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Los Angeles

Co-Processing of

Alkanes and Oxygenates on Metal-Exchanged Acidic Zeolites

A thesis submitted in partial satisfaction of the

requirements for the degree Masters of Science

in Chemical Engineering

by

Julie Ann Miller

2017

ABSTRACT OF THE THESIS

Co-Processing of

Alkanes and Oxygenates on Metal-Exchanged Acidic Zeolites

by

Julie Ann Miller

Masters of Science in Chemical Engineering

University of California, Los Angeles, 2017

Professor Dante A. Simonetti, Chair

Most sources agree that a solely renewable energy future is years off at best and therefore

carbon based fuel sources will continue to play a substantial role in energy production. For this

reason, this research focused on one path towards improving the efficiency and total usability of

carbon based resources. Current processing methods for biofuels produce many short chain

heavily oxygenated hydrocarbons at low yield. These molecules require further upgrading to be

useful as fuels or chemical intermediates, primarily, C-C bond formation to form longer

hydrocarbon chains and hydro-deoxygenation to remove O-atoms. This research focuses on

discovering catalyst site requirements for the selective formation of C-C bonds between aldehyde

molecules with the removal of O-atoms via dehydration/hydrogenation steps with H-atoms

derived from alkanes. Kinetic experiments show that butyraldehyde can be converted to 2-

ethyl-2-hexenal, via acid-catalyzed aldol-condensation at 200°C under a 4 kPa partial pressure of butyraldehyde on the acid site of BEA zeolite at a selectivity of 94% and rate of 8.16×10^{-10} mol s^{-1} Al^{-1}. The selectivity shifts toward aromatization products (triethylbenzene and xylenes) at a selectivity of 20% and cracking products (propene and pentene) at a selectivity of 18% as temperature increases from 200°C to 300°C. Addition of H-atoms as isobutane increases the rate of production of 2-ethyl-2-hexenal (from 8.16×10^{-10} mol s^{-1} Al^{-1} to 8.54×10^{-10} mol s^{-1} Al^{-1}) but shifts the selectivity towards triethylbenzene (from 6% to 14%).

Using a metal hydrogen transfer catalyst (in the form of Zn-exchanged BEA) causes a shift in the selectivity of butyraldehyde reactions toward 2-ethyl-2-hexenal (from 94% to 98%) which indicates metal catalyzed hydrogen transfer to unsaturated species formed during aldol-condensation. Using a different metal hydrogen transfer catalyst (in the form of Co-exchanged BEA) causes a shift in the selectivity of butyraldehyde reactions from 2-ethyl-2-hexenal (from 94% to 84%) towards cracking products (16% C_4 products from butyraldehyde, 17% C_5 products with the addition of isobutane) .

The thesis of Julie Ann Miller is approved.

Panagiotis D. Christofides

Philippe Sautet

Dante A. Simonetti, Committee Chair

University of California, Los Angeles

2017

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1 Background

Over the last several years, environmental concerns have driven the development of new technologies in an effort to decrease the impact of society's energy usage on the planet. For this reason, the focus of the energy industry has increasingly shifted towards renewable energy. However, it is clear that petroleum and other carbon based fuels will continue to play a critical role in the coming years[1,2]. Additionally, carbon based alternative fuels, such as biomass, are being heavily considered as an alternative to traditional fossil fuels. Because of these factors, further research is required to increase the efficiency of fuels and chemical intermediates derived from traditional and alternative, carbon-based energy resources.

Many biomass conversion processes predominantly produce short chain oxygenates (e.g., alcohols, aldehyde, and ketones)[3]. These products need to be both deoxygenated and upgraded to longer carbon chain lengths in order to be used as fuel. This conversion has been demonstrated to be feasible through the use of various material and biological catalysts[4,5,6]. However, the previously demonstrated methods have two main drawbacks. The first is that these methods produce a very wide product range[7,8]. The second drawback is that these processes require high levels of hydrogen for deoxygenation[9,10]. Both of these drawbacks can be mitigated by the method of co-processing discussed in this thesis.

Previous work has been done into determining the specific reaction mechanisms butyraldehyde (butanal) undergoes when exposed to zeolite catalysts. In general there are two major routes of reaction that are of interest from the butyraldehyde molecule. The first is a Trischenko esterification that eventually leads to the formation of a C_7 molecule. The second pathway begins with an aldol-condensation reaction that forms 2-ethyl-2-hexenal. This molecule can then undergo a wide array of reactions[11]. This general reaction matrix of butyraldehyde is

shown in Figure 1-1. Th butyraldehyde molecules can either undergo Trischenko esterification to a C_8 followed by a hydride transfer to heptene or it can undergo an aldol-condensation to 2-ethyl-2-hexenal. This second reaction can lead to either a further aldol-condensation reaction or a hydride transfer. The products of aldol-condensation reactions can additionally undergo aromatization and cracking. Through the use of specific zeolite and metal-exchanged zeolite catalysts this reaction matrix can be selectively tuned to a desired product(e.g. Y catalyst lead to Trischenko esterification and BEA leads to aldol-condensation)[12,13].

The reaction of isobutane over zeolite catalysts and metal exchanged zeolites has also been studied in detail. The general reaction scheme of isobutane can be seen in Figure 1-2. The isobutane molecules first undergoes a hydride transfer reaction followed by oligomerization. This oligomerization product can then either undergo a second hydride transfer reaction, an isomerization reaction, or beta-scission cracking.

