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WATER ENHANCEMENT OF HYDROCARBON CRACKING REACTIONS ON ZSM-5

A THESIS APPROVED FOR THE SCHOOL OF CHEMICAL, BIOLOGICAL AND MATERIALS ENGINEERING

BY

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This work is dedicated to my parents, whose patience, support, and lessons have been vital for everything I do.

Acknowledgements

The human mind plans the way,

but the Lord directs the steps.

– Prov. 16:9

There is a long list of people who also deserve thanks for helping me through my college years.

My parents have been extremely supportive of my academic endeavors since elementary school, but it has become more apparent as time passes. For all their help, I am so very grateful. It is difficult to outline everything they have done for me in so few words, so I would like to thank them each for one thing in particular. To my father, thank you for taking the time to meet with me once a week; the commitment has been dearer than I am able to express. To my mother, thank you for connecting me to OSSM; this is what has really allowed me to get to the level of excellence I have achieved.

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Abstract

Catalytic cracking of hydrocarbons is an extremely important process for the production of fuels and commodity chemicals from petroleum feedstocks. The effects of water on these reactions has been studied before at high temperatures and pressures; usually these results suggest that water decreases initial reaction rate in return for less deactivation. However, there is evidence that cracking reactions on ZSM-5 could be enhanced by the presence of small amounts of water. This work studies the response of zeolites to water and ultimately suggests that water has the ability to interact with extraframework alumina to form a new species that synergizes with acid sites.

Chapter 1: Introduction

Zeolites have been introduced to a variety of industrial processes as solid-acid catalysts. Common reactions that are aided by zeolite catalysts, many of which occur in the gas phase, include: aldol condensation, ketonization, methanol-to-gasoline, and alkylation [1]. These catalysts are favored in part due to the localization of highly acidic protons within the pores, which helps to keep equipment from corrosion while possessing the necessary acidity for catalysis. Additionally, because zeolites are solids while most other species in these reactions are gases, separation of products from the catalyst becomes trivial.

Aside from the reactions already listed, a particular reaction that is improved by the use of zeolites is the catalytic cracking of hydrocarbons. In the past, the petroleum industry would produce gasoline and commodity chemicals from petroleum by means of thermal cracking reactions. The introduction of fluidized catalytic cracking with zeolites allowed for substantial improvements to the process because the conditions required for the reactions were much less severe than those required for thermal cracking. Typically, the zeolite is designed for gasoline selectivity since this currently represents the highest profit; however, another commodity to consider is propylene due to its use in polymer manufacturing. If greater propylene selectivity is desired, ZSM-5 would be the favored zeolite for catalytic cracking. Optimization of ZSM-5 for the catalytic cracking of hydrocarbons

would be of great value for the production of propylene from petroleum or from other feedstocks consisting of large hydrocarbons [2].

The influence of water with regards to cracking reactions has been studied to a certain extent already [1, 3-9]. During zeolite synthesis, water is used as a solvent, so freshly made zeolites tend to be saturated with water prior to any reactions. Water may also be present in a reaction because steam is commonly used as a fluidizing medium for fluidized catalytic cracking units, though nitrogen is also common. Furthermore, water is not easily removed from the zeolite due to the presence of hydrophilic Bronsted acid sites. Therefore, the effects of water in zeolites have been of interest.

Usually, investigations into the effects of water on zeolites involve high temperatures and pressures, which are common conditions for zeolites in industry. At these conditions water is able to act as a diluent; by competing for active sites, water helps inhibit the formation of coke while also acting as a fluidizing medium [8, 9]. Thus, a reduction in initial rate leads to a reduction in catalyst deactivation, which is more useful in the long term. At more extreme conditions, water is able to remove aluminum species from the framework of the zeolite in order to reduce the number of active sites [3, 10]. While this may seem at first deleterious for the catalyst, it also helps reduce coking.

More recently, investigations have been performed on the rate enhancement of cumene while in the presence of water. These findings suggest that water can temporarily boost the activity of the zeolite [1]. This is particularly interesting

because the previous effects of water have all had negative effects on the initial rates. However, this effect seemingly is only possible when reaction conditions are mild. Further research in this area could help uncover techniques for enhancing rates for catalytic cracking.

Chapter 2: Hexane and 2-Methylpentane Cracking

Introduction

The catalytic cracking of hydrocarbons on zeolites is of commercial interest for converting petroleum feedstocks into high value molecules in the gasoline range. In addition, certain zeolites could be selected that produce high-value commodity chemicals, other than gasoline, also from petroleum or possibly even biofuel feeds [2]. ZSM-5 in particular is useful for this purpose since products from this catalyst tend to be selective for propylene [11, 12]. As a model feed, hexane and 2-methylpentane are excellent choices due to their ability to avoid coke during reaction. Of particular interest to this work is how the zeolite and feed respond to the addition of small amounts of water cofeeding since steam is often used industrially as a fluidizing medium.

Water has been well studied as an adsorbent that competes with the reactant of interest on ZSM-5. As site competition increases, the overall activity of the zeolite is diminished. However, site competition between water and the hydrocarbon feed does lead to a diluent effect that disallows coke precursors on adjacent sites to react irreversibly with each other [8, 9]. As a result, steam and nitrogen were reported to be helpful for preventing coke formation in addition to fluidizing the catalyst. An additional study, however, indicated that water may have a different effect at lower temperatures and partial pressures because the activation energy dropped in the experiments performed with water [13].

Cracking rates have been shown to increase by cofeeding water with a hexane or cumene stream into a reactor with ZSM-5 [1]. For zeolites that are selective for gasoline, such as USY, it is typical to expose the catalyst to superheated steam in order to remove aluminum from the crystal framework; this reduces the total number of acid sites in return for less catalyst deactivation by means of coking [11, 12]. As a result, fresh catalyst is less active, but it will be more stable over its lifetime. However, the conditions for zeolite steaming are significantly more severe than those required for hexane cracking. Furthermore, hexane does not yield coke at the reaction conditions studied, so reducing the number of acid sites should correspond to a strict decrease in cracking rates, not a rate enhancement.

