscopy image of Ni-Hβ

Parameterization Experiments

We conducted a systematic evaluation of the effect of process conditions with Ni-Hβ in the catalytic reactor. We evaluated the effects of pressure, temperature, and weight hourly space velocity. The base case condition was as follows: partial pressure of ethylene: 19.0 bar, T: 120ºC, WHSV: 3.1 hr^{-1}. To isolate the effect of each variable, we changed one variable, while keeping the others constant. The ethylene to nitrogen volumetric flow ratio was held constant at 1.12 in all experiments.

Effect of Ethylene Partial Pressure

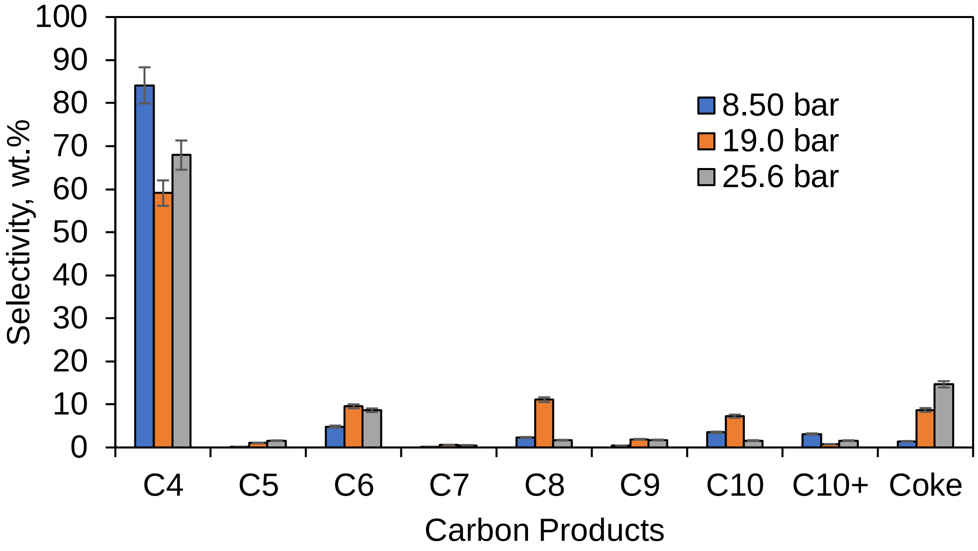

Figure 2.4. Selectivities of carbon products from ethylene oligomerization as a function of ethylene partial pressure. Reaction conditions, T: 120ºC, WHSV: 3.1 hr^{-1}

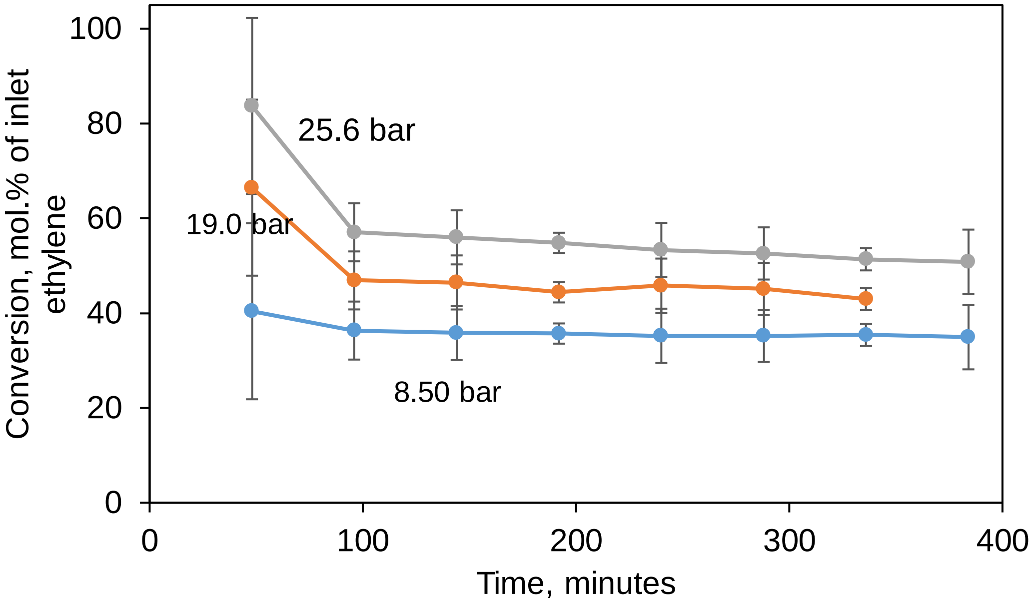

Figure 2.5. Ethylene conversion as a function of time on stream, at several partial pressures of ethylene. Reaction conditions, T: 120ºC, WHSV: 3.1 hr^{-1}

The effect of ethylene partial pressure on product selectivity is shown in Figure 2.4. At 8.5 bar, the primary product produced was butene at 84.1 wt.% selectivity. We observed high selectivities of octene (11.0 wt.%) and decene (7.3 wt.%) oligomers in the range of pressures tested. At 25.6 bar, the selectivity of the coke products increases, resulting in an overall decrease of the selectivity of the other pertinent oligomeric products. The coke selectivity appears to increase linearly with ethylene partial pressure, increasing from 1.4 wt.% at 8.50 bar to 8.7 wt.% at 19.0 bar, and to 14.7 wt.% at 25.6 bar. The conversion profiles, shown in Figure 2.5, show that the steady state ethylene conversion increases with the ethylene partial pressure.

All the reactions were conducted at the solid-gas interface in a packed bed reactor. This configuration contrasts with most of the previously reported literature, where ethylene oligomerization occurred in the liquid-phase by pressurizing the gas into a solvent, such as heptane, which held the solid catalyst. In this three-phase system, ethylene pressure was necessary to solubilize ethylene in the solvent to allow for increased contact with the entrained solid catalyst. Accordingly, the oligomerization rate increased proportionally with pressure in these slurry-bed studies. In packed bed reactors, some studies involving Ni-HY and nickel on silica-alumina substrates have observed an overall increase in ethylene conversion as a function of pressure[12,15,16]. The results presented in this section are consistent with that of the previous literature, with an increase in conversion with the reaction pressure. This result is consistent with other studies with Ni-HY, where butenes were observed to be the primary product at lower pressures[12]. A possible explanation of this phenomenon may be due to the increase of the velocity of the ethylene reactant gas at lower pressures, leading to lower residence times.

In the range of conditions tested, the highest steady-state conversion was achieved at an ethylene partial pressure of 25.6 bar. The increase in conversion may be attributed to a large amount of ethylene flowing through the reactor at high pressure and low velocity. Due to the lower velocity of the stream and the large availability of ethylene molecules, ethylene can more readily adsorb to the Ni and acidic active sites, allowing for an overall higher rate of reaction and conversion. The slower velocity at higher pressure results in a higher rate of adsorption and reaction due to the increased contact time with the active sites in the catalyst bed. This may also explain the high amount of catalyst coke at 25.6 bar. Higher ordered olefins past the dimer and trimer product could be produced due to the increased contact time, resulting in bulkier oligomers that would be unable to fully desorb from the catalyst bed.

Effect of Temperature

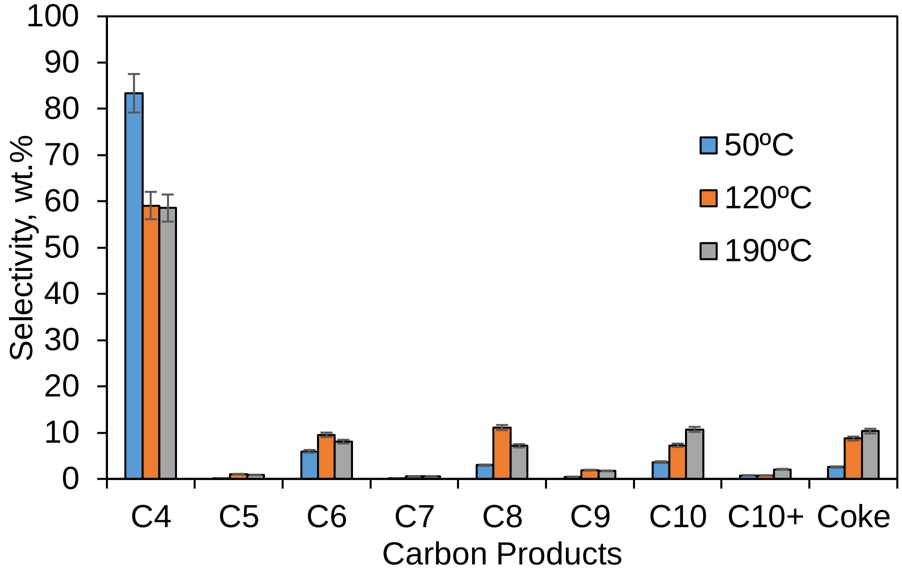

Figure 2.6. Selectivities of carbon products from ethylene oligomerization as a function of temperature. Reaction conditions, P_{C2H4}: 19.0 bar, WHSV: 3.1 hr-1

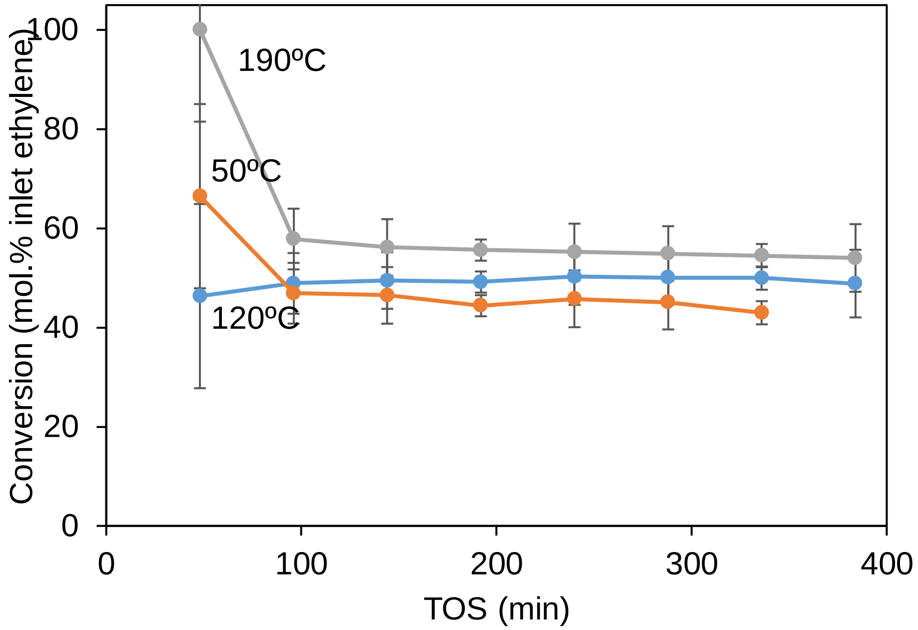

Figure 2.7. Ethylene conversion as a function of time of stream at several temperatures. Reaction conditions, P_{C2H4}: 19.0 bar, WHSV: 3.1 hr^{-1}

We verified the effect of the reaction temperature on ethylene oligomerization over Ni-Hβ by varying the temperature from 50ºC to 190ºC, with all other conditions held constant. As shown in Figure 2.6, butenes were the major product formed at 50ºC, with over 83% selectivity to dimers and roughly 6% selectivity towards hexenes, which comprise the trimer product. As the temperature increased to 120ºC, the product distribution varied drastically, with increased selectivities towards higher oligomeric products, such as hexenes, octenes, and decenes. Interestingly, the formation of odd-numbered carbon products did not noticeably increase with an increase in temperature in the range of conditions tested. The coke selectivity increased with the increase in the reaction temperature. Conversion generally increases as temperature increases due to higher rates of reaction. However, the effect of temperature on ethylene conversion with Ni-Hβ was small, without increase in conversion in the range 50ºC to 190ºC, as shown in Figure 2.7. It is possible that this unusual behavior is a consequence of potential hot spots (non-uniform temperature) in the reactor, as the reactor and catalyst bed in this work are significantly larger than in other studies. Larger reactors have heat transfer limitation that may lead to non-uniform temperatures in the bed[17]. This, in turn, led to large standard deviations and overlapping of the conversion curves.

The selectivity results are in accordance with previously published literature. At near room temperature, ethylene oligomerization has been previously observed to favor the formation of primarily butenes.[4,9,18,19] In prior studies with other nickel/silica-alumina species conducted in the range of 120ºC to 300ºC, an increase in the reaction temperature has generally been connected to the increase in the rate of acid-catalyzed reactions, namely secondary-cracking and isomerization reactions, which are responsible for the formation of both even and odd carbon products. Increasing the reaction temperature led to further oligomerization and cracking reactions that were responsible for the formation of the oligomers and coke, respectively. The upward trend in the selectivity of coke with reaction temperature could be a direct result of the interaction of the oligomers with the acid sites of the catalyst, leading to the formation of larger oligomers that were unable to diffuse out of the catalyst.

Effect of WHSV

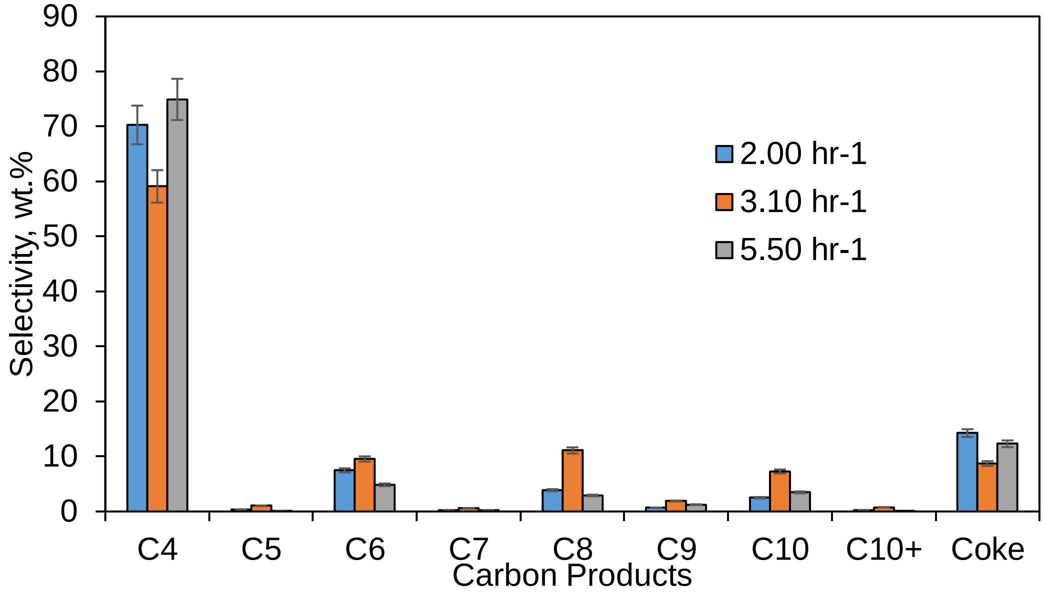

Figure 2.8. Selectivities of carbon products from ethylene oligomerization as a function of WHSV. Reaction conditions, P_{C2H4}: 19.0 bar, T: 120ºC

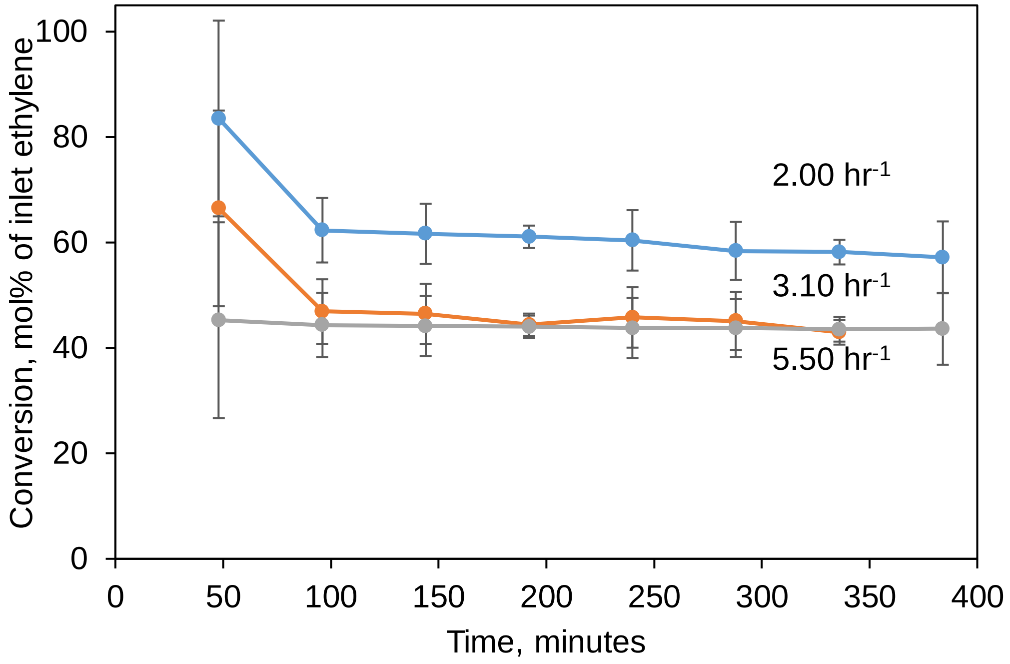

Figure 2.9. Ethylene conversion as a function of time on stream, for several values of WHSV. Reaction conditions, P_{C2H4}: 19.0 bar, T: 120ºC

We verified the effect of the weight hourly space velocity (hr^{-1}) by increasing the ethylene flow rate over a constant mass of Ni-Hβ catalyst in the bed. The selectivity and conversion data are shown in Figure 2.8 and Figure 2.9, respectively. In Figure 2.9, as the WHSV increased from 2.0 hr^{-1} to 5.5 hr^{-1}, the steady-state ethylene conversion decreased from 60% to 43%. An increase in the ethylene mass flow rate lowers the amount of time for ethylene to interact with active sites on the catalyst. At lower space velocities, the ethylene has more time to adsorb on the catalyst surface and can more readily undergo various types of surface reactions, such as oligomerization, isomerization, and even cracking reactions. As shown in Figure 2.8, at the highest space velocity, the most prevalent products formed were mostly the dimer product at 73 wt.% selectivity. Decreasing the space velocity led to the formation of heavier oligomers. This behavior was not entirely consistent, however, at 2.00 hr^{-1} as there was a high selectivity towards butenes (70 wt.%) and towards coke (14.2 wt.%). It is likely that heavier oligomers in the form of catalyst coke were formed due to the high amount of time of interaction at the lower space velocities. As the space velocity increases further, the lighter products can desorb faster before they can react further to form these long oligomers. As a result, the "coke" that is measured would be higher molecular weight molecules as these coke products are likely the result of large, bulky oligomers that were unable to thoroughly desorb from the bed. Interestingly, the conversion profiles at 3.1 hr^{-1} and 5.5 hr^{-1} are largely similar, yet the product distribution between the two experiments are markedly different. At 3.1 hr^{-1}, a myriad of oligomers is produced, ranging from butenes (59 wt.%) to decenes (7.3 wt.%), with coke accounting for 8.7 wt.% of the product distribution. However, at 5.5 hr^{-1}, butenes are the major product, with a selectivity of 70.2 wt.% and coke at 12.3 wt.%. At lower space velocities, the ethylene has much more time to interact with the surface for reaction.