The first reaction step of isobutane over zeolite catalysts is a hydride transfer reaction. The hydride transfer reaction is particularly important because it leads to the formation of alkanes. Desorption of species as alkanes improves catalyst stability by mitigating aromatization reactions that form coke depositions that deactivate the catalyst. Using alkanes during the oxygenate reactions shown in Figure 1-1 is advantageous because the alkanes have sufficient hydrogen to both remove oxygen atoms and to hydrogenate unsaturated hydrocarbons to prevent side

reactions that form aromatic species[11,14].
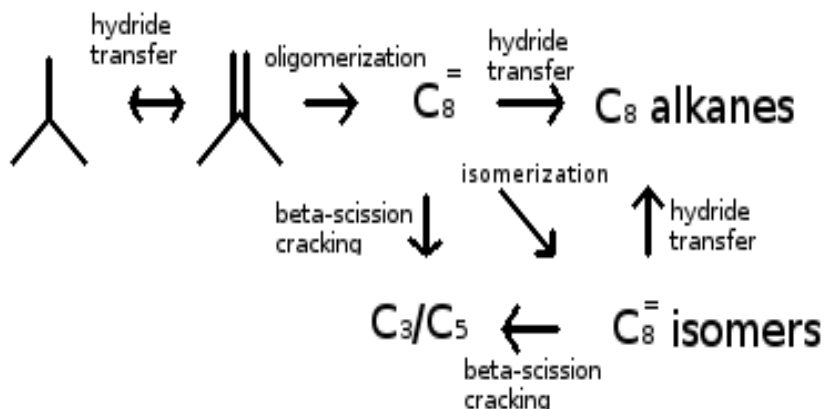
Figure 1-2: The general reaction pathways of isobutane over zeolite catalysts.

Over the course of this work, reaction kinetic measurements were used to study the effect of isobutane on acid-catalyzed aldol-condensation reaction networks and to probe the catalytic site requirements for hydrogen transfer reactions from isobutane to unsaturated the bond in aldehydes. The results of these experiments show that metal exchanged zeolites have a marked effect on the reaction product distribution as well as that changing the temperature and space velocity of the system allows for selective tuning of said product distribution[15].

2 Methods

Reaction experiments were conducted in an apparatus consisting of a stainless steel tubular reactor (6.4 mm outer diameter) containing the catalyst (50-100 mg; 180–250 μm particles) held in place by quartz wool. Temperatures were measured with a type-K thermocouple placed at the external reactor wall and held constant using a resistive heater (Applied Test Systems 3210-75-8-12) equipped with a digital feedback controller (Applied Test Systems 15-13093-2). All samples were heated to reaction temperature (at 1 °C min^{-1}) in flowing He (0.33 cm^3 s^{-1}) before introducing reactant mixtures. The chemical composition of the reactor effluent was determined by gas chromatography using flame ionization and mass selective detectors (Agilent Technologies 5977A/ Agilent Technologies 7890B). Reactant mixtures consisted of butyraldehyde (>99.5 Sigma-Aldrich) and/or isobutane (>99 Gas Innovations) mixed with He (Ultra-high purity, Airgas). Mass flow controllers (MKS GE50) were used to regulate the flow rates of isobutane and He. Butyraldehyde was added to the gaseous reactant stream by introducing liquid using a gas tight syringe and syringe infusion pump into a vaporization zone heated to 10°C above the normal boiling point of butyraldehyde at reaction pressure. Space velocities and reactant concentrations were varied by changing the flow rates of reactants and/or the catalyst bed size. Reactant feed lines (downstream of the vaporization zone) and reactor effluent lines were heated to 200°C to ensure all species remained in the vapor phase.

The ammonium forms of zeolites BEA (Si/Al = 12.5), MFI (Si/Al =11.5), MOR (Si/Al=10) and the acid form of Y zeolite (Si/Al = 15) were purchased from Zeolyst International. NH$_4$-zeolite samples were converted to their acid forms by heating to 500°C (at 1 °C min^{-1}) and holding for 4 h in flowing air (11.7 cm^3 s^{-1} g^{-1}). The air was treated for moisture and hydrocarbon removal using a Tsunami Regenerative Dryer (SR2 B121JD) prior to use. Metal-exchanged

BEA zeolites (Co-BEA and Zn-BEA) were synthesized via incipient wetness impregnation. H-BEA samples (4g) were impregnated with 10 mL of 0.69 M aqueous solutions of cobalt nitrate (98% Sigma-Aldrich) or zinc nitrate (98% Sigma-Aldrich). These samples were treated by heating to 500°C (at 1 °C min^{-1}) and holding for 20 hr followed by heating to 500°C (at 1 °C min^{-1}) and holding for 4 h in flowing air (11.7 cm^3 s^{-1} g^{-1}). This method has been previously shown to effectively exchange protons for Co^{2+} or Zn^{2+} ions within the cages of BEA[10, 14, 15].