The reaction mechanism for zeolite cracking is known to be complex. Hydrocarbons are known to react in three ways upon adsorption on the catalyst surface. If there is already a small species, like ethane or propane, on the active site, the adsorbed hydrocarbons react with the unreacted species in the gas phase in a process known as hydrogen transfer. The larger hydrocarbon becomes a carbocation associated with the active site by donating a hydrogen to the smaller hydrocarbon, which desorbs. Alternatively, the acid site might evolve hydrogen with the reactant, which becomes a carbocation intermediate; this is known as protolytic dehydrogenation. The final, and perhaps most interesting, interaction involves the formation of penta-coordinated carbon centers during protolytic cracking. These non-classical intermediates are unsurprisingly very unstable and can only form as a result of extreme temperature in the highly acidic environment, like that found in zeolite

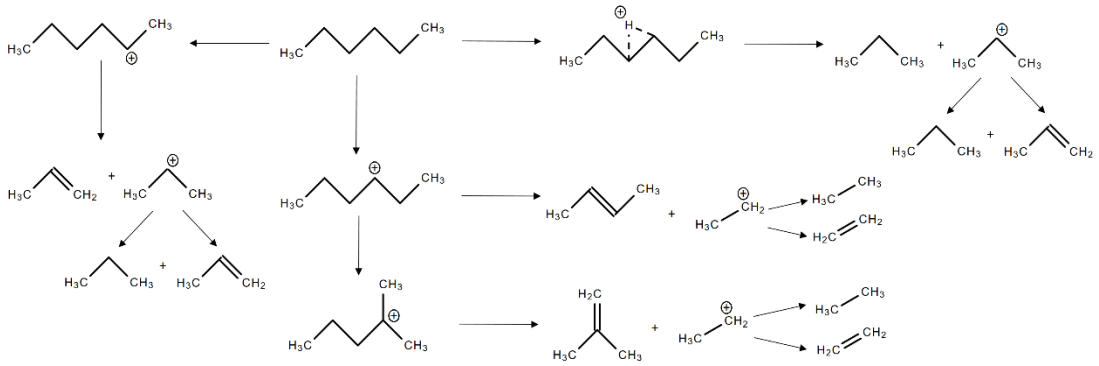

Figure 1. Reaction pathways for hexane cracking

pores. After the creation of the carbocation intermediates, these large intermediates are cracked into smaller products; this elementary step is referred to as β-scission. Two mechanisms are widely accepted for the removal of hydrocarbons from the active site, and both are known to take place in zeolite pores in varying proportions. These two mechanisms are known as monomolecular and bimolecular cracking for the number of hydrocarbons involved to complete the mechanism. For monomolecular cracking, the final step should be the desorption of the final product. Bimolecular cracking reactions instead undergo hydrogen transfer with larger reactant molecules, as described earlier. Isomerization steps to more substituted carbocations are not uncommon in catalytic cracking, though at times they can be difficult to notice in final product distributions [3, 14-18].

In this work, rate enhancements that occur in the presence of water will be clearly demonstrated. Moreover, the persistence of the rate enhancements after the subsequent removal of water will be examined as well. Necessary conditions for rate enhancement will be outlined. Ultimately, water is proposed to react with

extraframework alumina (EFAL) located in the zeolite pores to create a species that synergizes with acid sites in the framework to stabilize adsorbed molecules.

Experimental

Catalyst Preparation and Analysis

ZSM-5 catalysts, CBV 2314 (SiO_2/Al_2O_3 = 23, 425 m^2/g) and CBV 8014 (SiO_2/Al_2O_3 = 80, 425 m^2/g) were obtained from Zeolyst International in their ammonium form. In order to make the zeolite catalytically active, ammonia was removed from the framework by calcination in air at 600 °C for 5 hours. The air flow rate was set to 150 mL/min, which was sufficient for 1 gram of catalyst. A temperature ramp rate of 2 °C/min was used to prevent damage to the framework. Afterwards, the catalyst was pelletized, crushed, and sieved to a particle diameter of 90-250 microns.

The acid site densities of the zeolites were determined by isopropylamine temperature-programmed desorption (IPA-TPD). The catalyst samples, weighing about 40 mg, were packed in a quartz reactor between quartz wool. A thermocouple was attached to the side of the reactor level with the catalyst. Downstream of the reactor was an MKS Cirrus 200 mass spectrometer, which was used to measure relevant m/z signals including 4 (helium), 17 (ammonia), 41 (propylene), and 58 (isopropylamine). In order to remove any initially adsorbed species, the reactor was flushed with helium at a flow rate of 20 mL/min and heated to 300 °C. Afterwards, the temperature was reduced to 100 °C. Isopropylamine was injected in the reactor in

2 μL pulses until the mass spectrometer showed constant peak heights for m/z = 58 corresponding to different pulses. Temperature and helium flow rate were maintained for 4 hours to remove excess adsorbent. After excess isopropylamine was removed, the temperature was ramped at 10 °C/min to 600 °C. Calibration of propylene peaks was performed by injecting known volumes of propylene into the system and observing the peak area response.

During desorption, isopropylamine degrades around 350 °C to propylene and ammonia; ammonia for a time remains adsorbed to the catalyst bed while propylene is detected first. It is possible to determine acid sites from the number of ammonia molecules desorbing, but ammonia desorbs slowly from the catalyst bed, which makes peak integration less accurate. Instead, the propylene peak area was integrated and compared to propylene pulses sent through a blank reactor in order to quantify the amount of desorbed propylene. Assuming that desorbed propylene is stoichiometric with the number of acid sites in the sample, this implies an acid site density of 0.351 mmol/g for CBV 8014 and 0.894 mmol/g for CBV 2314. This is slightly lower than literature values of 0.396 mmol/g for CBV 8014 and 1.01 mmol/g for CBV 2314 [1].

Afterwards, X-ray diffraction (XRD) was performed in order to verify the crystallinity of the zeolite powders. The radiation source for the investigation was Cu-Kα and measurements were taken over an angle range of 5-50°. Diffraction patterns for Si/Al = 11.5 and Si/Al = 40 zeolites were compared to literature values and found to match the patterns for the MFI framework, as expected [19]. Steamed catalyst

samples were also prepared. These were pelletized, crushed, and sieved to diameters of 90-250 microns, then exposed to steam with a pressure of 27.5 torr. Samples were then ground back into a powder for XRD measurement. No difference could be discerned between the steamed and untreated samples, indicating that steaming of the catalyst was not severe enough to cause significant changes to the MFI framework.