Long Term Experiment

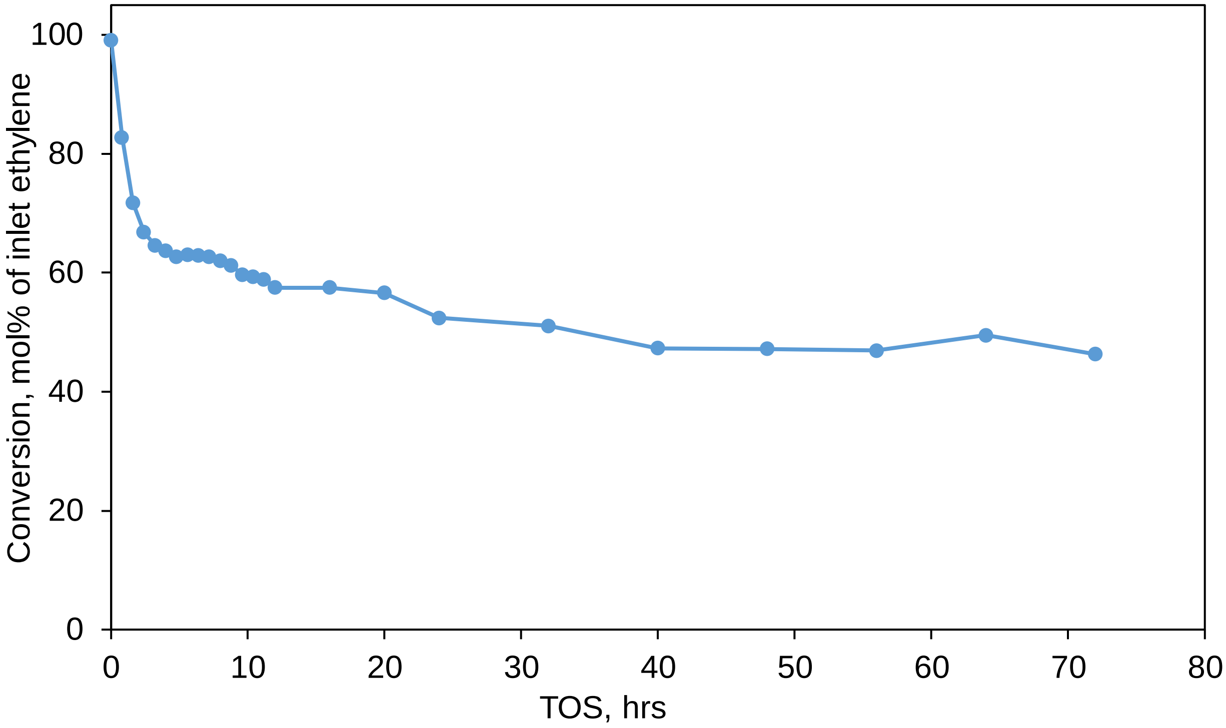

Figure 2.10. Conversion profile for Ni-Hβ over 3 days on stream. Reaction conditions, P_{C2H4}: 19.0 bar, T: 120ºC, WHSV: 3.1 hr^{-1}

To verify the deactivation of Ni-Hβ, we tested the catalyst continuously over the span of 78 hours on stream in the reactor. The conditions used were: 19.0 bar partial pressure of ethylene, 120ºC, and 3.1 hr^{-1} WHSV. The conversion profile is shown in Figure 2.10. After the typically observed drop in activity over the course of the initial 3 hours, the ethylene conversion did not diminish drastically after 78 hours on stream. The overall conversion approached a steady state plateau of approximately 50%. By the conclusion of the experiment, surprisingly, the amount of coke collected (8 grams) was approximately the same as that collected in the short-term experiment performed for 6 hrs. This result indicates that there is an initial buildup of coke at the beginning of the process that leads to a drop in the ethylene conversion. After this initial drop in activity, there is no additional coke accumulation throughout the course of the process, which is consistent with the steadiness of the conversion during this period.

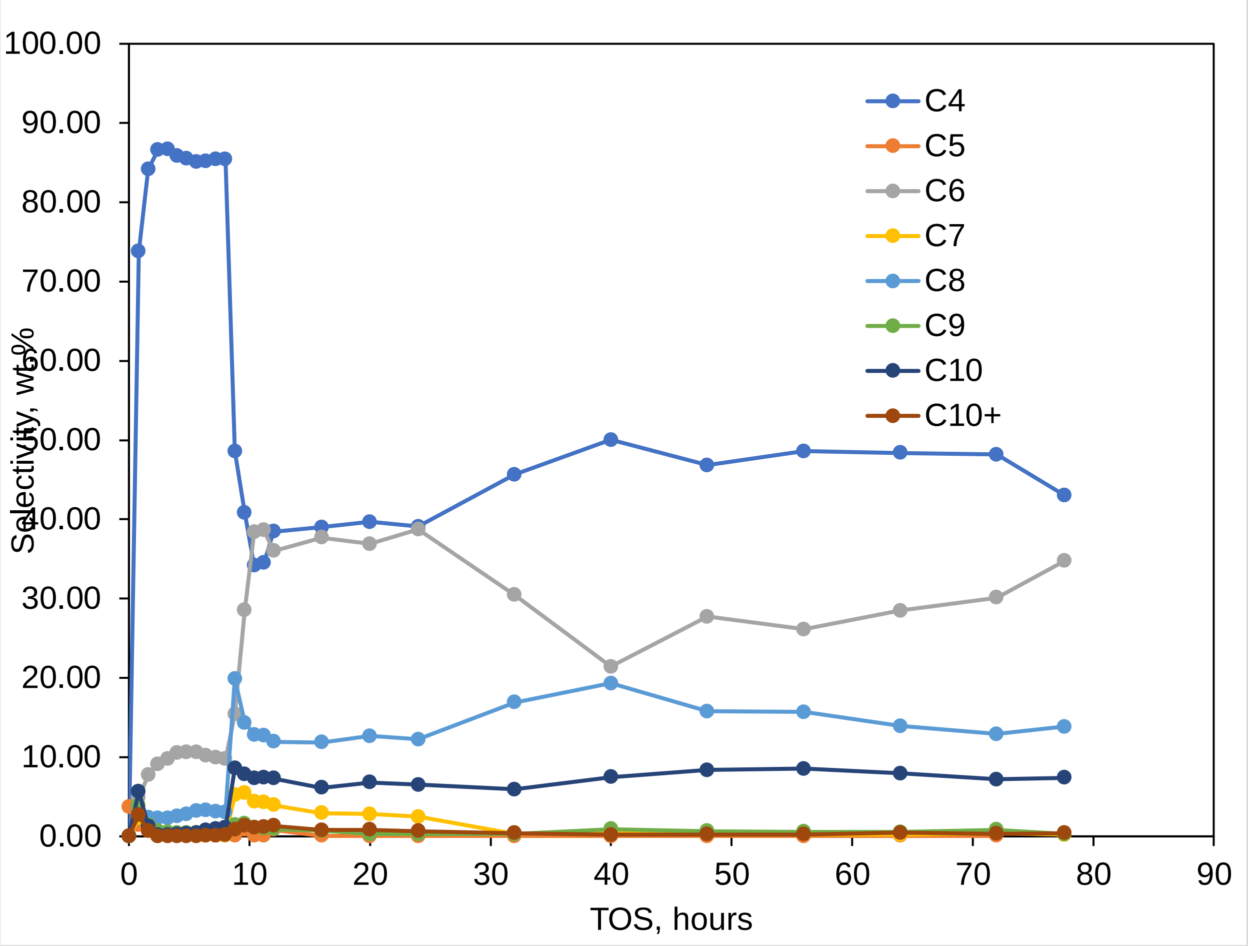

Figure 2.11. Selectivity profile of detected oligomeric products over 78 hours on stream. Reaction conditions, P_{C2H4}: 19.0 bar, T: 120ºC, WHSV: 3.1 hr^{-1}

The product selectivity profile of the carbon products is shown in Figure 2.11. The selectivity changes drastically throughout the 78 hours time on stream. The initial product distribution is similar to what we obtained previously for the shorter 6 hour experiments, with high selectivity to butenes and lower selectivities of the other typical even numbered olefins. However, after 8 hours, there was a sharp drop off in butene selectivity, and a large increase in selectivity towards hexenes, octenes, and decenes. The resulting product distribution remained approximately the same for the duration of the experiment and it nearly resembled a Schulz-Flory distribution, with C4 > C6 > C8 > C10 > C10+. After 8 hrs, the selectivity shifts towards the high molecular weight compounds.

To the best of our knowledge, long term experiments with Ni-Hβ have not been previously reported in the literature. We hypothesize that the ethylene adsorbed on the catalyst is more readily accessible to be dimerized into butenes during the startup of the process. Once the surface of the catalyst is covered with butenes, the adsorbed butenes further react to produce higher molecular weight products. In addition, adsorbed butene compounds can also react with one another, resulting in the formation in octenes.

Summary of the Work

We observed that Ni-Hβ is a viable catalyst for ethylene oligomerization in a single-pass packed bed reactor. To the best of our knowledge, this is the first report on the variation of pressure, temperature, and weight hourly space velocity on ethylene conversion and product selectivity for Ni-Hβ. The results from this work corroborated prior literature on pressure effects on ethylene oligomerization with other silica-alumina supports. In addition, this contribution adds important findings on the deactivation profile of Ni-Hβ over 78 hours on stream. The amount of coke observed after the 78 hour experiment was the same amount as the coke measured after a 6 hour experiment. As a result, the initial deactivation of the catalyst may be attributed to oligomeric coke building up on the catalyst during an initial timeframe, after which no further coke buildup occurs throughout the course of the reaction. Therefore, there is potential that this catalyst may be able to maintain a steady 47% ethylene conversion past 78 hours. Interestingly, we also learned that the product selectivity changes drastically after 8 hours on stream, with a major shift from a dominantly high butene selectivity towards a distribution consisting more of hexenes, octenes, and decenes. The findings from this work may be applicable towards the production of liquid hydrocarbon products.

Conclusion

This work expanded on the limited, published work on Ni-Hβ catalysts for ethylene oligomerization under a range of operating parameters, such as pressure, temperature, and space velocity. As the reaction pressure increased, the overall ethylene conversion increased steadily. We attributed this behavior to the decreased velocity at higher pressures, resulting in longer residence times at the active sites of the catalyst and availability of ethylene molecules. The effect of temperature on ethylene conversion was small, and we hypothesize the presence of hot spots in the reactor because of the larger diameter tubing and larger bed sizing. The product distribution, however, was affected by temperature, with more coking at higher temperatures. We also observed that the space velocity impacted ethylene conversion and product selectivity, with higher conversions at lower space velocities and higher selectivities to butene at higher space velocities. In addition, lower space velocities resulted in high conversion and high selectivity towards coke. To test the deactivation of the catalyst, a long-term study was conducted over a period of 72 hours-on-stream (19.0 bar partial pressure of ethylene, 120ºC, and 3.1 hr^{-1} WHSV). We found that catalyst coking from ethylene oligomerization occurred primarily during the startup of the process, with negligible coke formation occurring afterwards as the ethylene conversion was maintained at 47% throughout the duration of the study. The results of this work are relevant to the burgeoning industrial applications for ethylene oligomerization, where catalyst turnover can be a major expense, especially for companies entering the renewable energy sector.

Acknowledgements

The authors are appreciative of the funding provided by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30407 from the USDA National Institute of Food and Agriculture and the Weyerhaeuser Endowment in Paper Science and Engineering. We gratefully acknowledge the TEM imaging provided by Noah Ferguson. Part of this work was conducted at the Molecular Analysis Facility, a National Nanotechnology Coordinated Infrastructure site at the University of Washington which is supported in part by the National Science Foundation (grant ECC-1542101), the University of Washington, the Molecular Engineering & Sciences Institute, the Clean Energy Institute, and the National Institutes of Health.

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Chapter 3: Liquid hydrocarbon production via ethylene oligomerization over Ni-Hβ

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Abstract

We carried out oligomerization of ethylene using nickel supported on an acidic zeolite β (Ni-Hβ) in a laboratory-scale packed bed reactor for the synthesis of liquid hydrocarbons in measurable, milliliter-scale quantities. We evaluated the effect of several process variables (temperature, pressure, weighted hourly space velocity, and nickel loading) on the liquid hydrocarbon/coke yield, ethylene conversion, and oligomeric product selectivity. Increases in pressure resulted in higher ethylene conversion, corresponding to a liquid yield of 12.4 wt.% with 5.7 wt.% coke. As the pressure increased, the selectivity towards octenes doubled alongside a decrease in butenes, which suggested that higher pressures promoted butene dimerization. Under the conditions studied, a minimum temperature of 120ºC was required to produce liquid hydrocarbons. The liquid yield increased with temperature, with 17 wt.% observed at 190ºC. Higher reaction temperatures led to the formation of odd-numbered oligomers primarily due to acid-catalyzed cracking reactions. In the range of space velocities tested, a moderate WHSV of 2.0 hr^{-1} resulted in a local maximum of 10.6 wt.% of liquid hydrocarbon yield. A moderate nickel loading of 3.4 wt.% also resulted in the highest liquid yield out of the three loadings tested (10.6 wt.%). The variation in nickel loading revealed the importance of having a synergistic balance of nickel and acid sites on the catalyst to maximize ethylene conversion and maintain high liquid hydrocarbon yield.

Introduction

The Advanced Hardwood Biofuels (AHB) is a program funded by the National Institute of Food and Agriculture (NIFA) of the United States Department of Agriculture (USDA), whose goal is to start the biofuels and biochemical industry in the Pacific Northwest. The program is focused on the conversion of hybrid poplar from the Pacific Northwest into liquid hydrocarbons, that can be used either as drop-in transportation fuels or commodity chemicals. The conversion process involves sequential pretreatment hydrolysis and fermentation stages to biochemically isolate glucose monomers from polymeric cellulose and convert sugars to produce bioethanol. Once bioethanol is obtained, it can be converted into hydrocarbons in three steps: 1) dehydration of ethanol, that produces ethylene and water over an acidic alumina catalyst, 2) oligomerization of the ethylene to produce linear and branched alpha-olefins, and 3) hydrogenation of the alpha-olefins to produce a saturated, paraffinic hydrocarbon. Though the dehydration and hydrogenation reactions have been extensively studied, research into heterogeneous oligomerization of ethylene is much less documented and detailed in scope, particularly for their implementation in continuous flow systems.

Most the present literature for heterogeneous ethylene oligomerization involves the use of three-phase, semi-batch reactors in which the ethylene is pressurized into a liquid solvent. The solvent (such as n-heptane) is used to suspend the solid catalyst, usually consisting of a silica-alumina matrix[2–7]. Pressurized ethylene, the sole inlet flow, interacts with the catalyst after it is solubilized into the heptane solvent. However, the catalyst activity is strongly dependent on the solubility of ethylene in the solvent, resulting in major mass transfer limitations. In addition, the use of an organic solvent is not suitable from a green chemistry perspective, as future biorefineries will need to implement environmentally friendly processes that mitigate their usage[8]. Therefore, further research on alternative ways to incorporate heterogeneous catalysts is paramount to successful implementation of industrial ethylene oligomerization.

Studies involving packed bed reactors have been carried out using different types of silica-alumina catalysts, differing in their porosity and acidity. In particular, microporous and mesoporous species, such as Zeolite Y and SBA-15, respectively, have been used as substrates to support nickel metal for heterogeneous ethylene oligomerization[9,10]. The pore size of the support was found to be a major factor for determining the oligomerization activity of a catalyst, with larger pore sizes (mesoporous) being far more active than microporous materials[6,7]. Martinez et al investigated a unique zeolite consisting of both mesopores and micropores, Zeolite β, as a support for ethylene oligomerization[11]. The catalyst was bifunctional in nature, consisting of both nickel active sites as well as Brønsted acid sites in the form of acidic protons. Their research with Ni-Hβ led to encouraging results and investigated the connection between the nickel loading and the resulting conversion and product selectivity in a packed bed reactor[11].

The goal of the AHB program is to produce gallons of liquid hydrocarbons from hybrid poplar. However, initial attempts performed by industrial partners in systems larger than microreactors have faced severe difficulties to reproduce the work detailed by Heveling and coworkers due to the high productivity and selectivity reported by the aforementioned substrates[12,13]. From our previous parameterized work with Ni-Hβ, we observed favorable catalyst activity for ethylene oligomerization. As such, one of the major motivators for this work was to determine the possibility of producing liquid hydrocarbons using Ni-Hβ in a packed bed reactor.

Much of the previous work on heterogeneous oligomerization of ethylene involves thin tubular reactors, with the products typically analyzed online via gas chromatography, as opposed to collected as liquid products. To the best of our knowledge, the implementation of ethylene oligomerization catalysts has not been studied using a laboratory scale reactor capable of producing a liquid hydrocarbon product. In addition, the encouraging results from the previous work conducted with Ni-Hβ motivated its use in the present work. This research expands on the current limited research area on heterogeneous ethylene oligomerization and emphasize the effect of operating parameters that affect the liquid hydrocarbon yield.

Experimental Methods

Catalyst Synthesis

We synthesized Ni-Hβ catalyst using a dripping wet impregnation technique. We purchased a commercial zeolite, $NH_4\beta$, from Zeolyst (CP814E*, SiO_2/Al_2O_3=25, surface area=680 m^2/g) and used the material without prior pretreatment. To introduce the nickel species on the material, we continuously dripped nickel nitrate (Sigma Aldrich) on the powder over 5 hours at room temperature, achieving a liquid-to-solid ratio of 5 cm^3/g. The dripping wet impregnation technique was implemented to take advantage of strong capillary forces to further draw the nickel nitrate solution into the porous interior. After the nickel contact, we vacuum filtered the grey slurry to obtain a grey paste. Next, we then loaded the paste into a crucible, where it was dried at 110ºC in air overnight. After drying, we calcined the grey/green solid in an air furnace at 550ºC for 5 hours to liberate any remaining ammonia on the support, which resulted in a light grey powder known as Ni-Hβ. We crushed the powder with a mortar and pestle, and used it without any further treatment. We varied the nickel loading on the Ni-Hβ catalysts by changing the concentration of the nickel nitrate from 0.17 M to 0.85 M.