3 Results and Discussion

3.1 Isobutane Reactivity: In order for the study of the co-processing of short chain oxygenates and alkanes to be properly analyzed, both feeds had to be individually characterized. Initially, a mix of isobutane and inert helium was fed to the reactor in order to establish its product distribution. More specifically, isobutane was reacted over four different zeolite catalysts; MFI, MOR, BEA, and Y. The resulting product distributions (presented as carbon selectivities) are presented in Figure 3-1.
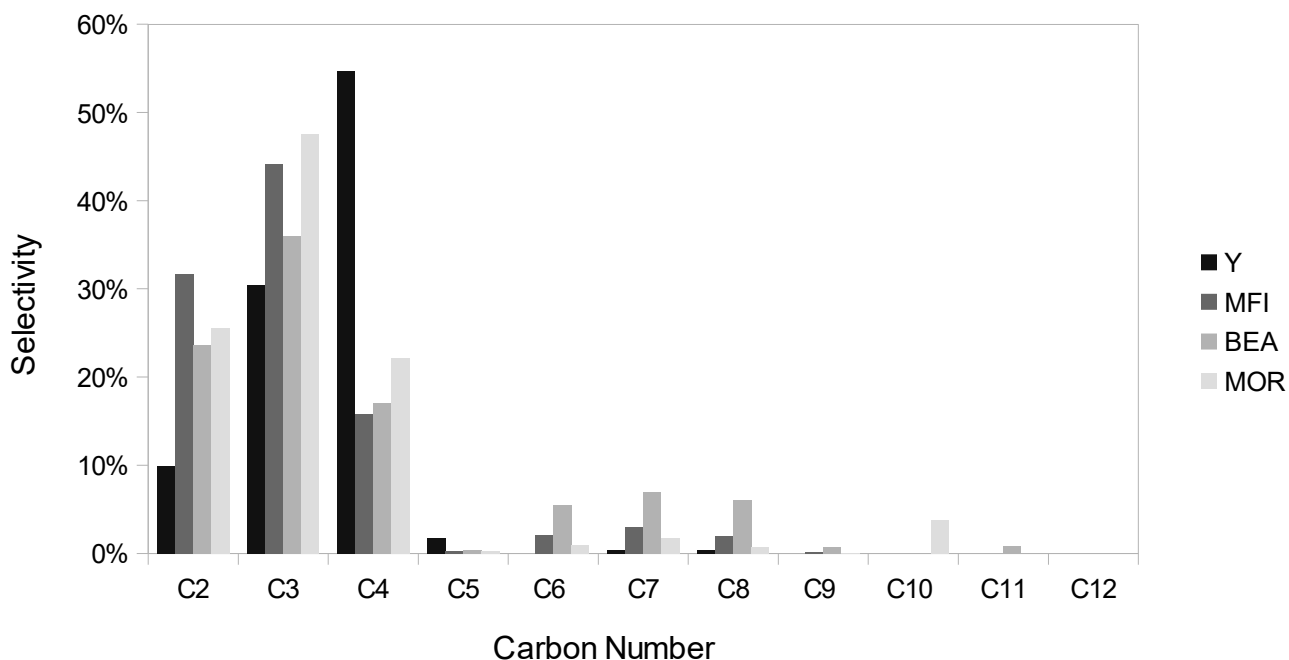
Figure 3-1: Selectivity to products with various carbon chain lengths from reaction of 4 kPa of isobutane on H-Y, H-MFI, H-BEA, and H-MOR zeolites at 300°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm).Total conversion of isobutane: Y-13%, MFI-74%, BEA-93%, MOR-61%.

The distributions in Figure 3-1 clearly indicate different reaction paths for isobutane conversion on each zeolite. The ideal co-processing material would be one that favors hydride transfer and minimizes isomerization. Additionally, oligomerization should be limited as this pathway leads to cracking and thus C_1-C_4 products from the alkene. BEA is clearly the most

effective at creating mid-range carbon chains (C_6-C_8) and was also able to produce some longer chain molecules. This is a strong indication that it is likely to be the best at promoting hydride transfer. Y showed significant selectivity towards the isomers of isobutane indicating high rates of isomerization as well as cracking of oligomerization products. MFI and MOR demonstrated similar reactivity in the lower carbon numbers but with MFI preferring mid-range products and MOR being more inclined to form even longer chains. For this reason, MOR was deemed not necessary for further study as it was similar to MFI but less favorable. From this set of experiments it is also clear that each catalyst demonstrated a different reactivity.

As can been seen above, BEA was the most reactive out of the four zeolites tested. This catalyst was able to produce naphthalene from the fed isobutane. This is a strong indication that almost all plausible reaction pathways were happening. Under conditions where oligomerization, cracking, isomerization and others can all take place it would be incredibly difficult to map a reaction network and changes to that network. For this reason, lower temperature conditions were necessary for further study.

Figure 3-1 shows that all four zeolites demonstrate high reactivity at a temperature of 490°C. However, the conversion drops to below one percent when operating at a temperature of 300°C. Therefore, below 300°C oligomerization-cracking reactions of isobutane will be negligible, and all products derived from isobutane-aldehyde feeds could be taken as the result of the aldehyde reaction network. These milder conditions would also allow for more detailed reaction studies as changes in the product distribution could be easily attributed to interaction changes with the surface and not just the pure excess of kinetic energy of the system. Therefore, further reactions would be performed at temperatures less than 300°C to eliminate alkane reactions dominating the reaction sequence.

3.2 Butyraldehyde Reactivity: As a result of the previous experiments, the initial condition for the butyraldehyde tests was selected at 300°C. Two microliters of liquid butyraldehyde per minute was chosen as the flow rate that would yield approximately 4 kPa of pressure in the system once converted to a gaseous form. The results of this experiment over Y, MFI, and BEA catalysts are presented in Figure 3-2.
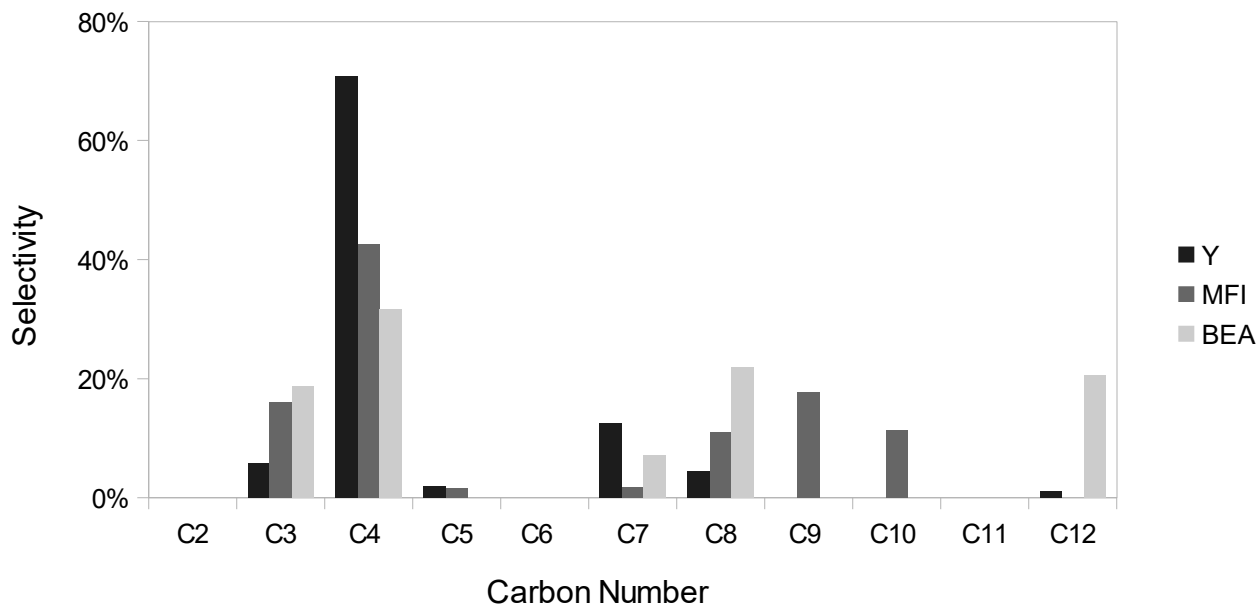
Figure 3-2: Selectivity to products with various carbon chain lengths from reaction of 4 kPa of butyraldehyde on H-Y, H-MFI, and H-BEA zeolites at 300°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm).