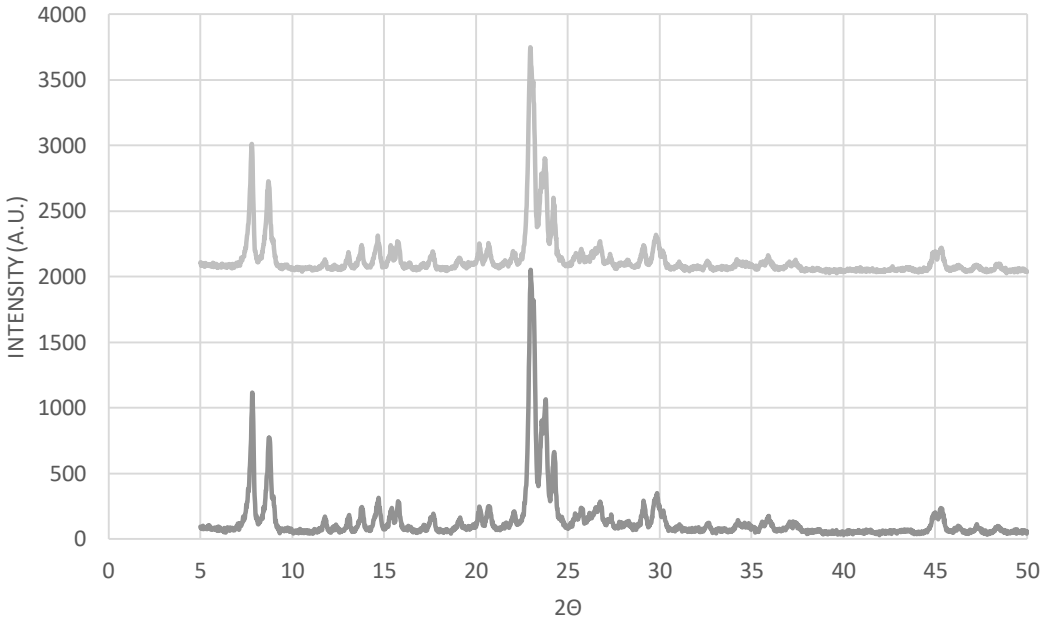

Figure 2. XRD patterns (Cu-Kα radiation source) of ZSM-5 (Si/Al-11.5), both steamed at 27.5 torr (above) and untreated (below), confirming presence of MFI framework; data are offset for clarity

Reactions at Continuous Flow Conditions

Cracking of n-hexane (Aldrich, 99% purity) on ZSM-5 was conducted at temperatures around 440-520 °C. For hexane cracking, 20 mg of Si/Al = 11.5 zeolite with 80 mg of glass beads or 80 mg of Si/Al = 40 and 20 mg of glass beads was loaded into a quartz reactor with an inner diameter of 0.15 inches between two layers

of glass wool. Helium was used as a carrier gas with a variable flow rate that most often was set to 120 mL/min; the pressure for the reactor was near atmospheric both before and after the catalyst bed. After reaching reaction temperature, the catalyst was left under flowing helium for 1 hour in order to remove any adsorbed species, especially water.

Hexane and water could then be flowed into the reaction system by means of a pair of syringe pumps; after injection of either species, data collection was delayed by thirty minutes to ensure the system was at equilibrium. The partial pressures for hexane and water ranged from 1.51-7.53 torr and 13.76-68.78 torr, respectively. Products from the reaction flowed through a heated sample loop that was connected to a Hewlett Packard 6890 gas chromatograph for analysis. Products were separated by a porous layer open tubular (PLOT) column and responses were measured by a flame ionization detector (FID). Because all products were hydrocarbons containing no heteroatoms, relative concentrations could be determined from comparing peak areas, and the actual concentration of hexane could be calibrated by using the peak areas of unreacted hexane of known concentrations.

Similarly, the cracking of 2-methylpentane (Aldrich, 99% purity) was performed on the temperature range of 420-510 °C with the same catalyst/glass beads proportions. For these reactions, the helium flow rate was set to 145 mL/min, but the pressure was still close to atmospheric. The partial pressures of 2-methylpentane ranged from 1.88 to 6.57 torr; water partial pressure was not varied and set to 27.5

torr, if present in the reaction at all. The pretreatment step of 1 hour for the catalyst was identical to that of the hexane pretreatment.

Results and Discussion

Selectivity

Changes in selectivity for ZSM-5 catalysts indicate a shift in reaction mechanisms. Product distributions give an indication of which mechanistic pathways are dominant. Although different pathways can yield the same products, oftentimes the ratios of the products can provide information. Hexane reaction selectivity is examined first. Hexane selectivity was compared to literature values and was found to be comparable [11].

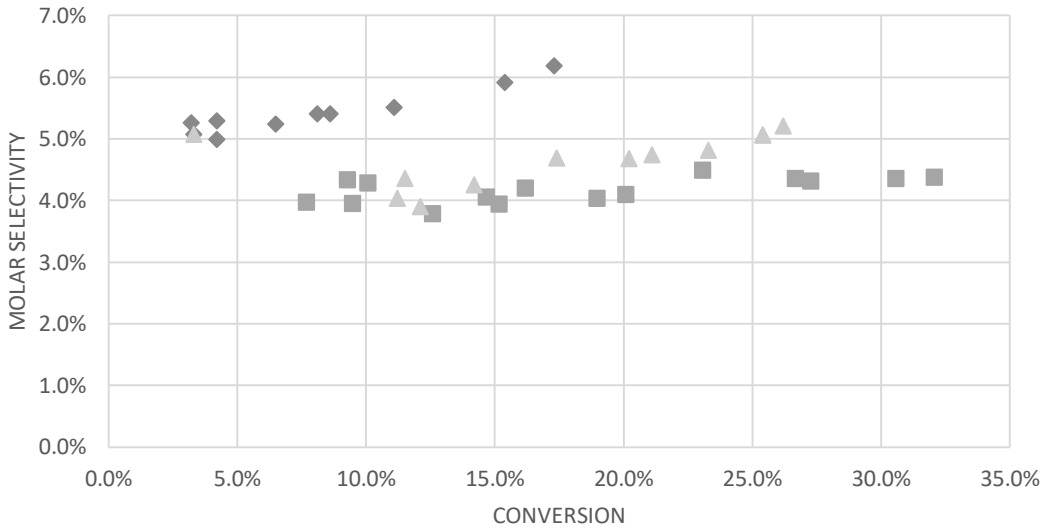

Figure 3. Methane selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

The presence of methane in product distributions is interesting; due to stability arguments, the formation of methane during catalytic cracking is widely accepted to be impossible. Instead, its formation can only be explained as a result of thermal

cracking. Due to the low amounts of methane in the product distribution, the contribution of thermal cracking to the results is considered to be generally negligible.