Catalyst Characterization

We determined the nickel loading for the Ni-Hβ catalysts by ICP-OES (inductively coupled plasma-optical emission spectroscopy) using EPA protocol 200.7. We contacted nitric acid with the catalyst to leach out the nickel content into the solution where it was then analyzed through ICP-OES. However, one limitation of this technique is that silica and aluminum are only partially soluble in nitric acid and for this reason cannot be measured accurately. Therefore, we assume that the SiO_2/Al_2O_3 ratio of 25 and surface area values provided by the manufacturer are correct.

We prepared catalyst samples for transmission electron microscopy (TEM) by sonicating the catalyst in ethanol solution and placing a drop onto a 250μm copper grid. We then loaded the sample using a single-tilt holder into the sample compartment of the TEM (Tecnai, G2 F20 Supertwin TEM). We previously conducted X-ray diffraction of the resulting Ni-Hβ catalyst in our previous paper.

Oligomerization System

We performed ethylene oligomerization experiments in a custom-made fixed-bed reactor constructed from 1" OD Schedule 80 SS316 tubing shown in Figure 3.1. Prior to each experiment, we loaded the reactor with approximately 8 grams of fresh catalyst in-between two beds of quartz wool. We pressure-tested and leak checked the reactor prior to every experiment. After pressure testing, we pretreated the catalyst at 300°C in N_2 at 200 mL/min for 16 hours under atmospheric pressure. The purpose of this pretreatment step was to purge any air or moisture from the system. An on-stream GC-FID-TCD Shimadzu GC-2014 coupled with a Carboxen 1000 packed column was used to monitor the gas composition from the reactor prior to testing. Once the pretreatment was finished, we lowered the temperature of the reactor to the desired reaction temperature and used nitrogen gas to pressurize the system using an Equilibar dome-loaded backpressure regulator. After the temperature and pressures were stable, we initiated the ethylene flow, mixing it with the nitrogen stream. The flow of ethylene gas and nitrogen gas were 300 and 294 mL/min, respectively. A heated transfer line to the condenser was implemented to prevent product condensation. The reactor effluent was then directed to a double-pipe condenser operating in countercurrent flow, with a 5ºC cold water stream provided by a mobile chiller (ThermoFlex 2500, Thermo Fisher). A liquid bottle connected to the condenser was submerged in ice and used to collect the condensate. We measured the noncondensable gases periodically with the on-line GC/TCD. A typical experiment was conducted for 6 hours of time-on-stream.

Once the experiment was complete, we depressurized the system and collected the liquid hydrocarbon product in the bottle for analysis and mass balance purposes. We also removed the spent catalyst from the reactor and gravimetrically weighed it to determine the mass of coke accumulated throughout the process. After the experiment, we analyzed the liquid using a GC/MS/FID Shimadzu QP2010 installed with a SHRXI-5ms capillary column. The high volatility of the liquid product and the setup of the collection system created difficulties in closing our mass balance. Typical mass balances, including the unreacted ethylene, were in the range of 80-95% with ethylene. If we exclude the unreacted ethylene, the mass balance obtained was in the range of 50-65%. We attribute this difference due to the high volatility of the liquid product. In comparison with our first work where we measured the entire effluent stream online, the addition of the downstream condenser system introduced a compromise between collecting a liquid hydrocarbon product and maintaining good mass balance closures. The reproducibility was tested by replicating three experiments at the following conditions: total pressure: 35 bar, T: 120ºC, WHSV: 2.0 hr^{-1}. and error bars are reported for subsequent experiments using these standard deviations.

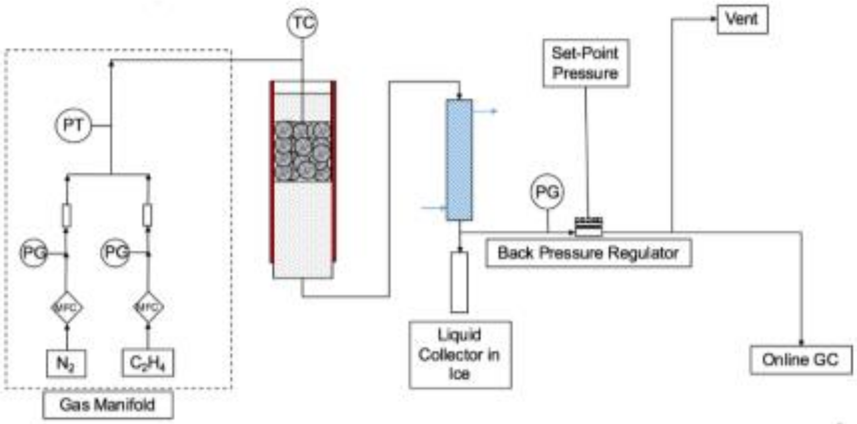


Figure 3.1. A process flow diagram for the ethylene oligomerization reactor used in these studies

In the following results, selectivity, S_i, and conversion, X, were calculated in this manner:

$$S_i\ (wt.\%) = \frac{mass\ of\ compound\ i}{mass\ of\ all\ measured\ compounds} \times 100$$

$$X\ (mol.\%\ of\ inlet\ ethylene) = \frac{molar\ flow\ rate\ of\ ethylene\ consumed}{molar\ feed\ rate\ of\ ethylene} \times 100$$

$$Liquid\ yield = \frac{mass\ of\ liquid\ product\ collected}{mass\ feed\ rate\ of\ ethylene * time} \times\ 100$$

$$Coke\ yield = \frac{final\ mass\ of\ catalyst\ bed - initial\ mass\ of\ catalyst\ bed}{mass\ feed\ rate\ of\ ethylene * time} \times\ 100$$

In reporting the selectivities, we group the hydrocarbons by the number of carbon atoms in the molecule (C4, C5, C6, etc.).

Results and Discussion

Catalyst Characterization

A full characterization of the catalyst is mentioned in our previous paper. The ionic exchange of the $NH_4\beta$ support with the nickel nitrate solutions produces a slurry with a grey color. The ammonium acts as a cation placeholder to maintain charge neutrality throughout the zeolite. After the exchange, the calcination steps decompose the ammonium ions on the support into ammonia gas and a proton, which remains on the support acting as a Brønsted acid site. As intended, the nickel loading of the as-synthesized catalysts increased proportionally with the concentration of the nickel nitrate solution. We determined that contacting the nickel nitrate solution with the ammonium form of the support was important for producing the appropriate catalysts for ethylene oligomerization. Contacting the nickel nitrate solution with the protonated form of the support (produced by calcination) resulted in negligible catalytic activity. We attribute this behavior to the higher ionic exchange potential of the nickel ion with the ammonium cation instead of the proton.

The TEM image shown in Figure 3.2 depicts the clusters of nickel, presumably located on the surface of the support. The major drawback to using wet impregnation for catalyst synthesis is the localization of the active metal near the mouths of the pores on the surface of the catalyst, where the nickel does not penetrate the pores. The nickel loading on the support, as shown in Table 1, increased as we increased the nickel concentration.

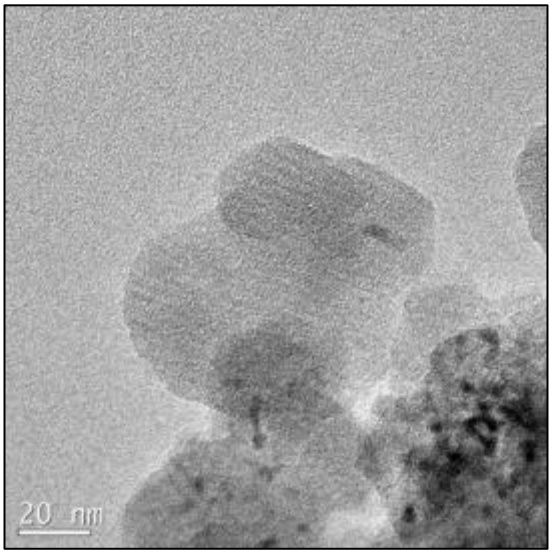


Figure 3.2. TEM image of the Ni-Hβ catalyst

Sample	$Ni(NO_3)_2$*$6H_2O$ concentration (M)	Ni Loading (wt.%)
Ni-1.5-Hβ	0.17	1.5
Ni-3.4-Hβ	0.51	3.4
Ni-6.0-Hβ	0.85	6.0

Table 1. Physical properties of the synthesized Ni-Hβ catalysts

Parameterization Experiments

We evaluated the performance of Ni-Hβ over a range of operating parameters. We arbitrarily selected a base-case condition as: T=120ºC, P_T= 35 bar, WHSV=2.00 hr^{-1}, and Ni loading=3.4 wt.%. From the base case, we changed one variable at a time, keeping everything else constant, in order to isolate the effect of the studied variable. Liquid yields were calculated as the total mass of liquid hydrocarbons collected relative to the amount of inlet ethylene over the course of the experiment. We computed coke yields in a similar manner, by measuring the difference between the mass of the catalyst bed before and after the reaction. The liquid product collected is shown in Figure 3.3. The liquid and coke yields for the parameterization experiments are shown in Table 2. Liquid hydrocarbons and coke yields (wt.%) over the parameterization studies

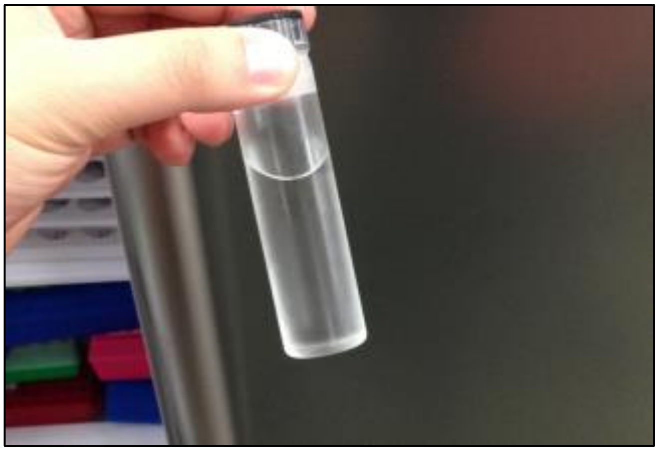
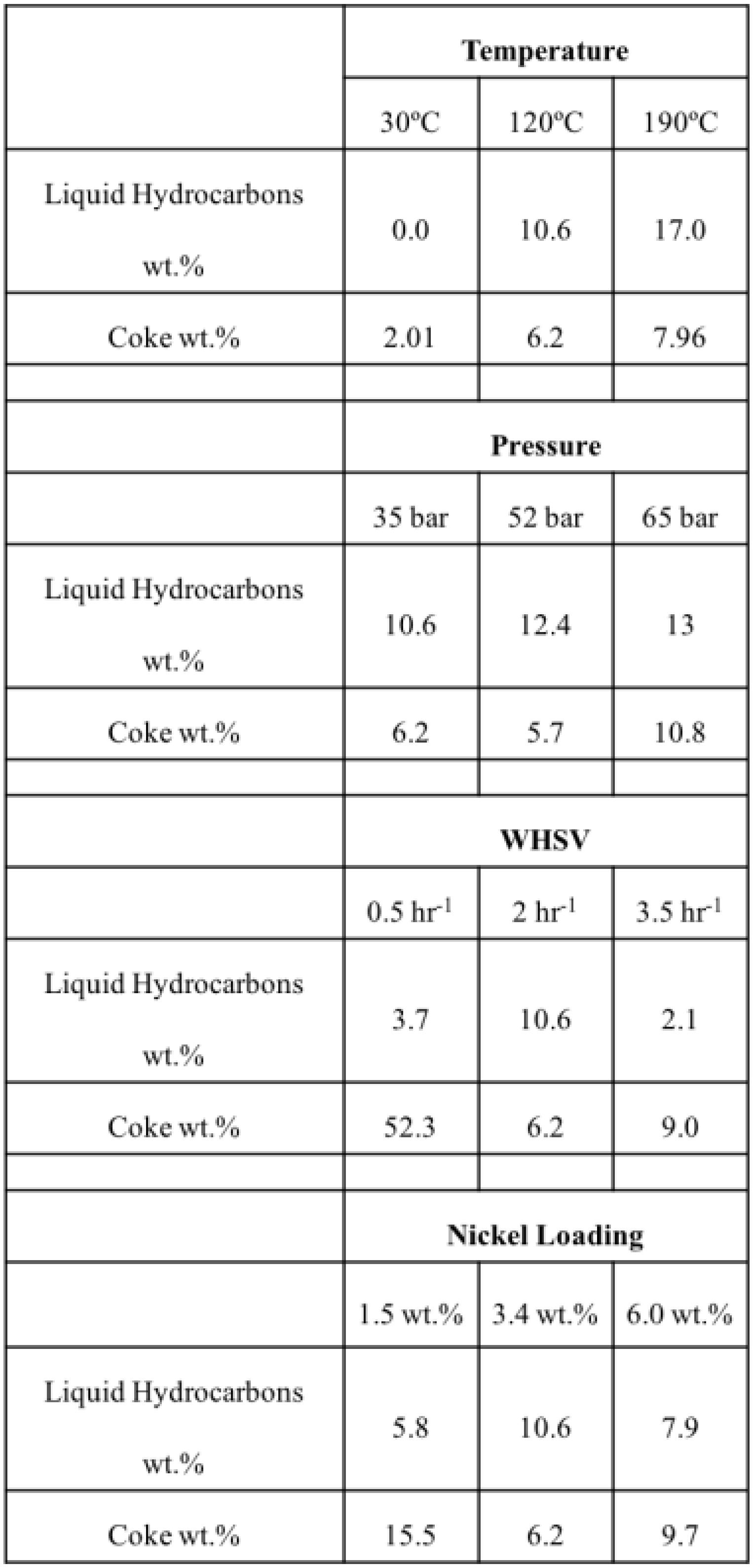


Figure 3.3. Liquid hydrocarbon product sample



	Temperature		
	30ºC	120ºC	190ºC
Liquid Hydrocarbons wt.%	0.0	10.6	17.0
Coke wt.%	2.01	6.2	7.96
	Pressure		
	35 bar	52 bar	65 bar
Liquid Hydrocarbons wt.%	10.6	12.4	13
Coke wt.%	6.2	5.7	10.8
	WHSV		
	0.5 hr^{-1}	2 hr^{-1}	3.5 hr^{-1}
Liquid Hydrocarbons wt.%	3.7	10.6	2.1
Coke wt.%	52.3	6.2	9.0
	Nickel Loading		
	1.5 wt.%	3.4 wt.%	6.0 wt.%
Liquid Hydrocarbons wt.%	5.8	10.6	7.9
Coke wt.%	15.5	6.2	9.7

Table 2. Liquid hydrocarbons and coke yields (wt.%) over the parameterization studies

Effect of Temperature

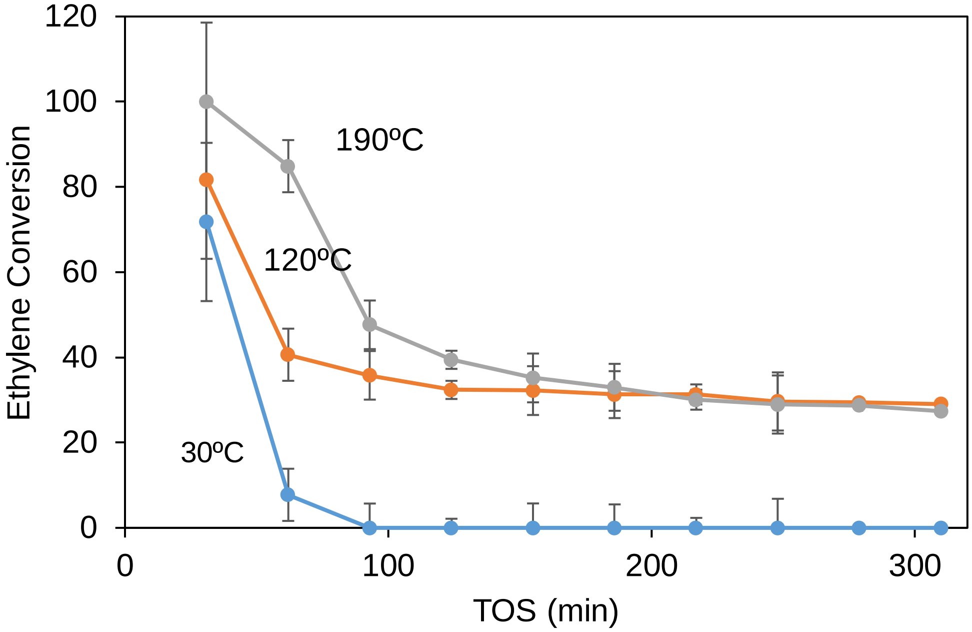


Figure 3.4. Ethylene conversion as a function of time-on-stream at several temperatures with Ni-Hβ. Reaction conditions: PT=35 bar, WHSV: 2.00 hr-1, Ni loading 3.4 wt.%