MFI catalyst displayed the highest selectivity to C_8 and C_4 products. However it also created quite a bit of C_9, C_{10}, C_2, and C_3 products. This array indicates that MFI facilitates aromatization to larger cyclic molecules as well as the cracking of these large molecules. Therefore MFI is capable of the hydride transfer reaction that is of interest, however all possible subsequent steps are then performed and it would be difficult to tune this reaction specifically to only incorporate the aldehyde for hydride transfer. These results show that MFI would be the preferred catalyst for further study into the aromatization reaction.

Y catalyst made a substantial amount of both butenes and of heptene. This indicates that Y is capable of performing isomerization and Trischenko esterification. The high concentration of heptanone found in the products further indicates this postulation. Y should thus be considered for further study into the hydride transfer reaction that occurs after the Trischenko esterification.

BEA demonstrated strong selectivity towards C_4, C_8, and C_{12} molecules. This is a strong indication that the major pathway followed over the BEA catalyst is the aldol-condensation reaction. Furthermore, the C_8 and C_{12} product distributions lean heavily towards 2-ethyl-2-hexenal and 1,3,5 triethylbenzene. This clear product distribution shows that BEA would be a good first candidate for further study of tuning the reaction matrix towards the aldol-condensation reaction products which could then be hydrogenated by isobutane via hydride transfer from the aldehyde.

Reactions of butyraldehyde on BEA zeolite were further studied because BEA gave the highest selectivity toward aldol-condensation dimers and trimers. Figure 3-3 shows the effect of decreasing temperature on the carbon selectivity for butyraldehyde conversion on BEA. As temperature decreases from 300C to 200C, selectivity shifts toward the aldol-condensation dimer at the expense of subsequent C-C bond formation reactions.
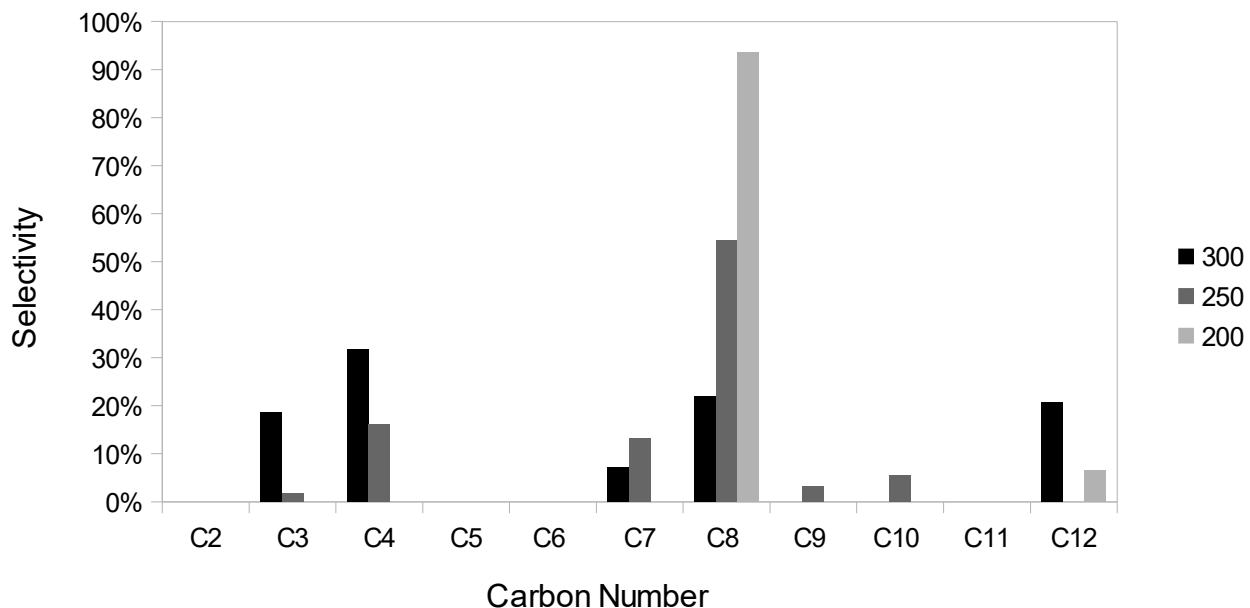
Figure 3-3: Selectivity to products with various carbon chain lengths from reaction of 4 kPa of butyraldehyde on H-BEA zeolite at 300°C, 250°C, and 200°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate over 0.1 g of catalyst at ambient pressure (~1 atm). Total conversion of butyraldehyde: 300-20%, 250-7%, 200-3%.