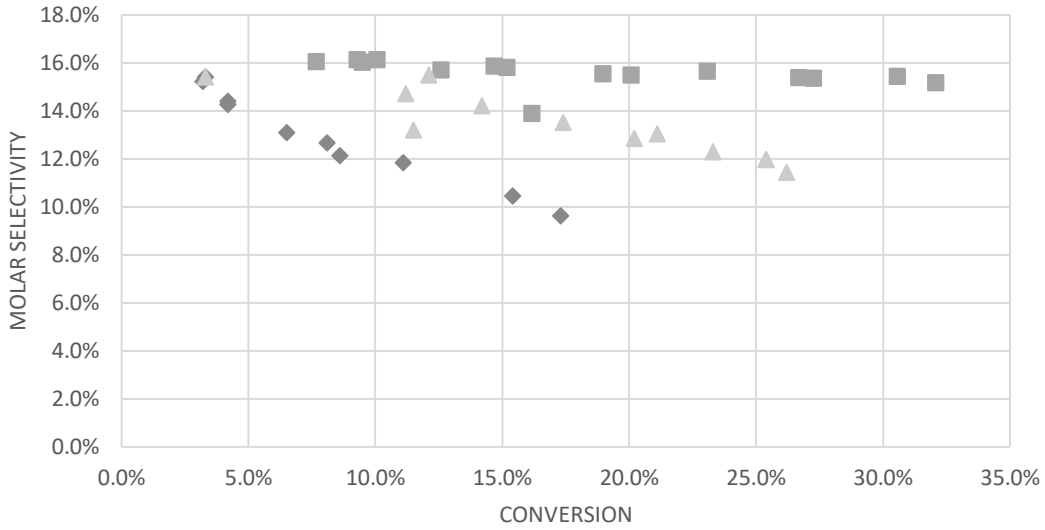

Figure 4. Ethane selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

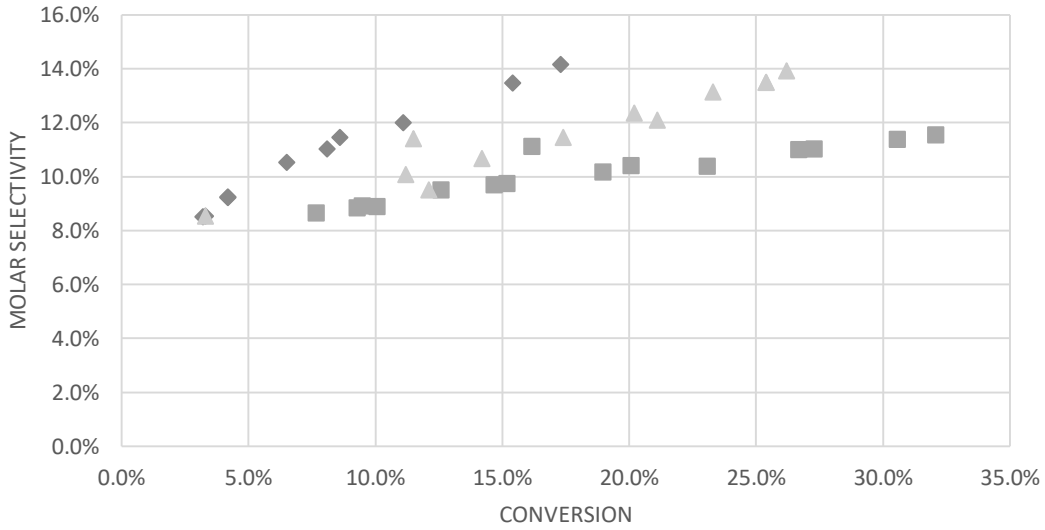

Figure 5. Ethylene selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

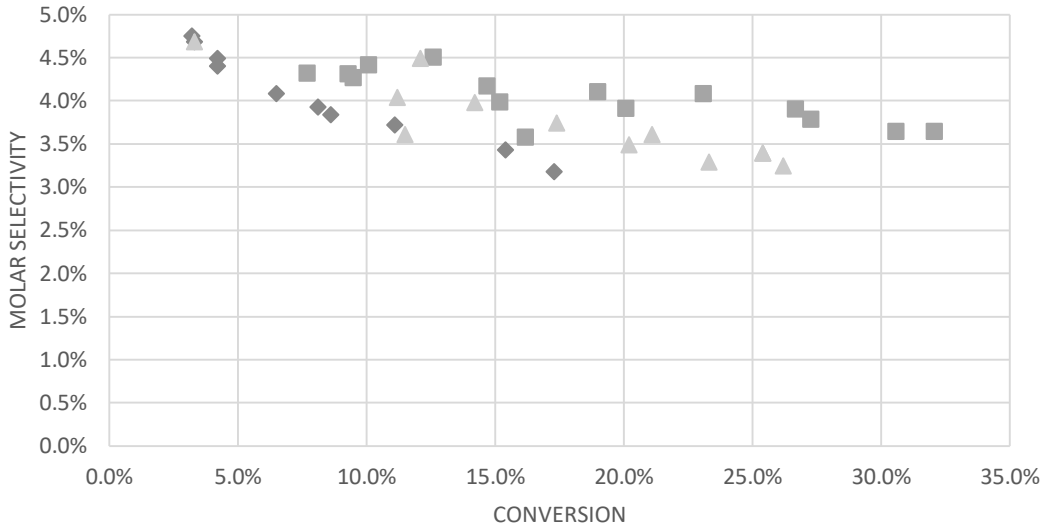

Figure 6. Trans-2-butylene selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

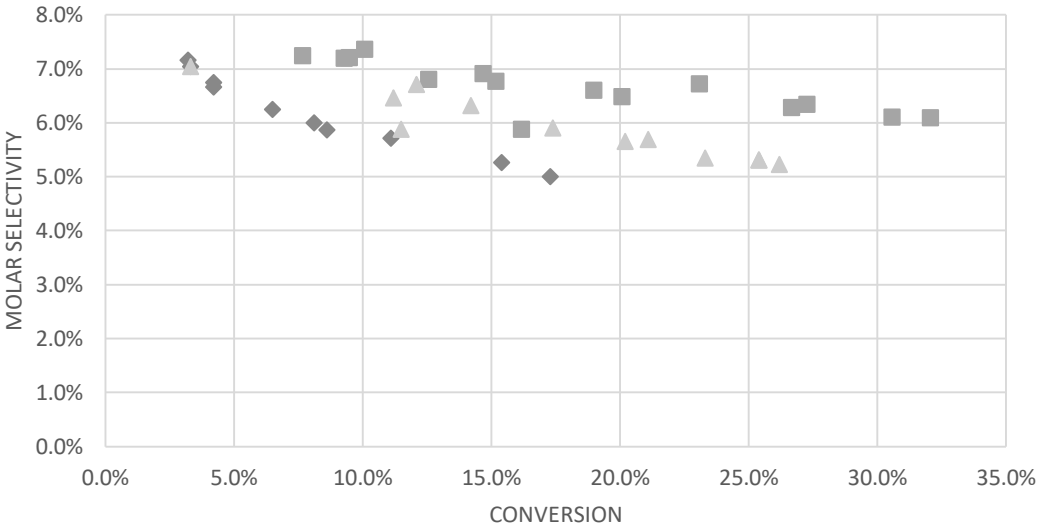

Figure 7. Isobutylene selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

It would be expected that the total selectivity of C2 products would be equal to the total selectivity of C4 products. Although it is surprising that this is not the case, the difference could be explained by the slight contribution of thermal cracking.