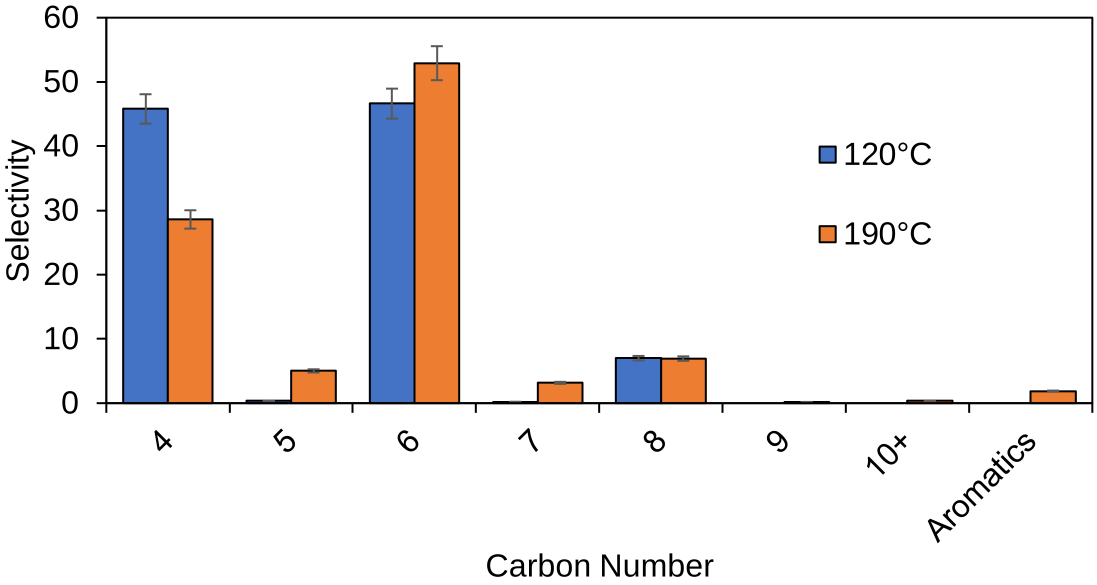
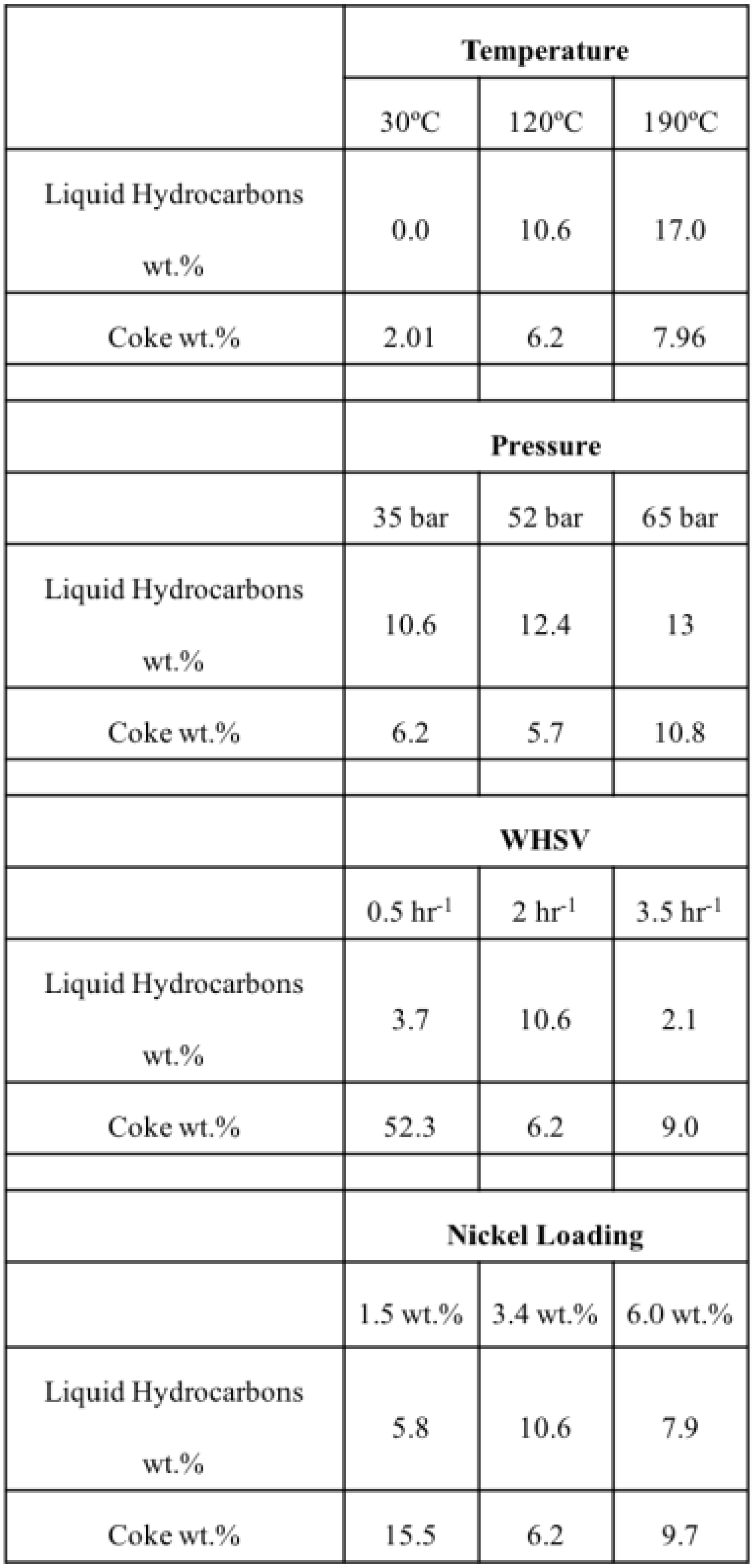


Figure 3.5. Relative product selectivities as a function of temperature with Ni-Hβ. Reaction conditions: P_T=35 bar, WHSV: 2.00 hr^{-1}, Ni loading 3.4 wt.%

The coke and liquid yields as a function of temperature are shown in



	Temperature		
	30ºC	120ºC	190ºC
Liquid Hydrocarbons wt.%	0.0	10.6	17.0
Coke wt.%	2.01	6.2	7.96
	Pressure		
	35 bar	52 bar	65 bar
Liquid Hydrocarbons wt.%	10.6	12.4	13
Coke wt.%	6.2	5.7	10.8
	WHSV		
	0.5 hr^{-1}	2 hr^{-1}	3.5 hr^{-1}
Liquid Hydrocarbons wt.%	3.7	10.6	2.1
Coke wt.%	52.3	6.2	9.0
	Nickel Loading		
	1.5 wt.%	3.4 wt.%	6.0 wt.%
Liquid Hydrocarbons wt.%	5.8	10.6	7.9
Coke wt.%	15.5	6.2	9.7

Table 2. As the temperature increased from 30ºC to 190ºC, the yields of the coke and the liquid fractions both increased steadily, with the coke yield increasing from 2.01 wt.% to 7.96

wt.% and liquid yields increasing from 0 wt.% to 17 wt.%. The conversion data are shown in Figure 3.4. In each experiment, the conversion reaches steady-state around 90 minutes after the initial system startup. A temperature increase in from 30ºC to 120ºC led to a significant increase from 0% to 35% ethylene steady-state conversion. However, increasing the temperature further from 120ºC to 190ºC did not increase the conversion. We hypothesize that higher temperatures increase the conversion until coke covers much of the catalyst surface, after which further increases in temperature do not increase the conversion. Other researchers have noted a bimodal distribution for optimal ethylene conversion as a function of temperature for ethylene oligomerization. For Ni-Y and Ni-SiO_2-Al2O_3 catalysts in a fixed bed reactor, Heveling and coworkers observed a maximum conversion at 120ºC and another high conversion region past 300ºC[9,12,13]. This polymodal behavior of other catalysts is consistent with ethylene conversion observed in the range of temperatures we tested. Despite the eventual plateau in ethylene conversion at 120ºC and 190ºC, the higher initial activity of the catalyst at 190ºC in the transient regime spanning the first 120 minutes may explain the difference in the liquid and coke yields between the two experiments.

The selectivities of the oligomers in the collected liquid fraction at 120ºC and 190ºC are shown in Figure 3.5. At 120ºC, the product consists primarily of four and six carbons (45% selectivity for each), with 8% selectivity to eight carbons. A liquid product was not collected at 30ºC so product selectivities for this temperature are not shown in Figure 3.5. As the temperature increased from 120ºC to 190ºC, changes in selectivity were evident, namely the formation of odd carbon products (C5 and C7) and an increase in the selectivity towards aromatic hydrocarbons. This behavior is consistent with previously observed studies, where higher temperatures appear to favor acid-catalyzed reactions[12]. Formation of odd numbered carbon products has been previously attributed to cracking and disproportionation reactions, which result in unstable hydrocarbon species that can further react to form coke[7]. The presence of aromatic hydrocarbons in the liquid fraction at 190ºC corroborates this hypothesis, as no aromatic hydrocarbons were observed at 120ºC. In addition, the highest liquid hydrocarbon yield (17 wt.%) along with a marked 13% increase in the selectivity towards hexenes were observed at 190ºC. The high selectivity towards hexenes is connected to the decrease in selectivity towards butenes at this temperature. As cracking reactions are more favorable at higher temperatures, it is likely that cracked oligomers led to an increase in the selectivity of hexenes, as well as odd carbon products. The rate of oligomerization could have also increased as well, with adsorbed butenes reacting further with adsorbed ethylene resulting in an increase in the hexene product.

Effect of Total Pressure

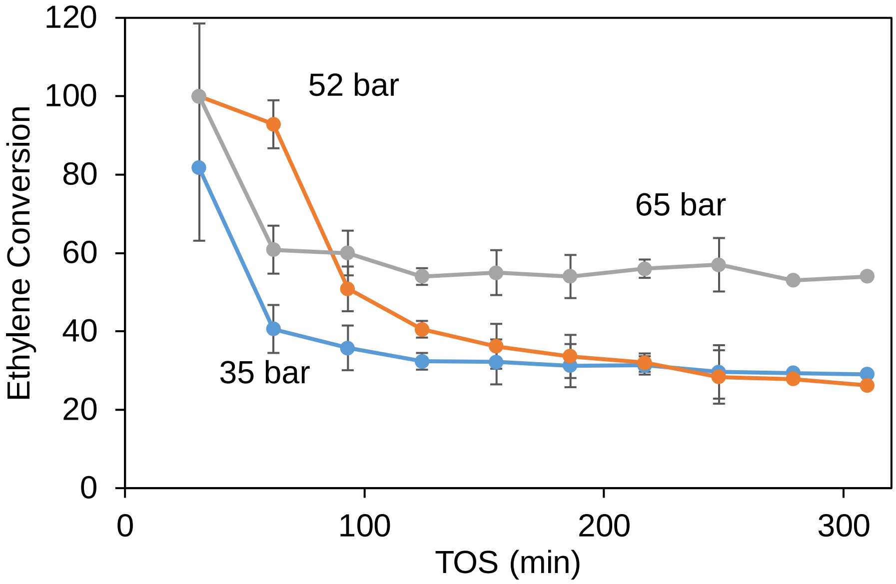


Figure 3.6. Ethylene conversion as a function of time on stream at several pressures with Ni-H**β**. Reaction conditions: T=120ºC, WHSV: 2.00 hr^{-1}, Ni loading 3.4 wt.%

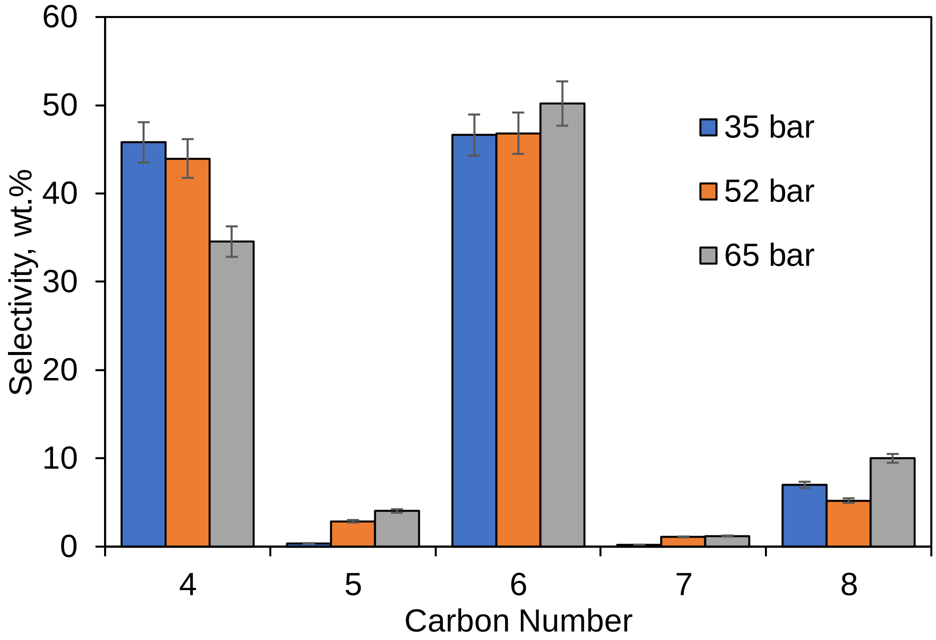


Figure 3.7. Relative productive selectivities as function of total pressure with Ni-H**β**. Reaction conditions: T=120ºC, WHSV: 2.00 hr^{-1}, Ni loading 3.4 wt.%

We carried out ethylene oligomerization at several total pressures in the range from 35 bar to 65 bar for Ni-Hβ. At 52 bar, we observed a 12.4 wt.% yield of liquid product along with a 5.7

wt.% yield of coke, which are nearly identical to the yields collected at 35 bar. At 65 bar, we obtained a slightly higher liquid (12.9 wt.%) and coke yield (10.8 wt.%). The conversion at 35 and 52 bar converge to a steady-state value of 30% after 3 hours of time-on-stream. At 65 bar, the ethylene conversion increased to 55%. Coke on the catalyst was also the highest at this condition, with 10.5 wt.% solids collected. We analyzed the liquid product collected at all experiments, with the selectivity results shown in Figure 3.7. The product distribution shifted from the lighter butenes (45.8 wt.%) at 35 bar to 34.6 wt.% at 65 bar. The selectivity shifted towards octenes, with an increase from 7 wt.% to 10 wt.% as the total pressure increased from 35 to 65 bar. Interestingly, the selectivity towards hexenes remained largely unchanged throughout the range of pressures tested. This behavior may indicate a shift in the oligomeric pathways on the catalyst at these conditions. Octenes can be formed via the dimerization of butenes, and our results indicate that it is likely that the increase in the total pressure promoted this reaction pathway. On the other hand, hexenes can be formed through the reaction of an adsorbed butene and an adsorbed ethylene. The selectivities of pentenes and heptenes also increased with pressure, which indicates that cracking reactions are also promoted at higher pressures. The results presented provide further insight onto the reaction pathways at moderate to high pressure for Ni-Hβ that have not been previously observed in the literature.

To the best of our knowledge, the effect of pressure has not been previously reported for ethylene oligomerization over Ni-Hβ catalyst. Prior literature evaluating the effect of pressure were based on semi-batch reactors where the reaction pressure was used to increase the solubility of the reactant ethylene in the liquid heptane solvent[2,6,7]. In these cases, the reaction rate increased favorably with pressure due to the increased solubility of the ethylene into the solvent. For fixed bed systems with catalysts such as Ni-HY, Ng and Creaser observed that the pressure also played a favorable role in the activity of the catalyst[14]. Higher reaction rates are expected at higher pressures, and we hypothesize that the high coke yields are due to increased catalyst activity. At 52 and 65 bar, odd carbon products ranging from pentenes to heptenes were observed in the liquid hydrocarbons. As noted in the previous section discussing the effect of temperature, the presence of odd carbon products has been attributed to coke formation due to the cracking and disproportionation reactions that would disrupt the formation of even carbon oligomers.

Effect of WHSV

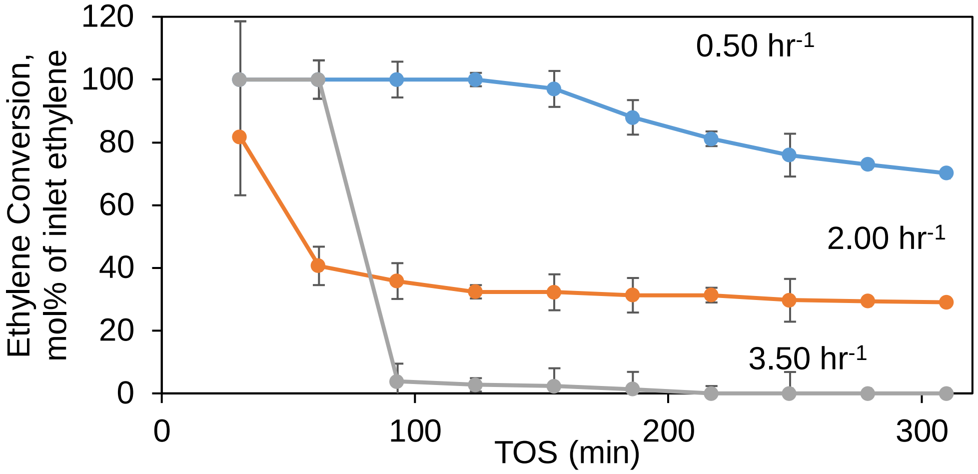


Figure 3.8. Conversion as function of time-on-stream for several values of WHSV with Ni-H**β**. Reaction conditions: T:120ºC, P_T=35 bar, Ni loading=3.4 wt.%

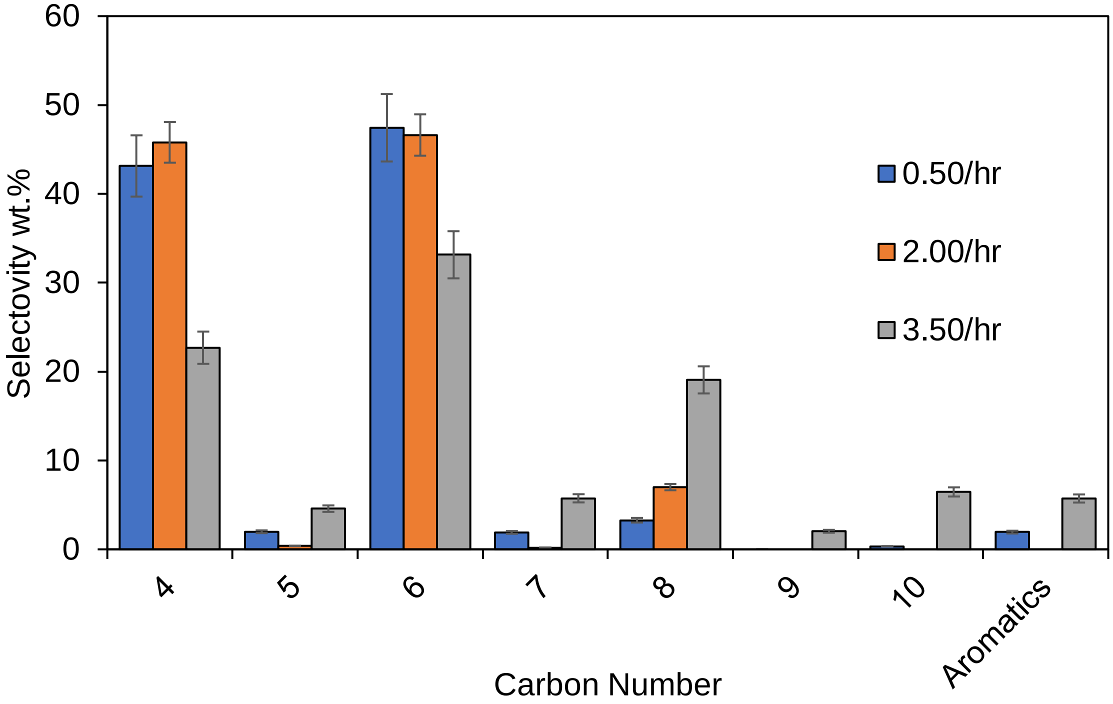


Figure 3.9. Relative product selectivities as a function of WHSV with Ni-Hβ. Reaction conditions: T:120ºC, P_T=35 bar, Ni loading=3.4 wt.%

We evaluated the effect of the ethylene weight hourly space velocity (WHSV) on oligomerization by adjusting the ethylene flow rate over a constant mass of catalyst. The lowest WHSV at 0.5 hr^{-1} resulted in nearly 52 wt.% of coke yield, along with a marginal 3.7 wt.% of liquid hydrocarbons. At WHSV of 2.0 hr^{-1}, there is a noticeable shift in the product distribution, with the yield of liquid product increasing three times, leading to a minimum of 6.24 wt.% of coke.