After one hour of reaction, the system was assumed to have reached steady state. The conversion of butyraldehyde at a temperature of 200°C was 3%. This was deemed a suitable conversion to continue investigating the reaction matrix at this temperature. Additionally it should be noted that the products at this temperature are almost completely C$_8$ and C$_{12}$. This indicates that the first reaction to take place inside the reactor is likely a dimerization of the butyraldehyde to 2-ethyl -2-hexanal. To further support this postulation, the same reaction was run at higher space velocities. The results of this experiment are presented in Figure 3-4.
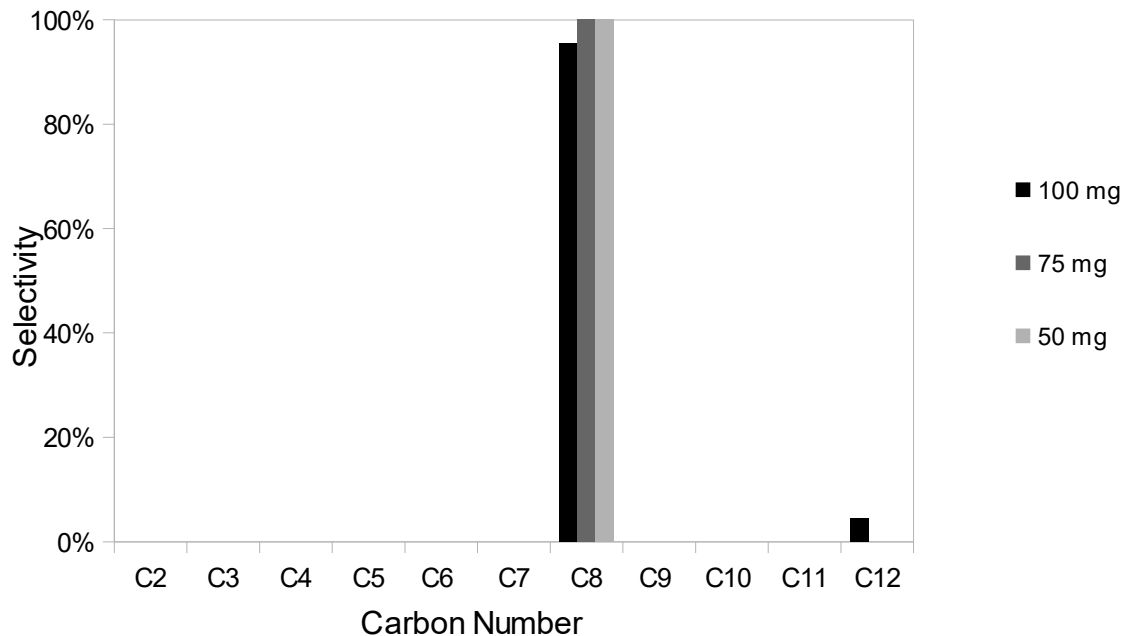
Figure 3-4: Selectivity to products with various carbon chain lengths from reaction of 4 kPa of butyraldehyde on H-BEA zeolite at 300°C. Reactions were carried out using a 20 cm³ min⁻¹ flowrate over 0.1 g, 0.075 g, and 0.050 g of catalyst at ambient pressure (~1 atm).

The graph of space velocities above shows that as the amount of catalyst decreases, the selectivity to the C_8 product increases. This is strong evidence that the dimerization to 2-ethyl -2-hexanal is indeed the primary reaction for butyraldhyde on BEA zeolite.

3.3 Co-Reactivity on Acid Sites: Once the behaviors of both individual molecules were established, experimentation could begin to elucidate their interactions. First isobutane and butyraldehyde were fed to a reactor at 300°C. This was done to examine the differences in interaction over different surfaces and to re-evaluate the assumption that BEA would be the best facilitator of the dimerization reaction. Specifically, these experiments were run to determine if the butyraldehyde products would activate the isobutane molecules to facilitate hydride transfer resulting in an increase in reactivity and a shift in the overall selectivity. The selectivity results of this experiment are presented in Figure 3-5. Because of the lower conversions at low

temperatures, these were performed at 300°C to clarify the differences between the three catalysts. The most notable differences between the reaction of butyraldehyde and the reaction that occurs during the co-processing of butyraldehyde and isobutane is the range of carbon chains formed. The comparison between the two reactions over the three different catalysts is presented below in Figure 3-6.