More interesting are the ratios of ethylene to ethane and isobutylene to butene. These describe the probability of hydrogen transfer as well as the probability of isomerization. From the results, it is fairly reasonable to assert that isomerization occurs with about 60% probability. Meanwhile, hydrogen transfer occurs about as often as desorption for the adsorbed ethylene species, though desorption is slightly less favored.

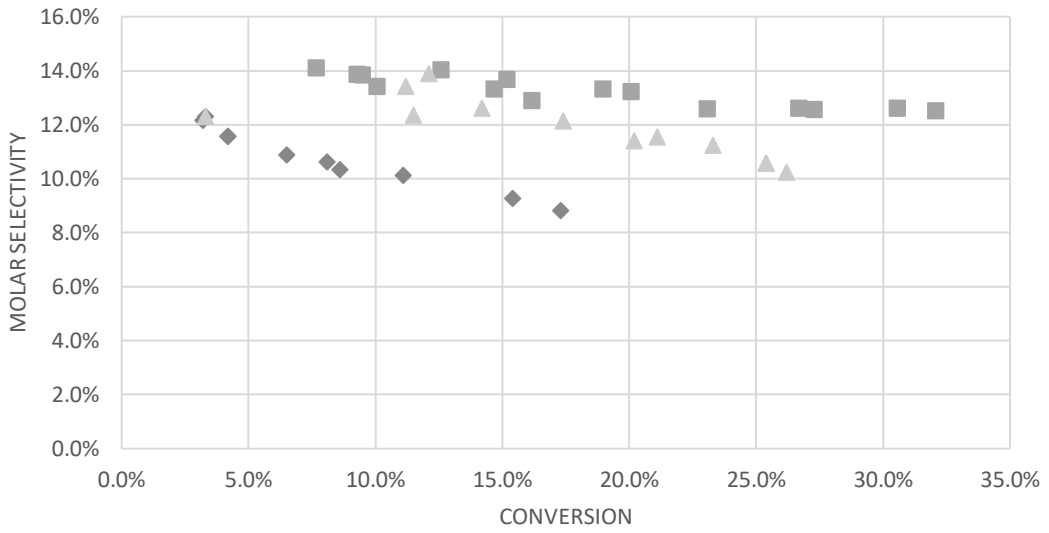

Figure 8. Propane selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

As mentioned previously, ZSM-5 is known to be selective for propylene, and these results reinforce this conclusion. Like the previously discussed ratios, the propylene to propane ratio helps describe the mechanistic pathways taken by hexane. The prevalence of propylene over propane suggests that protolytic cracking is strictly dominated by the other pathways. Moreover, the monomolecular and bimolecular mechanisms are about equally likely for the adsorbed propylene species. Regarding the selectivity of C3 hydrocarbons over C2/C4 hydrocarbons, energy barriers for the

production of propylene are unsurprisingly lower than those for ethylene because secondary carbocations are much more stable than primary.

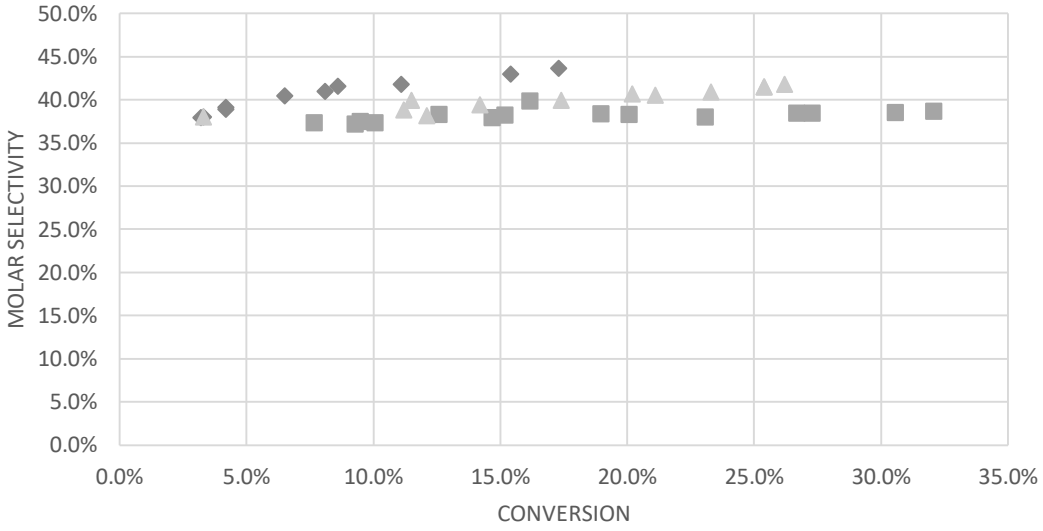

Figure 9. Propylene selectivity as a function of hexane (4.7 torr, 2.5 mL/hr) conversion on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

Selecitivities for 2-methylpentane show much less distribution among products. Olefins are much more favored, which implies that protolytic dehydrogenation is much more favored than hydrogen transfer. This can be attributed to the nature of the tertiary carbon; the attached hydrogen is surrounded by bulky groups that impede reactivity, thus making hydrogen transfer less favorable. Methane and C5 hydrocarbons from thermal cracking are present in small amounts, so thermal cracking is present yet for the most part is still considered negligible.

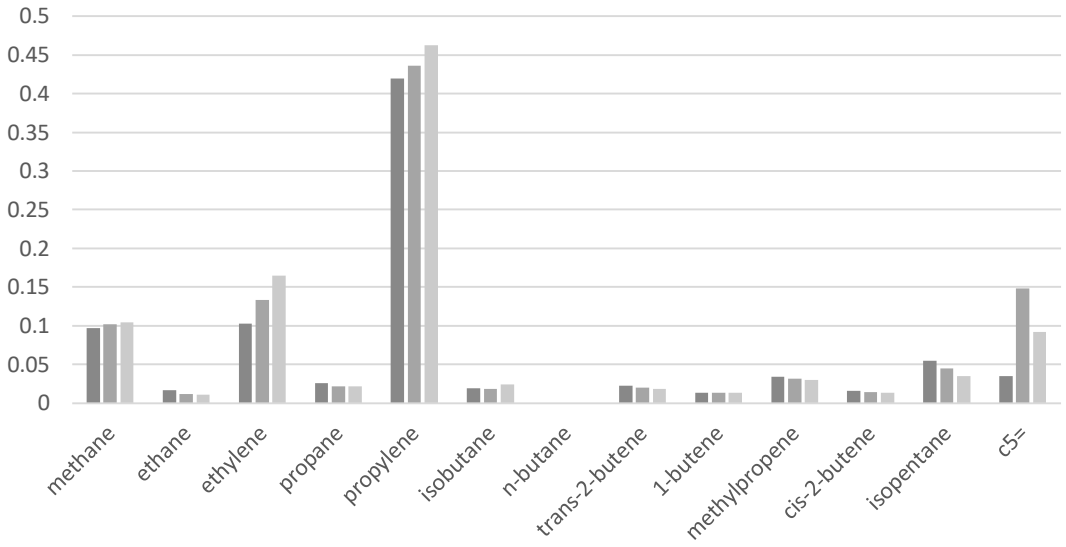

Figure 10. Selectivity of 2-methylpentane (4.0 torr, 2.5 mL/hr) cracking without water on ZSM-5 (Si/Al = 11.5, 20 mg); dark gray: 460 °C; gray: 480 °C; light gray: 500 °C