The residence time of the ethylene molecules at the catalyst bed is much higher at low WHSV than it is at higher values. We observed the highest yield of coke at 0.5 hr^{-1}. The longer residence time on the bed promoted high ethylene conversion, as shown in Figure 3.8. We hypothesize that the low ethylene flow rates promoted high conversion by allowing oligomeric chains to develop over an extended period of time. However, due to the low flow rates, the bulky chains were unable to fully desorb, thus remaining on the catalyst bed. An increase in the ethylene flow rate led to negligible ethylene conversion and low liquid product yield at 3.5 hr^{-1}. The noticeable decrease in ethylene conversion may be attributed to the decrease in the residence time in the bed, reducing overall contact with the catalyst. Despite the low conversion, the liquid product observed at 3.50 hr^{-1} presents a relatively high selectivity of C8 and C10 oligomers. These results are presented in Figure 3.9. The high ethylene flow rates likely force bulkier oligomers to desorb rather than to remain adsorbed on the catalyst.

Effect of Nickel Loading

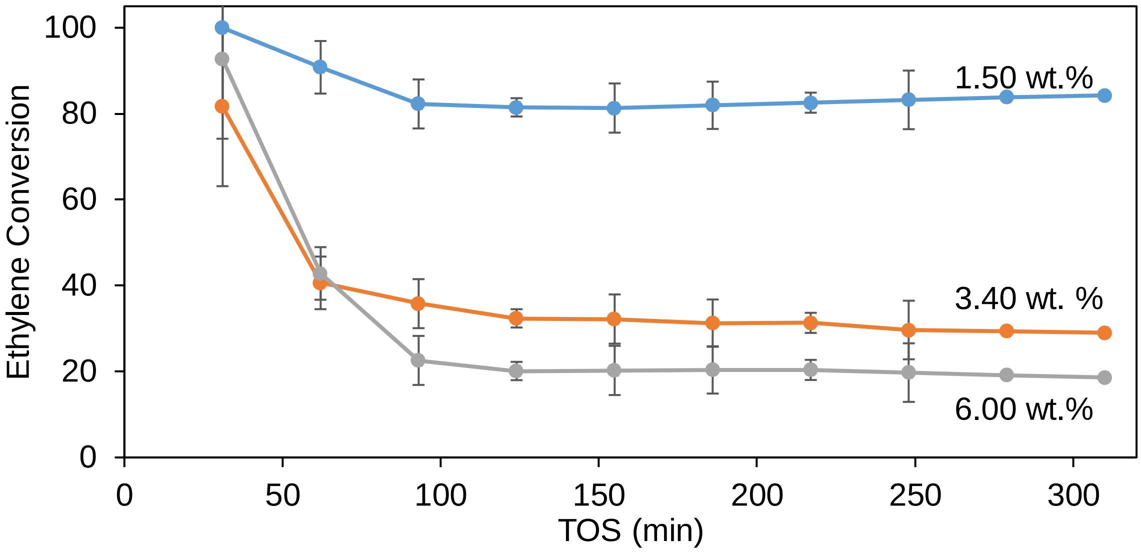


Figure 3.10. Ethylene conversion as function of time-on-stream at several nickel loadings with Ni-H**β**. Reaction conditions: T:120ºC, P_T=35 bar, WHSV: 2.00 hr^{-1}

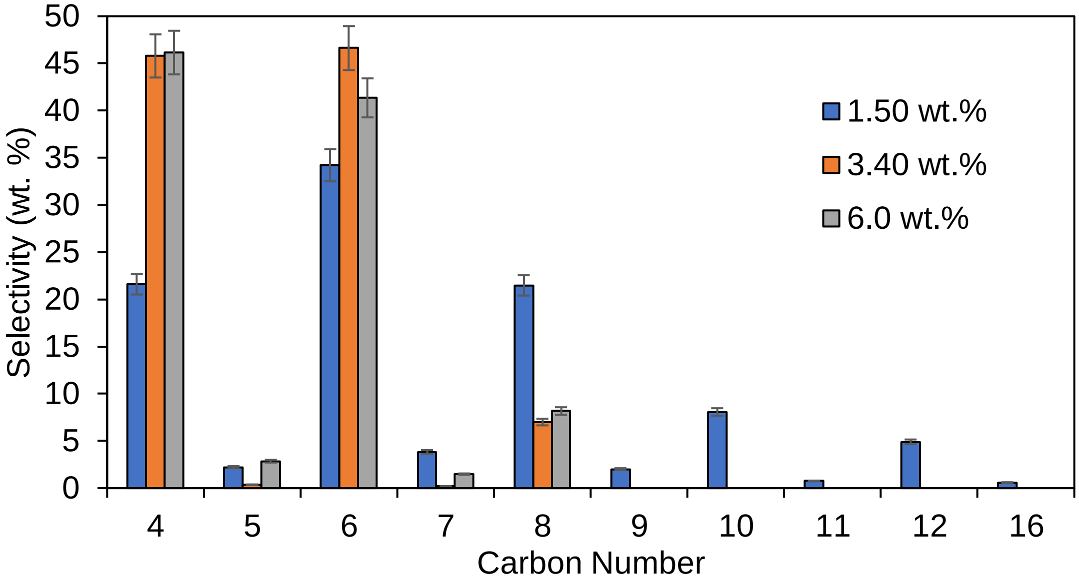


Figure 3.11. Relative product selectivities as function of nickel loading with Ni-H**β**. Reaction conditions: T:120ºC, P_T=35 bar, WHSV: 2.00 hr^{-1}

The effect of nickel loading on ethylene conversion and the resulting product selectivity are shown in Figure 3.10 and Figure 3.11. The overall conversion decreased from 84% to 18.6% as the nickel loading on the Hβ support increased from 1.5 wt.% to 6.0 wt.%. These trends are in agreement with previous reports for ethylene oligomerization and propylene oligomerization[15–17]. The increased activity at low nickel loadings may be attributed to a higher concentration of Brønsted acid sites across the catalyst, which have been attributed to secondary cracking/oligomerization reactions. The product selectivities as a function of nickel loading are shown in Figure 3.11. Decreasing the nickel loading resulted in a marked shift from a lighter oligomeric product (C4-C8) to a much heavier oligomeric product (C4-C16). However, the highest yield of coke (15.5 wt.%) was also observed at a nickel loading of 1.5 wt.%. The concentration of Brønsted acid sites in the catalysts with 1.5 wt.% nickel loading should be relatively higher compared to the catalysts with higher nickel loadings. Acid sites have been observed to facilitate several reactions, namely cracking and secondary oligomerization[7]. Therefore, it is likely that the higher concentration of acid sites on the support contributed to the formation of long oligomers. In addition to the presence of heavier products in the liquid hydrocarbon collected (5.8 wt.%), it is likely that the high coke yield (15.51 wt.%) is due to the accumulation of these species in the porous network of the catalyst. In contrast, the higher nickel loading resulted in a lighter oligomeric product (C4-C8). This behavior may be attributed to a decrease in the acid sites in the catalyst framework. The lack of odd carbon species in the collected hydrocarbons indicates that primary, nickel-catalyzed oligomerization was the dominant reaction at these conditions, instead of acid-catalyzed cracking and aromatization reactions. Within the range of conditions tested, there was a maximum liquid hydrocarbon yield of 11 wt.% and 6 wt.% coke at a nickel loading of 3.4 wt.%. This metal loading on the support, within the range of conditions studied, favors production of the olefins in the range of C4-C8. The conversion at this condition is more than 30%.

Summary of the Work

The results of the work performed will be helpful for pilot scale studies intending on producing liquid hydrocarbon products. Through our parameterization study over these processing variables, we obtained several insights on their effects on ethylene oligomerization for liquid hydrocarbon production over Ni-Hβ. The effect of temperature was found to be favorable towards liquid production, with a yield of 17 wt.% liquid hydrocarbons consisting of even and odd oligomeric products at 190ºC. The formation of odd carbon products was consistent with our previous temperature studies conducted over Ni-Hβ, as shown in Chapter 2. As we increased the total pressure from 35 to 65 bar, the conversion increased drastically from 30% to 54%. This increase in conversion, however, increased the coke yield while not significantly increasing the liquid yield. We theorized potential reaction pathways that resulted in the increase in selectivity towards octenes at 65 bar to be the dimerization of adsorbed butenes on the catalytic active sites. This phenomenon coincided with a decrease in selectivity towards butenes. We also studied the influence of WHSV and observed low liquid hydrocarbon yields and high coke yields at 0.5 hr^{-1}. This behavior was attributed to the increased contact time with the active sites of the catalyst, resulting in large, accumulated oligomers in the catalyst. We observed that a nickel content of 3.4 wt.% produced the highest amount of liquid (11 wt.%).

To summarize the results, the conditions that we observed for liquid production would be as follows: P_T: 52 bar, T: 120ºC, Ni loading: 3.4 wt.%, and WHSV: 2.0 hr^{-1}. The combination of these parameters led to the highest liquid production (12.4 wt.%), lowest coke deposition (5.7 wt.%), at 30% ethylene conversion. Due to the problems associated with our mass balance closures in this work, the selectivities of our products in this work were skewed towards the heavier oligomers (hexenes, octenes, etc.) resulting from the high volatility of the butenes in the liquid product. As a result, the other oligomers appear to be at much higher selectivities than the results shown in Chapter 2.

To extend this work, these results will be put to scale in a pilot facility at Southwest Research Institute in San Antonio, TX. The major difference that contrasts with the work we performed in Chapter 2 is that there is a compromise between maintaining a high mass balance and collecting a liquid product due to the high volatility of the liquid. This situation, however, was limited to the design of our product collection system. The issue of having proper mass balance closures can be remedied by installing appropriate unit operations downstream of the reactor and condenser, such as a distillation column and/or a recycle stream. The implementation of either of these systems will help immensely with maintaining a high mass balance.

Conclusion

We tested nickel metal supported on an acidic zeolite β (Ni-Hβ) in a laboratory-scale packed bed reactor for the synthesis of liquid olefinic hydrocarbons in a measurable, milliliter-scale quantity. The potential of the catalyst to produce a liquid product was measured through a parameterization of several process variables, such as temperature, pressure, weighted hourly space velocity, and nickel loading. We determined the effect of each of these variables on liquid hydrocarbon/coke yield, ethylene conversion, and product selectivity. Ethylene conversion was found to increase as the total reactor pressure increased from 35 bar to 65 bar, which resulted in a liquid yield of 12.4 wt.% with 5.72 wt.% coke. In addition, the yield of liquid hydrocarbon increased with temperature, with 17 wt.% observed at 190ºC. However, the increase in the reaction temperature also contributed to the formation of several odd-numbered carbon products, which is indicative of the occurrence of cracking reactions. In the range of space velocities tested, a moderate WHSV of 2.00 hr^{-1} resulted in a local maximum for liquid yield, whereas a WHSV of 0.5 hr^{-1} produced the highest amount of coke in the study (52.3 wt.%). A moderate nickel loading of 3.4 wt.% also resulted in the highest liquid yield out of the three loadings tested, with 10.6 wt.% liquids collected. This study provides a preliminary examination into potential reaction pathways and behavior at each of the parameters for this catalyst. Further study and incorporation of these results may help add valuable information for incorporating Ni-Hβ catalysts in a pilot or industrial scale facility for liquid hydrocarbon production. The results discussed in this paper will be extended to a pilot scale study for the AHB project.

Acknowledgements

The authors are appreciative of the funding provided by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30407 from the USDA National Institute of Food and Agriculture, and the Weyerhaeuser Endowment in Paper Science and Engineering. Part of this work was conducted at the Molecular Analysis Facility, a National Nanotechnology Coordinated Infrastructure site at the University of Washington which is supported in part by the National Science Foundation (grant ECC-1542101), the University of Washington, the Molecular Engineering & Sciences Institute, the Clean Energy Institute, and the National Institutes of Health.

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Chapter 4: Oligomerization of supercritical ethylene over silica-alumina catalysts

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Abstract

We used supercritical ethylene as both a solvent and as a reactant for ethylene oligomerization over two silica-alumina type catalysts: Ni-Hβ and Ni-Al-SBA-15. Specifically, the effect of pressure and temperature on the overall conversion and product selectivity were evaluated in the range from 0 to 65 bar and 30 to 120ºC. At subcritical conditions, the ethylene conversion reached a plateau of around 50%. By increasing the pressure past the critical point of ethylene, the conversion drastically increased to 71%. The increased conversion can be attributed to the solubility of certain oligomers, namely butene, in supercritical ethylene that promotes desorption from catalytic active site before further oligomerization. We also tested a mesoporous catalyst, Ni-Al-SBA-15 and observed conversion trends analogous to that of Ni-Hβ. At supercritical conditions, ethylene oligomerization over Ni-Al-SBA-15 was more selective towards the butene product, with nearly 74 wt.% butenes observed. The catalyst activity increased with temperature from 30ºC to 120ºC. The experiment conducted at 30ºC showed very little activity and ethylene conversion, however it effectively heavy molecular weight species from the catalyst. This condition, albeit being not effective for ethylene oligomerization, could be implemented as an *in-situ* technique to regenerate the catalyst during process operation.

Introduction

A fluid is said to be supercritical if its temperature and pressure exceed its critical point. This particular state has a unique combination of properties representative to both liquid and gaseous phases[1]. Supercritical fluids (SCFs) are characterized by liquid-like solubility and gas-like molecular diffusivities[2]. These unique properties allow these fluids to overcome transport limitations and for this reason SCFs are commonly used as solvents in chemical reactions[3]. SCFs, such as supercritical CO_2, have also been used as green solvents for the extraction of specialty chemicals from biphasic solutions.

The solubility of a compound in a solvent often drastically increases beyond the critical point of that solvent. Thus, higher reaction rates have been observed using a supercritical fluid as the reaction medium[2]. In addition to that, this enhanced solubility of supercritical fluids has been extended for applications other than for improving reaction rates. They have been theorized for potentially reducing carbon deposition on heterogeneous catalysts over the course of a reaction[4]. By suppressing the formation of these carbonaceous deposits, higher catalyst lifetimes can be achieved.

Several authors have reported reduction of coke accumulation on heterogeneous catalysts with SCFs. The work of Tiltscher et al. highlighted the application of SCFs as a reaction medium for 1-hexene isomerization. Gas-phase 1-hexene isomerization was tested over macroporous α-Al_2O_3 catalysts and it was observed that the formation of cis/trans 2-hexene was not affected by the temperature at pressures below the critical point[5]. Catalyst deactivation was typically observed to occur due to the accumulation of bulky, nonvolatile hexene oligomers in the pores and active sites of the catalyst. The solubility, however, changed abruptly at pressures above the critical pressure with very little coke deposition occurring. The modulation of the reaction pressure, therefore, can be a tool to prevent catalyst deactivation[5]. Subramaniam and coworkers extended the work on 1-hexene isomerization by performing the same reaction over a microporous Pt/ γ-Al_2O_3[6]. They noted that the activity of the catalyst was lower at subcritical conditions, whereas the activity was sustained above the critical pressure. The authors attributed this behavior to the solvating properties of the dense SCFs that mitigated the formation and deposition of hexene oligomers in the catalyst pores[6,7]. Hassan et al. observed that, during naphthalene hydrogenation, the coke deposition was 38% lower at supercritical conditions on $NiMo/Al_2O_3$ catalysts[4]. The pressure had a pronounced effect on the overall conversion of naphthalene, with nearly 100% conversion at 60 bar and 300ºC. The mole fraction of naphthalene (a common precursor molecule for coke) dissolved in supercritical ethylene increased sharply after the ethylene partial pressure increased above the critical point. There also appears to be a strong dependence on the temperature; right above the critical pressure (50.4 bar), the solubility of the naphthalene in ethylene is substantially higher at 12ºC than at 35ºC[1]. The critical temperature and pressure of ethylene are 9.5ºC and 50.4 bar, respectively.

Ethylene oligomerization is responsible for the production of a myriad of industrially-relevant products. Companies such as Shell and Chevron have incorporated ethylene oligomerization to generate higher olefins. However, the optimal conditions have yet to be fully evaluated in heterogeneous systems, as most of the prior work was performed over homogeneous catalysts and slurry batch systems[8–12]. The development of a greener and solvent-free heterogeneous process using solid catalysts is desirable for the environmental benefits and ease of product separation at a process standpoint. Compared with heterogeneous processes, the separation and recovery of homogeneous catalysts from the solvent and products is a nontrivial unit operation. The problem of heterogeneous systems, however, is the deactivation of the catalyst over time on stream which requires an auxiliary regeneration step to burn off the existing coke to regenerate the catalyst. The application of supercritical conditions for ethylene oligomerization has not been previously studied, and thus it is currently unknown on their impact on coke mitigation or catalyst activity.

In the present work, we report the effect of supercritical conditions on ethylene oligomerization. This work expands on the limited scope of knowledge available in heterogeneous ethylene oligomerization and offers an extended outlook on using supercritical conditions on Ni-Hβ and Ni-Al-SBA-15 catalysts. This work uses, for the first time, ethylene as both a reactant and as a supercritical medium for ethylene oligomerization. We report how pressure and temperature affect ethylene conversion and product selectivity. We start by comparing results from runs at subcritical conditions to runs at supercritical conditions, by varying the pressure for oligomerization over Ni-Hβ. Then, to verify how the effects observed depend on the catalyst, we repeat the same analysis for a mesopore catalyst, Ni-SBA-15. Finally, to determine process changes within supercritical conditions, we performed experiments at a range of supercritical temperatures with Ni-Hβ.