Figure 3-5: Selectivity to products with various carbon chain lengths from reaction of 4 kPA of isobutane and 4 kPa of butyraldehyde on H-Y, H-MFI, and H-BEA zeolites at 300°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm).
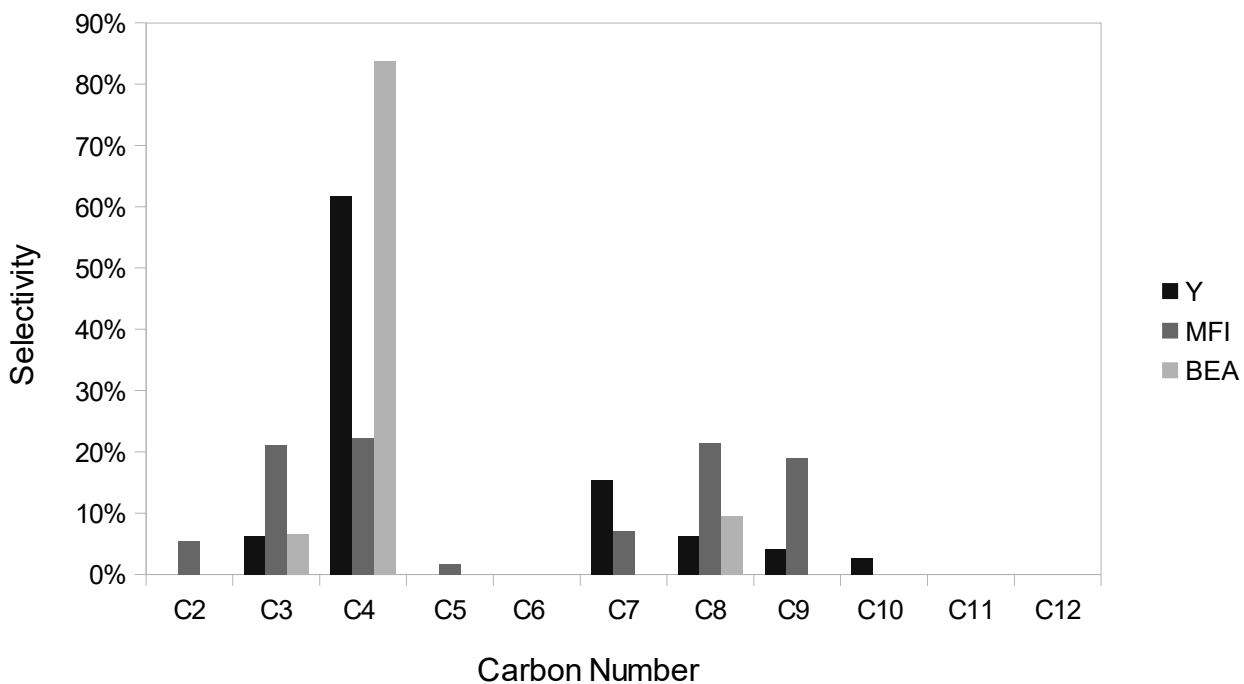
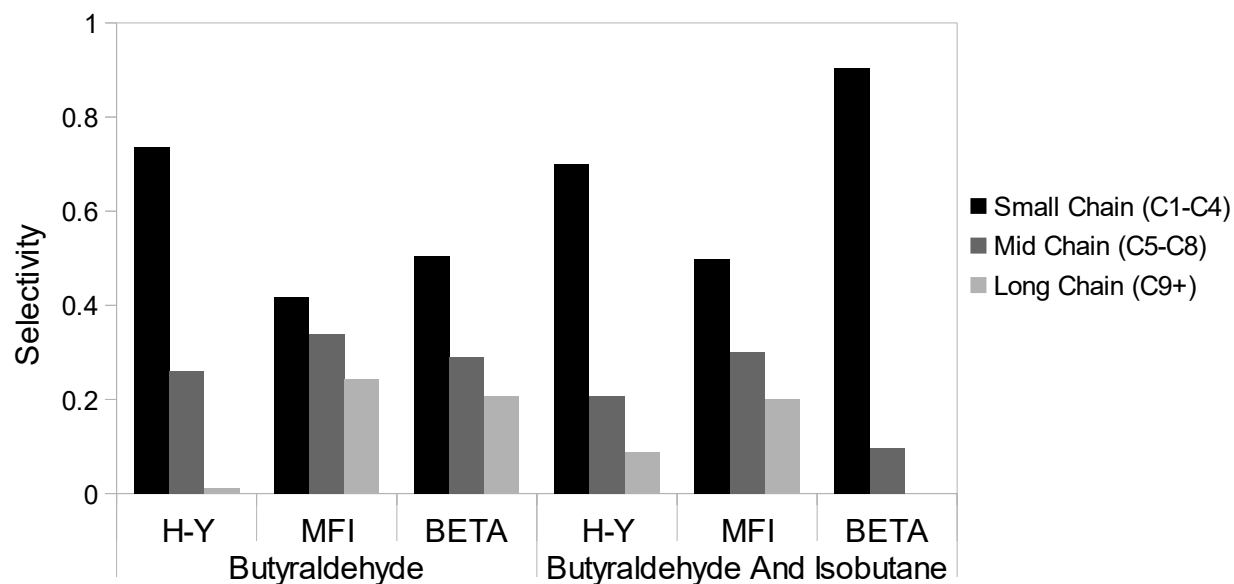**Figure 3-6:** Selectivity to products with various carbon chain lengths from reaction of 4 kPA of butyraldehyde on H-Y, H-MFI, and H-BEA zeolites at 300°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm).

Using this reaction data, the effect on the reaction matrix of co-processing with isobutane can be seen. When co-processing, it is important to take note of the new species of products that are the result of inter-molecular interactions. Under these conditions, isobutane was postulated to be mainly a hydrogen donor that helped to cut off side reactions by saturating molecules. As such, it was also reasonable to expect that the addition of isobutane would affect the reaction differently over the different catalysts due to their predilection to facilitate certain reactions.

Over MFI, butyraldehyde by itself was capable of producing C$_{10}$, however this product almost disappeared once isobutane was added. The selectivity to C$_8$ and C$_7$ products also decreases. This would indicate that isobutane does not hinder the aldol-condensation reaction over MFI but it does donate hydrogen so as to prevent aromatization.

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The ability of isobutane to act as a hydrogen donor is further demonstrated by the shift in selectivity over Y. The addition of isobutane over this catalyst led to a dramatic increase in selectivity to longer chain molecules. In order to form heptene molecules, butyraldehyde undergoes Trischenko esterification followed by a hydride transfer reaction. Therefore the ability of isobutane to donate hydrogen to desorb Trischenko esterification products is useful to furthering this path and an increase in the selectivity to the final product is evident.

BEA catalyst was studied extensively above for its ability to selectively convert the feed to 2-ethyl -2-hexenal through an aldol-condensation reaction. Figure 3-7 shows the difference in the product distribution between the butyraldehyde reaction and the co-processing of butyraldehyde and isobutane. It is easy to see that isobutane hinders the production of this molecule. This is likely through its ability to donate a hydrogen and saturate bonds. The fact that there is a large uptick in the production of C_4 molecules further supports this theory.