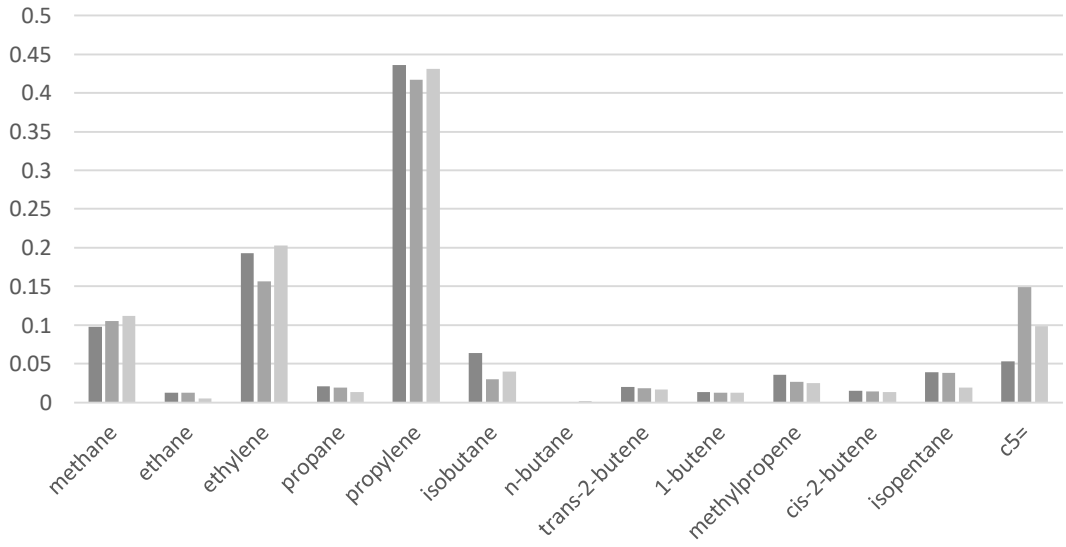

Figure 11. Selectivity of 2-methylpentane (4.0 torr, 2.5 mL/hr) cracking with water (27.5 torr, 2.0 mL/hr) on ZSM-5 (Si/Al = 11.5, 20 mg); dark gray: 460 °C; gray: 480 °C; light gray: 500 °C

Water enhancement did not seem to have a radical change for methylpentane selectivity. Ethylene saw the greatest change and is slightly more favored at the expense of heavier species, but largely the results are similar. However, it is notable

that ethylene does not appear stoichiometrically with methylpropene. The presence of thermal cracking may be sufficient to explain some error, but would be unsuitable in this case. Further investigation for this result is required.

For both hexane and 2-methylpentane cracking, water enhancement did not appear to affect selectivity significantly. Mechanistic pathways can be assumed to be unchanged between the cases with and without water. Interestingly, 2-methylpentane also demonstrated a much greater selectivity for olefins than hexane, which is evidence for the preference of methylpentane for protolytic dehydrogenation. Protolytic and thermal cracking are negligible pathways for the reactions at these conditions.

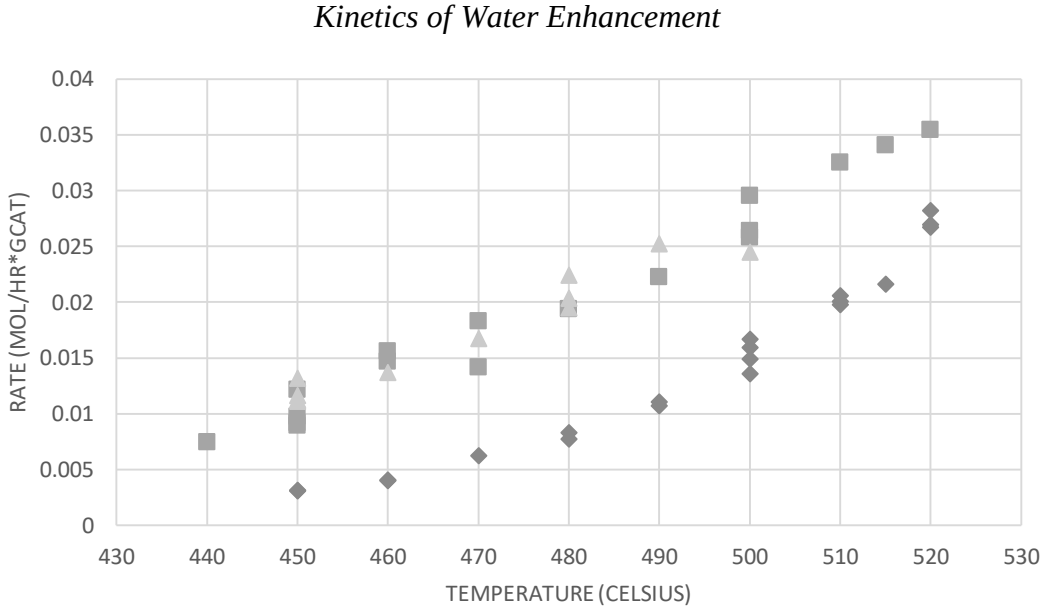

Figure 12. Reaction rates of hexane (4.7 torr, 2.5 mL/hr) cracking on ZSM-5 (Si/Al = 11.5, 20 mg) as a function of temperature; diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

Reactions for hexane cracking were studied for CBV 2314 at a variety of temperatures to find activation energies in the presence and absence of water. Deactivation was negligible throughout the experiments and all values were at steady state. Conversion in most cases was kept below 35% to avoid equilibrium effects. The carbon balances for these reactions are at least 95%.