Materials and Methods

Catalyst Synthesis

We conducted ethylene oligomerization experiments with two catalysts, Ni-Hβ and Ni-Al-SBA-15. The β zeolite was a commercial support from Zeolyst, and the SBA-15 support was synthesized in the laboratory.

Ni-Hβ

We purchased a commercial beta zeolite from Zeolyst (CP814E, $SiO_2/Al_2O_3=25$, ammonium form) and used without prior treatment. To introduce nickel onto the support, we slowly dripped a 0.34M solution of nickel nitrate onto the powder for over 5 hours at room temperature to achieve a liquid-to-solid ratio of 5 cm^3/g. After mixing, we washed the resulting dark grey slurry and vacuum filtered it to obtain a grey paste. We then dried the resulting paste overnight at 110ºC overnight for 12 hours, which resulted in a pale green powder. After drying, we calcined the powder at 550ºC for 5 hours in an air furnace, which resulted in the Ni-Hβ catalyst. We then crushed the powder using a mortar and pestle and used it without any further treatment.

Ni-Al-SBA-15

We adapted the synthesis of Ni-Al-SBA-15 from methods detailed by Andrei et al.[13] We synthesized pure siliceous SBA-15 by stirring a mixture of Pluronic P123 (Sigma-Aldrich), tetraorthosilicate (TEOS, Sigma-Aldrich) and HCl (Sigma-Aldrich) in water. The molar ratio of the resulting slurry was 1 TEOS/0.016 P123/ 4.9HCl/40.5 H_2O, per the methods from Andrei et al[13]. We then mixed the slurry using a magnetic stirrer for 24 hours at 40ºC and then transferred it to a drying furnace at 100ºC for 48 hrs without stirring. We then washed the resulting solid, vacuum filtered it under deionized water, and dried it overnight at 110ºC. Afterward drying, we then calcined the yellow/white solid in air at 550ºC for 5 hrs to expel the organic template formed from the synthesis, resulting in a white powder.

To introduce the eventual Brønsted acid and nickel sites, we had to add aluminum to the SBA-15 framework. This was conducted by grafting the parent SBA-15 material with 0.1M sodium aluminate ($NaAlO_2$, Acros). We mixed the slurry for 15 hrs and subsequently filtered, washed, and dried the solids overnight at 100ºC. We then calcined the solids in air at 550ºC for 6 hours. The solid product that remained was denoted as Na-Al-SBA-15. Afterwards, we contacted the resulting Na-Al-SBA-15 with a 0.1M solution of ammonium nitrate (NH_4NO_3, Sigma-Aldrich), resulting in NH_4-Al-SBA-15. Finally, the final form of the catalyst was produced after contacting NH_4-Al-SBA-15 with 0.51M nickel nitrate, resulting in a mixture of Ni-NH_4-Al-SBA-15. To obtain the protonated form of the catalyst, we calcined the Ni-NH_4-Al-SBA-15 in air to expel ammonia from the template, resulting in Ni-H-Al-SBA-15, otherwise known as Ni-Al-SBA-15.

Catalyst Characterization

We determined the nickel loading in the catalyst using ICP-OES (inductively coupled plasma-optical emission spectroscopy). Catalyst samples were also imaged using transmission electron microscopy (TEM). The catalyst powder was sonicated in ethanol to create a fine dispersion, which was then dripped onto a 250 μm copper grid. We then loaded the copper grid into the microscope using a single-tilt holder into the sample compartment of the Tecnai G2 F20 Supertwin TEM. To complement the TEM images, we also took scanning electron microscopy images using a Sirion XL30 SEM. We prepared the catalysts imaged using SEM by sputter coating the samples with silver paint to mitigate electron charging during imaging. We collected the diffraction profiles of the materials using a Bruker D8 Discover with a high-power rotating Cu anode x-ray source.

We analyzed the chemical composition of the surface of the fresh and spent catalysts using Fourier transform infrared (FTIR) spectroscopy. We used an attenuated total reflectance (ATR) attachment with a diamond surface. Several milligrams of each material were analyzed at a time, spanning wavenumbers of 400-4000 cm^{-1} at a scan rate of 40 images per sample.

Catalytic Reactor

We performed oligomerization experiments in a continuous flow fixed-bed reactor constructed with 1” OD Schedule 80 SS316 tubing. Prior to each experiment, we loaded the reactor with approximately 8 grams of fresh catalyst in-between two beds of quartz wool. We pressure-tested and leak checked the reactor prior to every experiment. After pressure testing, we pretreated the catalyst was pretreated at 300ºC in N_2 at 200 mL/min for 16 hours under atmospheric pressure. This pretreatment step was intended to purge any air or moisture from the system, as moisture has been previously observed to severely hinder the catalyst performance. We used a downstream GC-FID-TCD Shimadzu GC-2014 with a HP-PLOT-Q column (30 m, 0.53 mm, 40 µm film thickness) to monitor the gas composition online from the reactor prior to testing. After pretreatment, we lowered the temperature of the reactor to the desired reaction temperature and nitrogen gas was used to pressurize the system. We set and controlled the pressure using an Equilibar dome-loaded backpressure regulator. After stabilizing the set point temperature and pressures, we started the ethylene flow, mixing it along with the nitrogen to initiate the reactions in the catalytic bed. The nitrogen and ethylene flow rates were kept at 109 and 467 mL/min, respectively, with the ethylene to nitrogen volumetric flow ratio kept constant at 4.29. We kept a heated transfer line downstream of the reactor at 120ºC to prevent product condensation and measured product gases periodically through on-line GC/TCD. We determined the coke yield gravimetrically by measuring the weight of the reactor contents before and after the reaction. Mass balances (excluding the unreacted ethylene) for all reported experiments were closed above 90%. The reproducibility was tested by replicating three experiments at the following conditions: total pressure: 35 bar, T: 120ºC, WHSV: 5.5 hr^{-1}. and error bars are reported for subsequent experiments using these standard deviations.

The selectivity, S_i, and conversion, X, have been defined as follows:

$$S_i\ (wt.\%) = \frac{mass\ of\ compound\ i}{mass\ of\ all\ measured\ compounds} \times 100$$

$$X\ (mol.\%\ of\ inlet\ ethylene) = \frac{molar\ flow\ rate\ of\ ethylene\ consumed}{initial\ molar\ flow\ rate\ of\ ethylene} \times 100$$

$$Coke\ yield = \frac{final\ mass\ of\ catalyst\ bed - initial\ mass\ of\ catalyst\ bed}{mass\ feed\ rate\ of\ ethylene * time} \times\ 100$$

In reporting the selectivity, we group the products according to the number of carbon atoms in the molecule (C4, C5, C6, etc.)

Results and Discussion

Catalyst Characterization

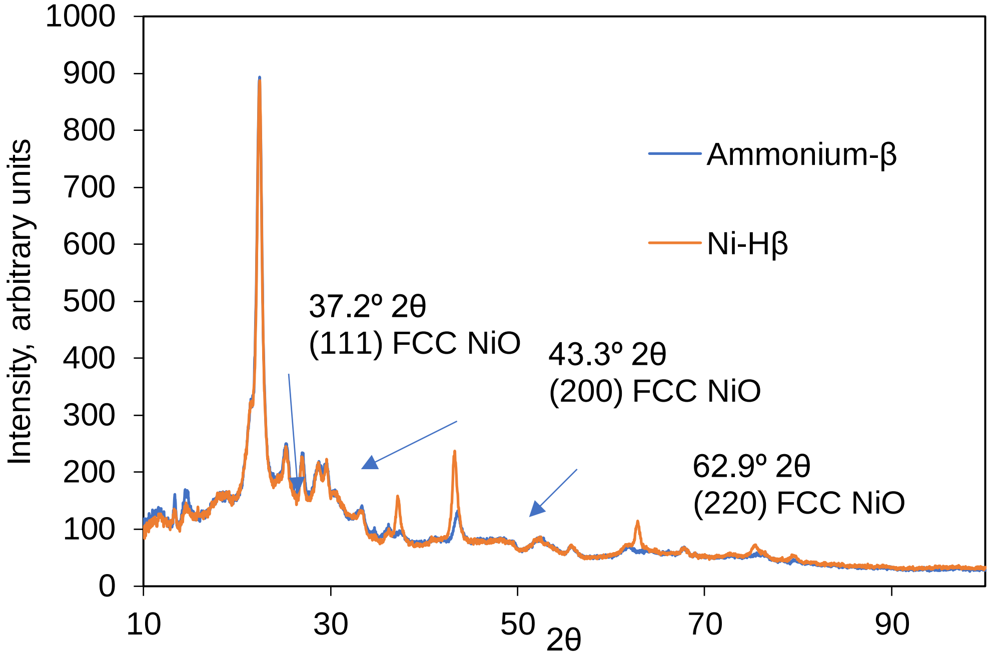

Figure 4.1. Diffraction patterns between NH_4-β and the Ni-Hβ, as adapted from Chapter 2

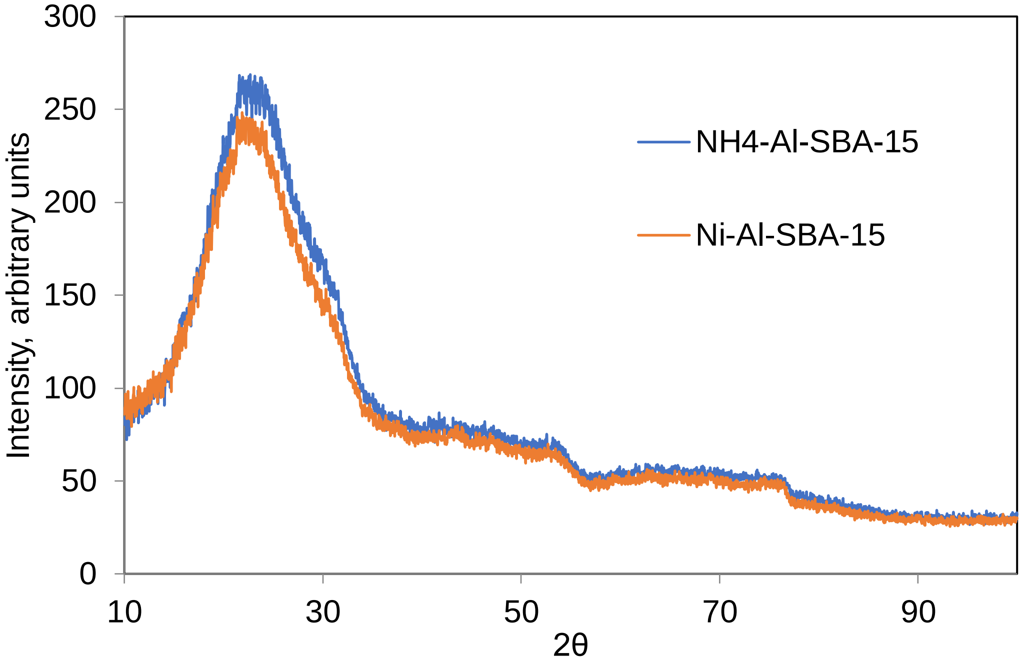

Figure 4.2. Diffraction patterns for NH_4-Al-SBA-15 and the Ni-Al-SBA-15

Through ICP-OES, we determined the nickel content for the Ni-Hβ and Ni-Al-SBA-15 materials to be 3.4 and 0.9 wt.%, respectively. Diffraction patterns comparing the parent forms and the nickel forms of the catalysts are shown in Figure 4.1 and Figure 4.2. In Figure 4.1, it is apparent that there are distinct differences between the parent NH_4-β and the Ni-Hβ materials, expressed by the appearance of three peaks in Ni-Hβ. These peaks are the (111), (200), and (220) Miller plane indices for NiO occurring at 37.2º, 43.3º, and 62.9º 2θ, respectively. In contrast, the diffraction patterns between the NH_4-Al-SBA-15 and the Ni-Al-SBA-15 materials, shown in Figure 4.2, show no distinct peaks at these distinct values of 2θ for NiO. This behavior is consistent with that of the work done by Andrei et al, in which none of the long-range order of their Al-SBA-15 support was disturbed by the incorporation of nickel into the framework[13]. This may also be attributed to the low weight percentage of nickel on the Ni-Al-SBA-15 material. Other authors have attributed that nickel loadings of under 1.8 wt.% are primarily ion-exchanged with the material, and cannot be detected by XRD. After a certain threshold, the exchange sites on the material will be occupied and the remaining the nickel will exist as NiO[11,14]. This may explain the absence of the NiO peaks for the Ni-Al-SBA-15 material we synthesized.

Transmission electron microscopy images of the Ni-Hβ catalysts are shown in Figure 4.3. The darker spots on the image represent the clusters of nickel present on the exterior surface of the zeolite. To the best of our knowledge, this is the first TEM imaging performed on this material. SEM images of fresh and spent Ni-Hβ after reaction are shown in Figure 4.4. From the microscale resolution of the images, it appears that the bulk structure of the catalyst remains largely intact, with very little difference from the fresh catalyst as compared with the spent catalysts after supercritical reaction conditions.

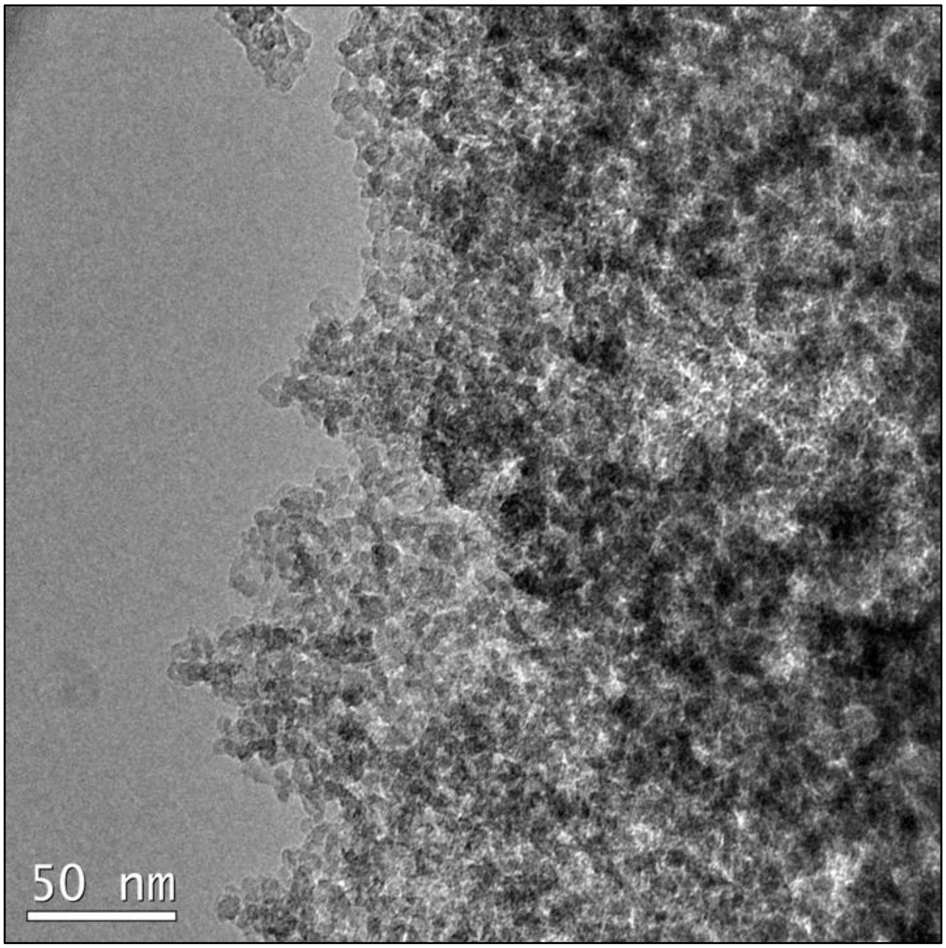

Figure 4.3. TEM image of Ni-Hβ

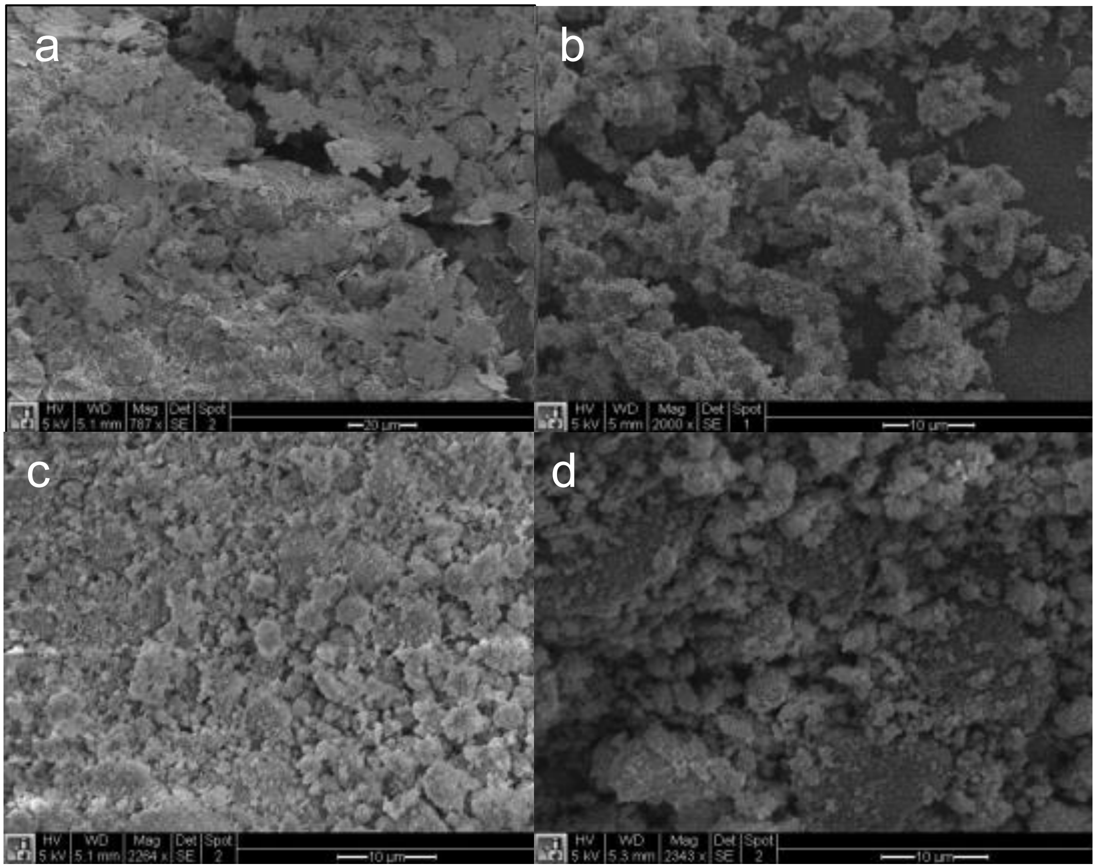

Figure 4.4. SEM images of a) Ni-Hβ before reaction b) Ni-Hβ after reaction at 120ºC, 27.6 bar c) Ni-Hβ after reaction at 30ºC and d) Ni-Hβ at 120ºC, with both b) and c) at supercritical reaction conditions