Figure 3-7: Selectivity to C_4 and C_8 products from reaction of 4 kPA of butyraldehyde (black bars) compared with the reaction of 4 kPa of butyraldehyde and 4 kPa of isobutane (grey bars) on H-BEA zeolite at 300°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm).
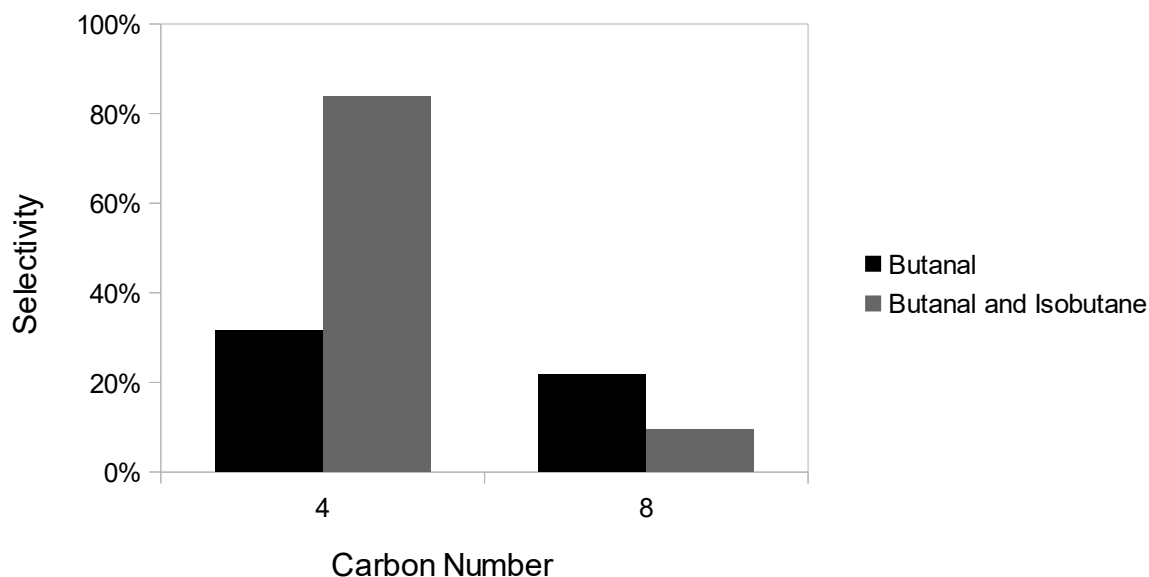
Overall, the initial hypothesis of isobutane acting as a hydrogen donor and reducing the production of side products was proven to be true. The one noted exception is that over Y the hydrogen donation was shown to further the reaction to heptene as hydrogen donation in this case is necessary. Furthermore, the co-processing reaction over BEA further shows that BEA is the most advantageous catalyst for further study as the addition of isobutane directly effects the first aldol-condensation reaction of the butyraldehyde molecule.

3.4 Co-Reactivity on Metal-Exchanged Zeolites: After establishing reaction paths of butyraldehyde and isobutane/butyraldehyde on solid acids, the next investigation involved adding a hydrogenation-dehydrogenation functionality to the catalyst (in the form of Zn and Co ions). Using the incipient wetness method of impregnation, protons within the BEA zeolite

micropores were exchanged with Zn and Co. This was carried out to a 10% by mass loading of metal ions for a final M/H^+ ratio of approximately 11. Further reactions were then carried out over these metal-BEA zeolites. Again, the two reactants by themselves had to be characterized over the surface as well as the co-processing reaction. Isobutane demonstrated almost no reactivity at 200°C, and the product selectivities for butyraldehyde and isobutane/butyraldehyde mixtures are shown in Figures 3-8 and 3-9 for Zn-BEA and Co-BEA respectively. Zn-BEA selectively forms 2-ethyl-2-hexenal from reactions of butyraldehyde. However, when isobutane is added to the system, the product selectivity shifts toward the formation of C_5 and C_7 alkanes. The formation of C_7 hydrocarbons indicates that the presence of Zn ions facilitates the H-transfer from isobutane to adsorbed Trischenko esterification products, thus increasing the rate of this reaction pathway at the expense of aldol-condensation.