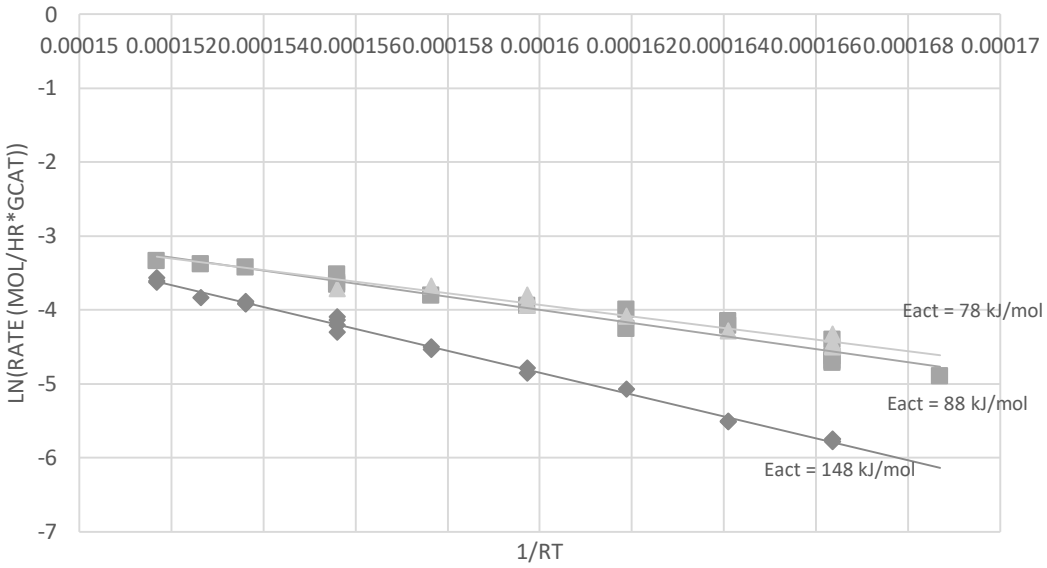

Figure 13. Arrhenius plots for hexane (4.7 torr, 2.5 mL/hr) cracking on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; squares: water cofeeding (27.5 torr, 2.0 mL/hr); triangles: after water treatment

A rate enhancement was observed at all studied temperatures while cofeeding water, which is observable in Fig. 12. For reactions without water, an Arrhenius plot (Fig. 13) was used to determine the observed activation energy: 148 kJ/mol, which corresponds well with values found in the literature [9, 11]. This value decreased to 89 kJ/mol for reactions when water was cofed.

In addition, reactions that continued after water was removed from the reaction system showed the persistence of the rate enhancement. In some cases, the

reaction system was shut down overnight before data collection continued the next day. This suggests that water caused some kind of change within the catalyst during the cracking of hexane; moreover, this change is at least metastable for the timescales of the experiments and possibly permanent. The activation energy was determined to be 78 kJ/mol for the catalysts that had been treated with water and then continued to possess rate enhancement.

Importantly, the reaction order also changes for the two cases; the orders for the reactions without and with water are 0.56 and 0.92, respectively. In the case of catalytic cracking, a reaction order of 1 is associated with the apparent activation energy whereas a reaction order of 0 implies that the observed activation energy is in fact the true activation energy barrier. As a result, the increase in reaction order suggests that water affects hexane cracking in part by shifting the observed activation energy closer to the apparent energy barrier. The heat of adsorption for hexane (86 kJ/mol) is slightly greater than the difference between the measured activation energies, which helps to support the idea that observed activation energy is linked with changing apparent reaction order [11].

Usually the reason for shifts in observed activation energy are due to changes in partial pressure for species that can adsorb onto the catalyst surface. Alternatively, changes in observed reaction energy could be due to changes in conversion. However, the latter explanation is not sufficient for the case of hexane cracking; the overall conversion of hexane is still small (below 35%) for reactions with or without water. A change in conversion would have to be much more extreme in order to be so

noticeable on an Arrhenius plot. Regarding the former explanation, hexane partial pressure can remain constant for experiments with or without water, which initially makes a change in rate order seem unlikely to be caused by changing hexane pressures. However, it is important to consider that although hexane partial pressures may be kept constant at the reactor inlet, competitive adsorption of water on the active site might make the hexane pressure in the catalyst seem lower. This is in fact the case with hexane cracking. Water is known to be able to adsorb onto the zeolite surface with a heat of adsorption around 50.6 kJ/mol [20]. For both hexane and water, the product of the adsorption constant and the respective partial pressures is on the order of 1. As a result, the reaction order should be expected to be around 0.5 for reactions without water, and it will approach 1 as the water partial pressure increases.

Methylpentane reactions on CBV 2314 were conducted similarly to the hexane reactions. In all cases, it was noticed that after a couple hours of data collection, reaction rates would steadily increase over the course of the experiment despite the steady state nature of controlled variables. These enhancements could increase rates by as much as 20-40% over three hours. Increasing the timescales of the experiments to wait until the point of steady state did not improve results. Rate data was used to extrapolate for rates at 0 time on stream (when methylpentane is first introduced to the catalyst). The definite cause for this transient behavior is still unknown at this time, but it may be possible that very small amounts of water were present in the hydrocarbon feed, which led to rate enhancements similar to those

purposefully imposed in this work. Carbon balances were within 10% error, and conditions were selected so that conversions were mostly below 35%.

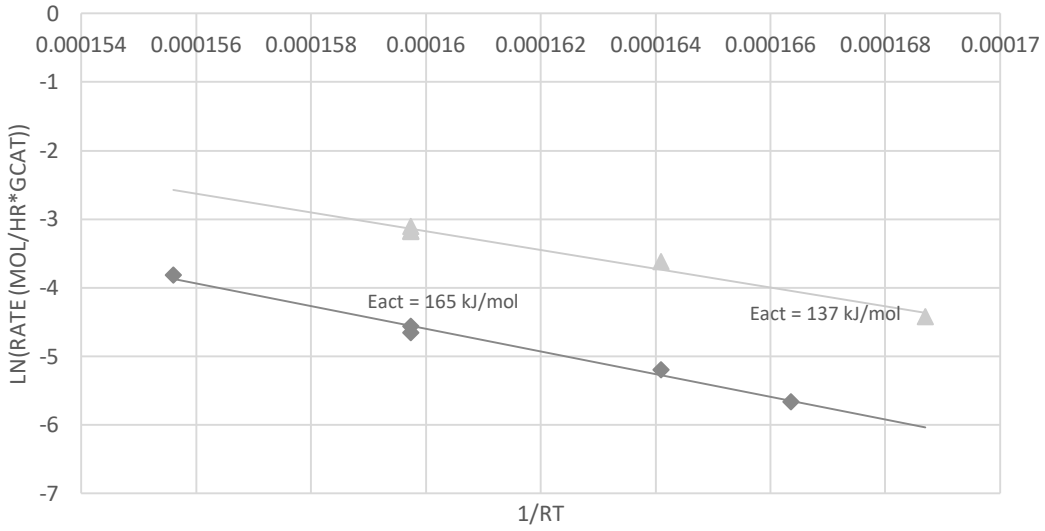

Figure 14. Arrhenius plots for 2-methylpentane (4.0 torr, 2.5 mL/hr) cracking on ZSM-5 (Si/Al = 11.5, 20 mg); diamonds: no water; triangles: after water (27.5 torr, 2.0 mL/hr) treatment

Again, rate enhancements were observed when water was involved in the reaction, but unlike the hexane reactions, there was no rate enhancement during water cofeeding. In fact, competitive adsorption for sites drove rates down slightly. Rate enhancements only appeared for methylpentane cracking after water was removed from the system. Observed activation energies for methylpentane cracking before and after the introduction of water were 165 and 137 kJ/mol respectively.