Effect of Total Pressure

Ni-Hβ: Effect of Total Pressure

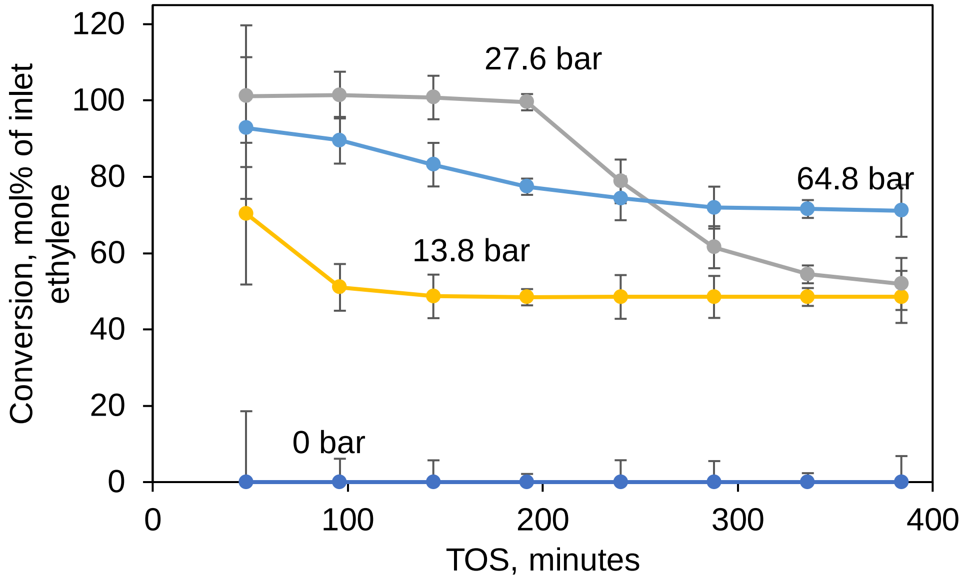

Figure 4.5. Conversion as a function of time-on-stream at several total pressures with Ni-Hβ. Reaction conditions: T: 120ºC, Ni loading: 3.4 wt.%, WHSV: 5.5 hr^{-1}

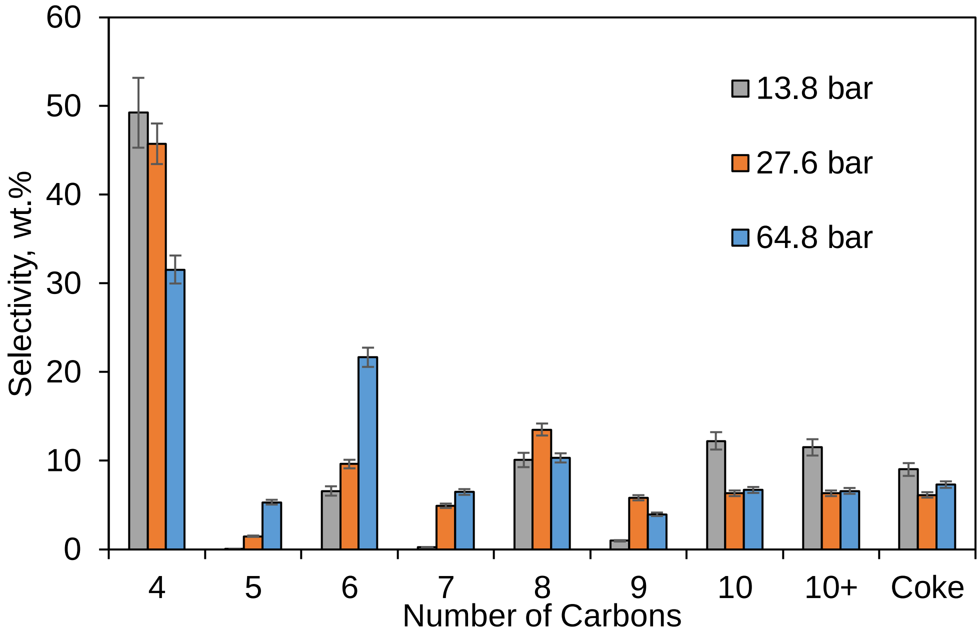

Figure 4.6. Product selectivities as a function of pressure with Ni-Hβ. Reaction conditions: T: 120ºC, Ni loading: 3.4 wt.%, WHSV: 5.5 hr^{-1}

The critical point of ethylene is 9.4°C and 50.6 bar. In the section, we present results at subcritical and supercritical conditions on ethylene oligomerization for Ni-Hβ. Transient conversion curves are shown in Figure 4.5. The steady state conversion was negligible at 0 bar, which indicated that ambient pressure was not sufficient to drive any chemical reaction. There was a significant increase in ethylene conversion at 13.8 bar, with steady state conversion approaching 45-48 mol.%. The product selectivity towards the butene dimer product at 13.8 bar was approximately 50 wt.%. Interestingly, the steady state ethylene conversion at 27.6 bar was approximately equivalent to the conversion obtained for the 13.8 bar experiment, though conversion values were higher at 27.6 bar for most of the 6 hours. The steady state ethylene conversion increased substantially to 71% only after increasing the pressure to 64.8 bar, above the critical point of ethylene. In general, selectivity towards heavier oligomers increased with ethylene pressure. The change in coke selectivity was small in the range of 13.8-64.8 bar.

The unique behavior at supercritical operating conditions can be further explained by referring to the product selectivities. Selectivities of hexenes increased 100% (from 9.6 wt.% to 21.7 wt.%) from 27.6 to 64.8 bar, coinciding with a stark 50% decrease in butene selectivity. The observed increase in hexene selectivity and resulting decrease in butene selectivity may provide insight into the reaction pathways taking place at the catalytic active sites. For ethylene oligomerization reactions at subcritical conditions, the selectivity for butene is high, which is consistent with the Schulz-Flory weighted statistics on product distributions (C4 > C6 > C8 > C10 > … > C_n)[15]. However, tuning the reaction pressure past the critical point of ethylene resulted in a drastic increase in the selectivity for hexenes. This indicates that supercritical ethylene may be influencing the rate of the dimerization and trimerization reaction networks responsible for butene and hexene synthesis, respectively.

For Ni-Hβ, we observed a 50% increase in ethylene conversion and a sharp increase in hexene selectivity switching from subcritical to supercritical conditions. As mentioned previously, supercritical fluids are efficient reaction mediums due to the fluid having gas-like diffusivity and simultaneously having liquid-like solubility[2]. For ethylene oligomerization reactions, deactivation in silica-alumina catalysts has been previously attributed to sequential oligomerization, resulting in the formation of bulkier oligomers on the active sites of the catalyst[15]. The inability of these larger oligomers to desorb from the active sites prevents further ethylene adsorption/reaction steps from occurring, thus resulting in catalyst deactivation and decreased overall activity. However, by incorporating a supercritical fluidic medium, there is a higher likelihood that sequential oligomerization and thereby oligomeric accumulation would be reduced. This behavior could be explained due to supercritical fluids having both higher solubility and improved diffusivity, where primary products, such as smaller oligomers (i.e., butene and hexene) would be formed, desorbed, and solubilized in the bulk fluid more rapidly at supercritical conditions compared to subcritical conditions.

Ni-Al-SBA-15: Effect of Total Pressure

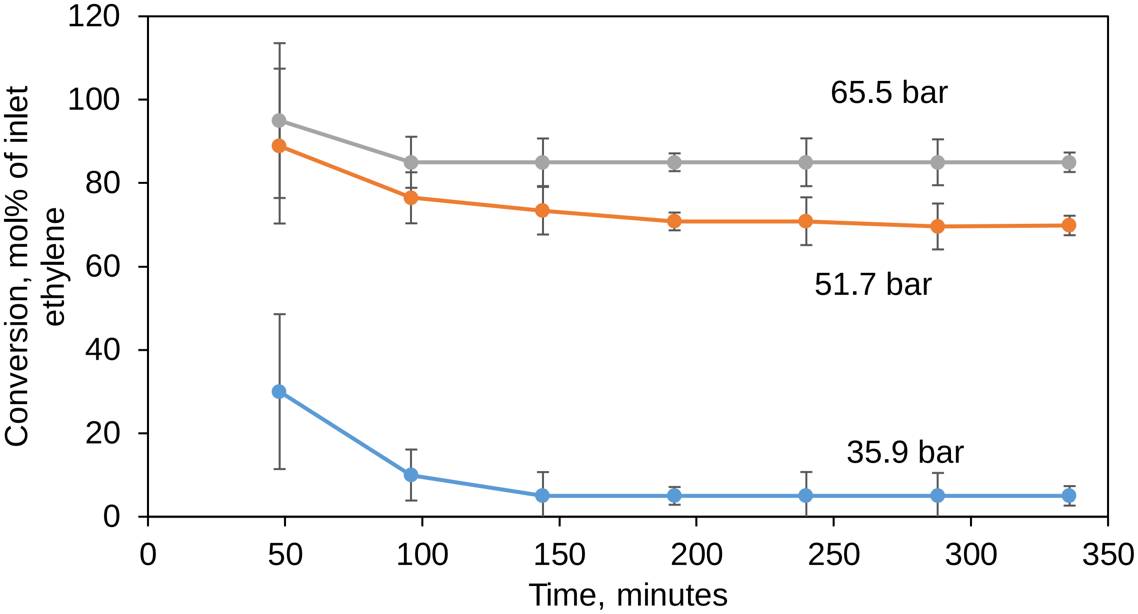

Figure 4.7. Conversion as function of time-on-stream at several pressures for Ni-Al-SBA-15. Reaction conditions: T: 120ºC, Ni loading: 0.9 wt.%, WHSV: 5.5 hr-1

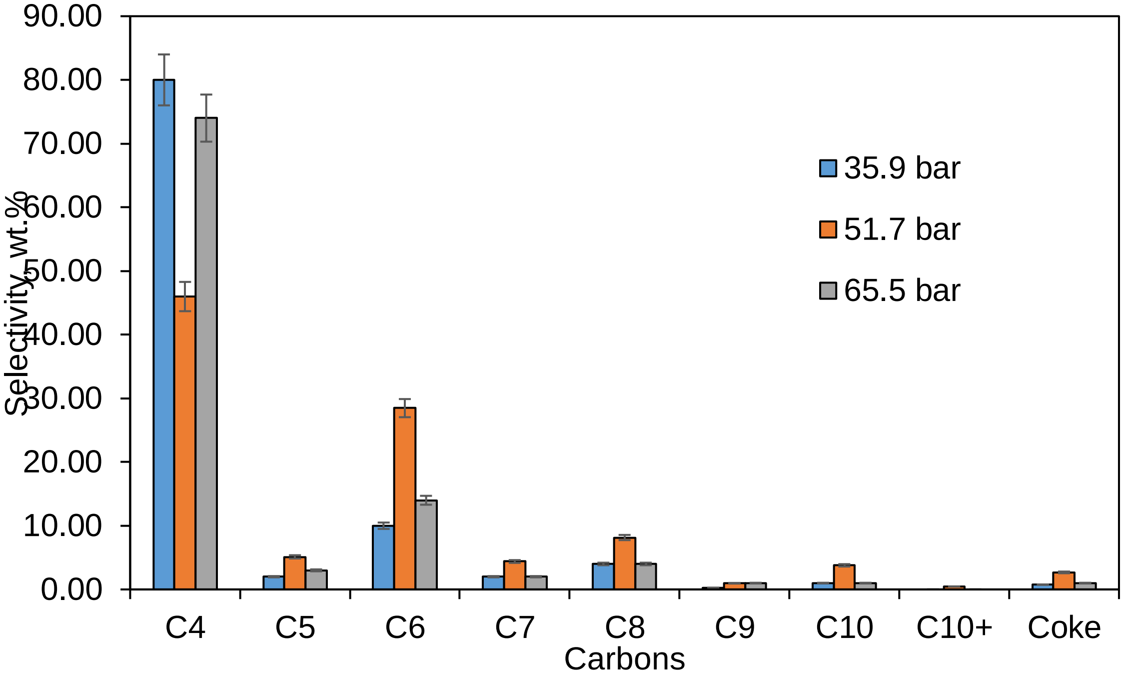

Figure 4.8. Product selectivities as a function of pressure with Ni-Al-SBA-15. Reaction conditions: T: 120ºC, Ni loading: 0.9 wt.%, WHSV: 5.5 hr^{-1}

To determine how the effects observed in the previous section depend on the catalyst, a purely mesoporous catalyst, Ni-Al-SBA-15, was also tested in the packed bed reactor at similar conditions. Ni-Al-SBA-15 has been previously shown to be a suitable catalyst for ethylene oligomerization by Andrei et al[13]. According to Figure 4.7, the ethylene conversion increased with pressure with the Ni-Al-SBA-15 catalyst, which is consistent with the results observed for Ni-Hβ. In contrast, SBA-15 is a mesoporous support with pore diameter of 8.4 nm, so Ni-Al-SBA-15 is not as readily susceptible to coking and accumulation of longer oligomers trapped inside the pores of the support as Ni-Hβ would be, due to the latter consisting of a matrix of micropores and mesopores. The low selectivity towards coke (less than 2.7 wt.%) reflects the effect of the large pore size of the support. Interestingly, compared to Ni-Hβ, higher ethylene partial pressures are necessary to drive the process. At 35.9 bar, small activity was observed, with 5% ethylene conversion. A drastic increase in ethylene conversion (~68%) was observed when the pressure was increased to 51.7 bar. The conversion increased to nearly 85% at 65.5 bar (supercritical conditions).

At 35.9 bar, the selectivity towards butenes is high at 80 wt.%. As we increased the pressure to 51.7 bar, the butene selectivity drops to 46 wt.%. This decrease in butene selectivity is accompanied by increases in hexene selectivity and other higher olefins. This behavior suggests that the reaction pressure is beneficial for facilitating higher oligomerization activity, which is consistent with previous literature[11,16]. Increasing the pressure further past supercritical conditions for Ni-Al-SBA-15, we observed that the butene selectivity increases up to 74 wt.% from 46 wt.%. We hypothesize that butenes are the favored product at supercritical conditions due to their increased solubility in supercritical ethylene at supercritical conditions. As butenes are the direct result of the dimerization reaction, it is likely that the butene is desorbed from the catalyst active site before further ethylene can react to form hexenes, octenes, and longer oligomers. This is apparent as there is a diminished selectivity towards these longer oligomers at supercritical conditions as compared to the product distribution at non-supercritical conditions.

Whereas butenes are the favored product in Ni-Al-SBA-15 at supercritical conditions, hexenes are the more selective product for Ni-Hβ. We propose that the reasons for this discrepancy are due to the inherent steric constraints between the two materials presented by their respective porosimetry. As previously mentioned, Ni-Hβ is a mixture of mesopores and micropores, which would indicate that products are unable to desorb as easily due to the smaller pore sizes present in the material. Meanwhile, SBA-15 is a mesoporous material that has larger pore sizes, which means that products should more easily escape the pores. Due to the increased solubility and diffusivity of the oligomeric products in supercritical ethylene, it is likely that the butenes produced were desorbed and swept away the catalytic active sites, preventing further reaction. This may explain the drastic increase in selectivity towards butenes at 64.8 bar.

The results of the two substrates (SBA-15 and Hβ) demonstrated that the differences between the two materials may only partially be attributed to their pore sizes, as there are multiple differences between the two materials, namely the nickel loading as well as the acid site concentration. At supercritical reaction conditions, butene (74 wt.%) was the prevalent product for SBA-15 (mesoporous) whereas a mixture of butenes (31.6 wt.%) and hexenes (21.7 wt.%) were the prevalent products for the Hβ substrate(microporous/mesoporous).

Effect of Temperature

Ni-Hβ: Effect of Temperature

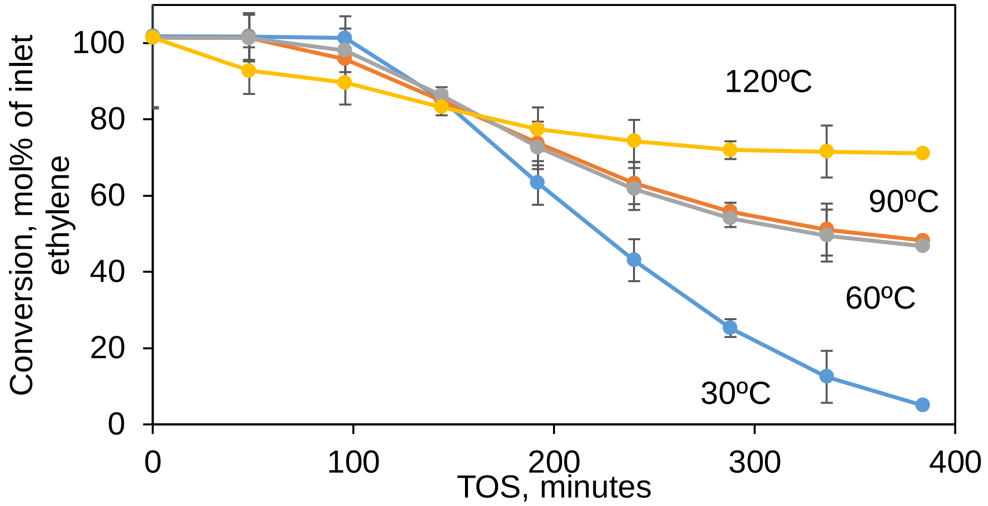

Figure 4.9. Conversion as a function of time at several temperatures with Ni-Hβ. Reaction conditions: P_T: 64.8 bar, Ni loading: 3.4 wt.%, WHSV: 5.5 hr^{-1}

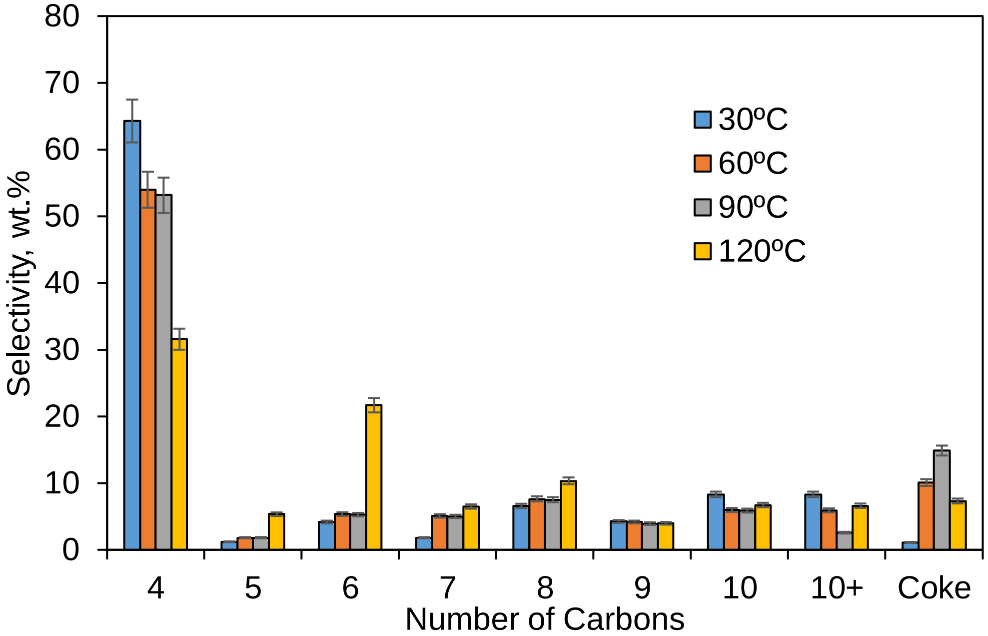

Figure 4.10. Product selectivities as a function of temperature with Ni-Hβ. Reaction conditions: P_T: 64.8 bar, Ni loading: 3.4 wt.%, WHSV: 5.5 hr^{-1}

In this section, we worked with Ni-Hβ at several temperatures, with all experiments in the supercritical range. The temperature had a dramatic effect on the overall ethylene conversion, with steady state conversions as high as 71 wt.% at 120ºC, as shown in Figure 4.9. The higher activity at 120ºC is in stark contrast to the low conversion at 30ºC, with a decrease to nearly 0% conversion by the conclusion of the experiment. The selectivity data is shown in Figure 4.10. We observed that the reaction temperature, at 64.8 bar, is consistent with that of the subcritical results in our previous published work with Ni-Hβ. As the temperature increased, the activity of the catalyst increased as indicated by the higher conversions and progressive increase in selectivity towards hexenes and octenes. As expected, the selectivity towards odd-numbered carbon products increased with temperature. This behavior has been attributed to the increase in the rate of cracking and disproportionation reactions with temperature.