The presence of Co sites influenced the reactivity of butyraldehyde and isobutane/butyraldehyde feeds (Figure 3-9). The presence of Co sites leads to an increase in the formation of butenes during reactions of butyraldehyde and to the formation of butenes and C_5 hydrocarbons during reactions of isobutane/butyraldehyde. This shift in product selectivity suggest that Co ions facilitate cracking of aldol condensation products. This hypothesis is further substantiated by the increase in the production of C_5 products from mixtures of isobutane/butyraldehyde because five carbon length molecules are likely formed from cracking of a C_8 species into C_5 and C_3 fragments.
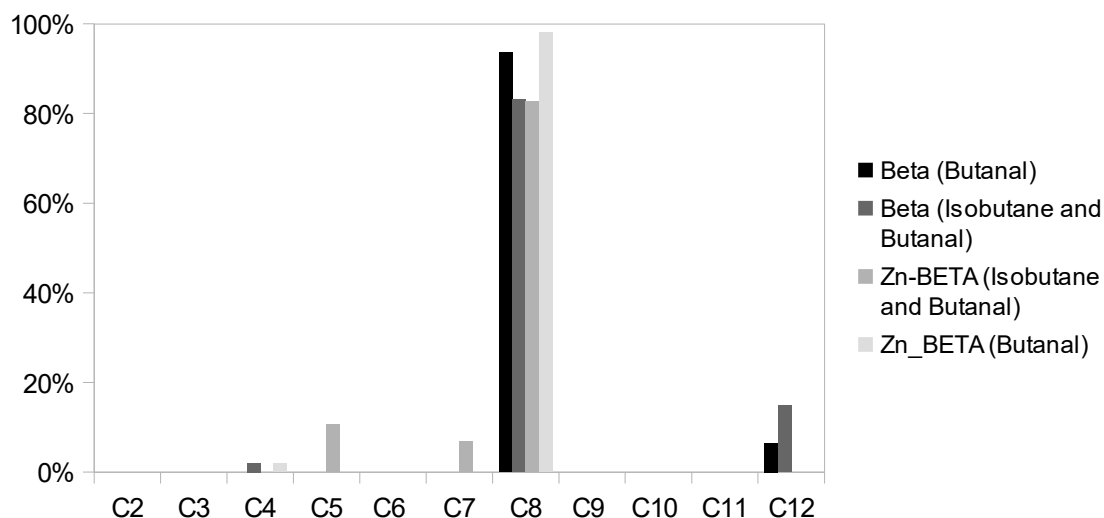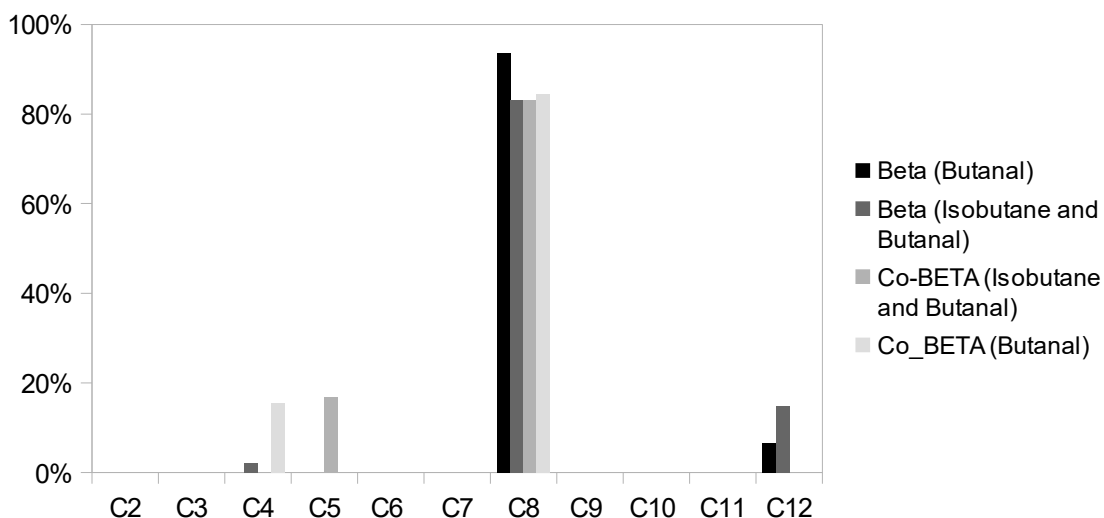
Figure 3-8: Selectivity to products with various carbon chain lengths from reaction of 4 kPa of butyraldehyde compared with the reaction of 4 kPa butyraldehyde and 40 kPa isobutane on BEA and Zn-BEA at 200°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm). Production rates of 2-ethyl, 2-hexenal: BEA (Butanal)-8.16x10^{-10} mol/s/Al, BEA (Butanal and Isobutane) 8.54x10^{-9} mol/s/Al, Zn-BEA (Butanal)-4.06x10^{-9} mol/s/Al, Zn-BEA (Butanal and Isobutane) 2.09x10^{-9} mol/s/Al.

Figure 3-9: Selectivity to products with various carbon chain lengths from reaction of 4 kPa of butyraldehyde compared with the reaction of 4 kPa butyraldehyde and 40 kPa isobutane on BEA and Co-BEA at 200°C. Reactions were carried out using a 20 cm^3 min^{-1} flowrate and 0.1 g of catalyst at ambient pressure (~1 atm). Production rates of 2-ethyl, 2-hexenal: BEA (Butanal)-8.16x10^{-10} mol/s/Al, BEA (Butanal and Isobutane) 8.54x10^{-9} mol/s/Al, Co-BEA (Butanal)-3.65x10^{-12} mol/s/Al, Co-BEA (Butanal and Isobutane) 2.88x10^{-12} mol/s/Al.

4 Summary

As carbon based molecules will continue to play an important role in our energy future, it is important to develop technologies that will optimize their usage. Current biofuel production technologies produce a large amount of short chain byproducts. Acid-catalyzed reactions of these molecules can be used to convert them to higher value products. However, catalyst compositions and reaction and reaction conditions need to be carefully selected to avoid the formation of a wide range of products. This work has shown that metal-exchanged BEA can be used to selectively convert butyraldehyde to 2-ethyl-2-hexenal at 200°C.

This work also indicated several avenues for further research. Y catalyst is the next logical path for study into the hydride transfer properties of metal-exchanged catalysts as it was shown to be selective towards C_7 molecules. Additionally, the ratio between the oxygenated and deoxygenated heptene seems to be very responsive to isobutane addition. Further study could also be performed in the area of metal-exchanged zeolites. The zinc and cobalt exchanged catalysts clearly demonstrated a different selectivity profile to the BEA catalysts. Additional metals such as copper or gallium have also been shown to be highly reactive metal sites in these kinds of reactions. For this reason, these metals could also be tested for how they affect the selectivity profile.

This research combined with further experimentation could yield sets of conditions to selectively tune to the reaction conditions to any desired product. It also lays the ground work for further exploration into further exploration into different beneficial reactions that are currently performed at high temperatures on acid catalysts and that lead to a wide range of products. Specifically, the co-processing reactions studied give a clear indication of the use of alkanes as H-donors in hydride transfer reactions over acidic zeolites.

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