As mentioned in previous research with supercritical ethylene, naphthalene solubility was impacted dramatically by simply altering the temperature at elevated pressures[1]. At lower temperatures, the solubility of naphthalene was orders of magnitude higher than that at higher temperatures. This uptake of the aromatic hydrocarbon would be beneficial for removal of coke deposits in the pores and surface of the catalyst. Based on the previous literature, one would expect that the mitigation of the formation of the coke deposits could potentially improve the overall conversion, activity, and stability of the catalyst to help impact its overall longevity.

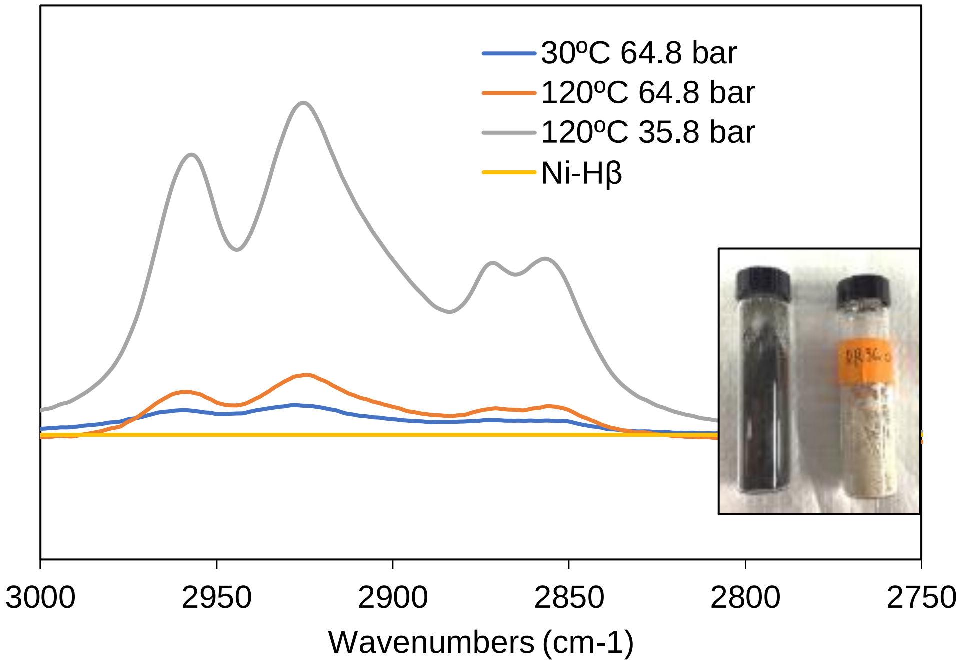

Figure 4.11. FTIR spectra comparing spent catalysts for subcritical conditions (grey, supercritical at 120ºC (orange), and supercritical at 30ºC (blue), with the fresh Ni-Hβ catalyst (yellow). Inset image is of spent catalysts after reaction, with the 30ºC trial shown on the right, and the 120ºC trial shown on the left

After reaction, the catalysts collected from the reactor were analyzed using Fourier Transform infrared (FTIR) spectroscopy. An example of some spent catalysts from the supercritical experiments are shown in the inset of Figure 4.11. The comparison of the infrared (IR) bands from 2800 cm^{-1} to 3100 cm^{-1} from the FTIR spectra are shown in Figure 4.11. With the exception of the fresh Ni-Hβ catalyst, all of the spent catalysts share distinct bands at approximately 2950 cm^{-1}, 2930 cm^{-1}, and 2860 cm^{-1}, which are located in an IR region primarily occupied with C-H bands of asymmetric $-CH_2$ and $-CH_3$ stretching[4]. No bands associated with aromatic =C-H stretches, usually seen in the range of 3200-3000 cm^{-1}, and C=C stretching (1630-1580 cm^{-1}) were observed in the spectra. This result further indicates that the coke residue on the catalyst consists of residual oligomeric compounds instead of solely aromatic hydrocarbons. The IR bands of the coke collected from subcritical conditions (120ºC, 35.8 bar) are more pronounced than that of the bands observed from the catalysts under supercritical conditions. The spectra collected from the two supercritical experiments show decreased bands in these specific wavelengths. This result may be attributed to the increased solubility of the coke at supercritical conditions, which led to the weak bands in the FTIR spectra. The results suggest that supercritical ethylene participates as both a reactant and as a potential solvent for coke precursors during supercritical ethylene oligomerization.

From the temperature studies, we observed that, while there is minimal coke formation observed at 30ºC, there is also minimal catalyst activity due to the low temperature. This behavior, in turn, implies that there is an inherent tradeoff between higher solubility of coke-like material or heavier oligomers and a high enough temperature to impact the overall kinetics of the reactions. The kinetic rate constant for a reaction is a strong function of the temperature and it is likely that, at these low temperatures, that the reactions were unable to proceed. This perspective has also been shared by several authors, where catalytic activity was severely compromised during reaction in supercritical fluids when the reaction temperature was close to the critical temperature[2]. Low temperature supercritical ethylene could still be a viable solvating agent. From a processing standpoint, these low temperature/high pressure conditions for ethylene could be applied to solubilize the coke from the catalyst *in-situ*, serving to regenerate the catalytic active sites without needing to wholly replace the catalyst.

Summary of the Work

This study presented supercritical ethylene as both a reactant and a solvent for ethylene oligomerization reactions. To the best of our knowledge, this is the first time this reaction has been studied at supercritical conditions. We analyzed the influence of reaction pressure over two catalysts with different pore structures, Ni-Hβ (microporous and mesoporous) and Ni-Al-SBA-15 (mesoporous). For both materials, we saw that ethylene conversion increased with pressure, with a noticeable increase in conversion only after increasing the pressure above the critical point of ethylene. In the range of conditions studied, the maximum conversions occurred at 64.8 bar (71%) and 65.5 bar (85%) for Ni-Hβ and Ni-Al-SBA-15, respectively. We also conducted experiments to determine the effect of temperature on ethylene conversion as well as to take advantage of the high solubility properties at lower temperatures. Analogously to pressure, ethylene conversion increased with temperature over Ni-Hβ. We observed negligible coke content at 30ºC, the lowest temperature in our experimental range. However, the activity of the catalyst was greatly affected by the low temperature as the conversion steadily decreased to 5% by the end of the experiment. We attributed this diminished activity due to the influence of the low temperature on the overall reaction kinetics. Low temperature supercritical ethylene could be a useful process fluid to solubilize the coke *in-situ*, but not as a condition for oligomerizing ethylene.

Conclusion

We examined the behavior of ethylene as both a subcritical and supercritical fluid for oligomerization of ethylene. For Ni-Hβ, we found that the ethylene conversion reached a plateau of around 52% at subcritical conditions. The conversion increased again beyond the critical pressure of ethylene, with steady-state conversion approaching 71%. In addition to the conversion, the selectivity of the products was also affected by the change from subcritical to supercritical conditions. Supercritical conditions resulted in a more evenly distributed oligomeric spread because of the increased pressure, whereas subcritical conditions primarily favored the butene product in terms of its selectivity. To further evaluate the impact of supercritical conditions on ethylene oligomerization, we synthesized and tested Ni-Al-SBA-15, a mesoporous catalyst, in the reactor. We observed that the ethylene conversion increased to 85% at supercritical conditions, and the butenes were the prevalent product. To better understand the effects of solubility in supercritical fluids, we also varied the temperature for Ni-Hβ from 30ºC to 120ºC. Our results showed that, at 30ºC, Ni-Hβ was not as active compared to the trial conducted at 120ºC. The diminished activity was attributed to the impact of the low temperature on the kinetics of the reactions. Despite the low activity, we theorize that operating at temperatures near the ethylene critical temperature and exceeding the critical pressure may provide a suitable environment for solubilizing coke, providing a tool for *in-situ* removal of coke from the catalyst.

Acknowledgements

The authors are appreciative of the funding provided by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30407 from the USDA National Institute of Food and Agriculture and the Weyerhaeuser Endowment in Paper Science and Engineering. We gratefully acknowledge the TEM imaging provided by Noah Ferguson and SEM imaging by Heather Wise. Part of this work was conducted at the Molecular Analysis Facility, a National Nanotechnology Coordinated Infrastructure site at the University of Washington which is supported in part by the National Science Foundation (grant ECC-1542101), the University of Washington, the Molecular Engineering & Sciences Institute, the Clean Energy Institute, and the National Institutes of Health.

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Chapter 5: Dissertation Summary and Future Work

Dissertation Summary

In this chapter, we conclude the major study and findings of the present work conducted on ethylene oligomerization. From the addition of our research to existing literature, we outline several potential future experiments that can expand on the gap of knowledge that still exists with heterogeneous catalytic oligomerization of ethylene.

Throughout this work, we reported results for the oligomerization of ethylene over Ni-Hβ in a packed bed reactor. We performed a parameterized study over temperature (30ºC-190ºC), pressure (8.5-25.6 bar), and weighted hourly space velocity (2.0-5.5 hr^{-1}). We observed that the ethylene conversion increased with reaction pressure due primarily to the slower velocities at higher pressures. Increasing the temperature of the reactor led to the formation of larger oligomers and coke, but its effect on the conversion was small. The space velocity played an important role on ethylene conversion and product selectivity, with higher conversions observed at lower space velocities and higher selectivities to butene at higher space velocities. We also conducted a long experiment to determine the activity of the Ni-Hβ catalyst over 72 hours-on-stream at 19.0 bar partial pressure of ethylene, 120ºC, and 3.1 hr^{-1} WHSV. We observed that catalyst deactivation occurred only during the startup period largely due to coke formation. Despite this initial deactivation, negligible coke formation occurred after 8 hours time-on-stream, as the conversion remained steady at 47% for the duration of the experiment.

We also carried out oligomerization of ethylene using Ni-Hβ in a laboratory-scale packed bed reactor for the synthesis of liquid hydrocarbons. We evaluated the effect of several process variables (temperature, pressure, weighted hourly space velocity, and nickel loading) on the liquid hydrocarbon/coke yield, ethylene conversion, and oligomeric product selectivity. The liquid product that we collected, however, was volatile in nature. Because of this high volatility, the mass balances for these experiments were unable to be satisfactorily closed. This volatility also contributed to the skew in the product selectivities, as butenes were the primary volatile component. Increases in pressure resulted in higher ethylene conversion, corresponding to a liquid yield of 12.4 wt.% with 5.7 wt.% coke. As the pressure increased, the selectivity towards octenes doubled alongside a decrease in butenes, which suggested that higher pressures promoted butene dimerization. In the range of temperatures tested, a minimum temperature of 120ºC was required to produce liquid hydrocarbons. The liquid yield increased with temperature, with 17 wt.% observed at 190ºC. Higher reaction temperatures led to the formation of odd-numbered oligomers primarily caused by acid-catalyzed cracking reactions. In the range of space velocities tested, a moderate WHSV of 2.0 hr^{-1} resulted in a local maximum of 10.6 wt.% of liquid hydrocarbon yield. A moderate nickel loading of 3.4 wt.% also resulted in the highest liquid yield out of the three loadings tested (10.6 wt.%). The variation in nickel loading revealed the importance of having a synergistic balance of nickel and acid sites on the catalyst to maximize ethylene conversion and maintain high liquid hydrocarbon yield.

Lastly, we used supercritical ethylene as both a solvent and as a reactant for ethylene oligomerization over two silica-alumina type catalysts: Ni-Hβ and Ni-Al-SBA-15. Specifically, the effect of pressure and temperature on the overall conversion and product selectivity were evaluated in the range from 0 to 65 bar and 30 to 120ºC. At subcritical conditions, the ethylene conversion reached a plateau of around 50%. By increasing the pressure past the critical point of ethylene, the conversion drastically increased to 71%. The increased conversion can be attributed to the solubility of certain oligomers, namely butene, in supercritical ethylene that promotes desorption from catalytic active site before further oligomerization. We also tested a mesoporous catalyst, Ni-Al-SBA-15 and observed conversion trends analogous to that of Ni-Hβ. At supercritical conditions, ethylene oligomerization over Ni-Al-SBA-15 was more selective towards the butene product, with nearly 74 wt.% butenes observed. The catalyst activity increased with temperature from 30ºC to 120ºC. The experiment conducted at 30ºC showed very little activity and ethylene conversion, however it effectively heavy molecular weight species from the catalyst. This condition, albeit being not effective for ethylene oligomerization, could be implemented as an *in-situ* technique to regenerate the catalyst during process operation.

Proposed Future Work

Recycle stream

We conducted all the reactor experiments in a single-pass packed bed reactor, observing the effects of temperature, pressure, weight hourly space velocity, and nickel loading on ethylene conversion and product selectivity. While the results are useful at a single-pass standpoint, an interesting way to further expand on the potential industrial application of the catalysts used in this study would be to incorporate them in a packed bed reactor consisting of a recycle stream. The purpose of the recycle stream would be to take the permanent gas components of the reactor effluent (primarily unreacted ethylene and butene) and recycle these compounds back into the inlet feed of the reactor. This work would expand on the area of knowledge in several ways. The first is that, the potential reactions that could occur would involve butene oligomerization over Ni-Hβ. To the best of our knowledge, this type of reaction has not yet been explored in the literature. In addition, the incorporation of a recycle stream in a laboratory reactor may generate new insights into online gas chromatography sampling methods and process control not previously discussed. The incorporation of a single-pass reactor, at a laboratory scale, is straightforward. However, the expansion of such a system to incorporate a recycle stream would deliver new insights as precise process control and monitoring would be paramount to the success of such a system. Due to the nature of such a system, it is likely that a recycle stream would improve the overall ethylene conversion. This, in turn, could lead to higher production of oligomers and overall catalyst activity. However, it remains to be seen whether a recycle stream may induce butene oligomerization reactions as well. The incorporation of a recycle stream for the ethylene oligomerization reactor would be relevant at both an academic and industrial standpoint.

Investigation of the nature of the nickel active site

The nature of the nickel metal site is still an area of debate. The oxidation state has been a highly contested topic, with several authors suggesting a range of oxidation states of Ni^{2+} and Ni^{+} as the nickel active site[1]. In the present work, the catalysts we synthesized consisted of Ni^{2+} cations derived from nickel (II) nitrate ($Ni(NO_3)_2*6H_2O$, Sigma-Aldrich). To better understand the state of the nickel species, adjusting the exchange capacity of the support may provide further insight into this area. Deimund et al. explored the use of nickel metal support on zincosilicates instead of aluminosilicates for propylene oligomerization in a fixed bed reactor. The rationale behind using a zincosilicate is due to the presence of zinc affecting the framework charge of the material, as suggested in Figure 5.1.

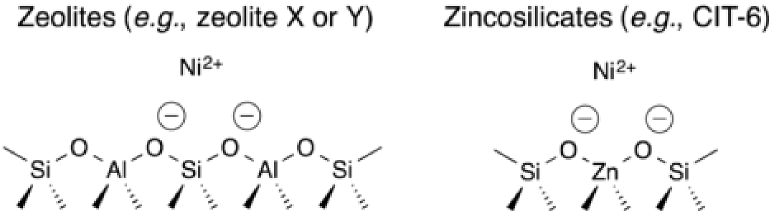

Figure 5.1. Comparison of the framework charge compensation in zeolites versus that of zincosilicates[2]

The authors suggest the incorporation of zinc instead of aluminum due to the drawback that aluminosilicate materials necessitate the incorporation of two nearby framework aluminum atoms to compensate for the charge of Ni^{2+}. In addition, a Brønsted acid site is generated for every aluminum site that is nonexchanged, which can generate undesirable side reactions, such as cracking[2,3]. On the other hand, framework Zn^{2+} creates two anionic charge vacancies for each zinc atom incorporated in the framework, allowing for a 1:1 exchange ratio. A future experiment could entail expanding on the work conducted by Deimund and coworkers by synthesizing a similar zincosilicate and observing the difference in Brønsted acidity and nickel loading in the material.

The source of nickel used could be varied as well, as the nickel used in our studies was divalent. A source of monovalent nickel (Ni^+) can be used as well in the synthesis procedure to determine how the oxidation state of the metal ion impacts its incorporation in the framework.

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