Interestingly, the effect on observed activation energy is much less noticeable for methylpentane cracking than for hexane. Comparing reaction orders, methylpentane was already near first order kinetics when reactions were performed for dry experiments. It can thus be concluded that since both observed activation energy values for methylpentane cracking experiments are already near the apparent

activation energy values, the difference in observed activation energy will be less noticeable than for hexane.

As mentioned previously, water must affect the catalyst in order to induce a stable change to the rate. The steaming of Y zeolites to form more stable (less coking) USY zeolites is the most well-known interaction between steam and framework species, but such interactions take place at higher temperatures. More importantly, USY catalysts actually have lower initial rates than untreated Y zeolites (though this lower rate does not decrease as easily due to coking, making it better overall). Coking on ZSM-5 in this work was unnoticed, so greater stability would be meaningless for hexane or methylpentane cracking. Therefore, the destruction of the MFI framework during steaming would be an insufficient explanation for the rate enhancement of zeolites; furthermore, destruction of the MFI framework would have been detected by XRD measurements.

A better explanation is that water interacts with EFAL present in the zeolite pores to form a species that acts synergistically with acid sites in the framework [3, 22-27]. At first, it may be tempting to assert that EFAL reacts with water to form additional active sites, but this ultimately would be incorrect. Measurements of Bronsted acidity with IPA-TPD indicate no increase in the number of active sites. Therefore, the presence of water-affected EFAL as synergistic sites with framework acid sites would be a much more suitable explanation for water enhancement phenomena at these reaction conditions.

Characteristics of Diffusion Limited Reactions

There is a possibility that reactants are limited by external or internal diffusion in any catalyzed reaction. These limitations can become apparent during experiments by changing fluid velocity, particle size, or temperature. If the reaction is limited by external diffusion, the apparent reaction rate varies linearly with temperature and with the square root of the fluid velocity, though the rate would vary exponentially with temperature and be independent of velocity if the rate were limited by internal diffusion or kinetics [28]. It is more difficult to determine whether internal diffusion limits reaction rates, though particle size can be used. The apparent rate would be inversely proportional to particle size if internal diffusion is limiting, but kinetically limited reactions are not influenced by particle size [28]. Unfortunately, this is not easily investigated without purposefully synthesizing the zeolite to have different particle sizes.

A rate order of 1 is associated with external diffusion limitations. However, since hexane did not exhibit mass transfer limitations before the addition of water since the rate order was not 1 for those experiments, it is reasonable to disregard external mass transfer for all cases and consider only internal diffusion limitations. Rate order for internal diffusion limited reactions depends on the kinetics of the particular reaction; in the case of hexane cracking, internal diffusion would have a rate order of 1. Since there are reactions at high rates with a rate order of 1, rate order is not sufficient to disregard internal diffusion in all cases, though it would be unlikely for the reaction to transition to the diffusion limited case in the range of the

experiments. Apparent activation energy would also be different in the case of internal diffusion limited reactions. As mentioned previously, the apparent rate varies exponentially with temperature, and an activation energy could be calculated; if the value is between 8 and 24 kJ/mol, the reaction is likely diffusion limited [28]. From this, the reaction is known to be limited by kinetics since all activation energies discussed so far have been greater than 75 kJ/mol.

Additionally, the Weisz-Prater criterion can be used to determine the likelihood of internal diffusion limitations affecting results. Calculations of the Weisz-Prater criterion for the highest observed rates of hexane and methylpentane gave values that were less than 0.001; this implies that internal diffusion can be ignored for all cases.

Water Rate Enhancement and Acid Site Density

Hexane reactions with and without water were also considered for CBV 8014 at 500 °C. It is noteworthy that the turnover frequencies are smaller than those for CBV 2314 at otherwise identical conditions. However, it is particularly notable that the rate enhancements were less impressive than that for CBV 2314. Likewise, methylpentane cracking showed similar trends; in fact, reactions with CBV 8014 showed no noticable enhancement after the removal of water at all. This is slightly more extreme than the observations with hexane, which do show marginal

enhancement. From this, it could be concluded that the acid site density of the zeolite is also relevant for affecting water's rate enhancement.

	0 Torr Water	13.8 Torr Water	27.5 Torr Water	13.8 Torr % Enhancement	27.5 Torr % Enhancement
CBV 2314	21.98	29.47	32.11	34	46
CBV 8014	8.85	9.24	10.48	4.3	18.3

Table 15. Turnover frequencies for CBV 2314 and CBV 8014 catalysts exposed to different partial pressures of water; hexane partial pressure: 4.7 torr; temperature: 500 °C

The lack of rate enhancements while Si/Al ratio is high suggests that the density of aluminum has a role. Indeed, EFAL is known to be less prevalent in zeolite samples with high Si/Al ratios. These results support the idea that EFAL and water together are needed to create synergistic sites. More investigation is needed to confirm this claim. Selective removal of EFAL during catalyst preparation by means of ammonia hexafluorosilicate could give an indication of how necessary EFAL is for rate enhancement [23]. Additionally, further experiments with low EFAL are necessary to determine whether acid site density, rather than EFAL, is necessary for enhancement.

Conclusions

Rate enhancements in the presence of water allow for significant gains in catalyst rate with very little downsides regarding selectivity at the temperatures and pressures studied. Site competition of water is able to explain certain effects present during these reactions, but not rate enhancements. Enhancement has been shown to

persist, even in the subsequent absence of water. The only ZSM-5 catalysts capable of rate enhancements are those with low Si/Al ratios. Thus, EFAL in zeolite pores is believed to react somehow with water in order to form synergistic sites that stabilize molecules adsorbed on acid sites.

Chapter 3: Cumene Cracking

Introduction

Currently, most interest in petroleum catalytic cracking is for the production of gasoline, but ZSM-5 is another commonly used zeolite on account of its high propylene selectivity. Aromatic compounds form a significant proportion of typical petroleum feeds, and they are also prevalent in biomass, which may become important as gasification technology improves [2, 29]. Investigations of catalytic cracking of these feeds also require investigations of different classes of compounds within the mixture of hydrocarbons. Cumene is a decent model compound for aromatic hydrocarbons, but this compound should be exceptionally helpful for determining how water affects zeolite performance at low partial pressures. First, cumene cracks to form propylene and benzene exclusively in equimolar ratios, so product selectivity would be certain. Second, cumene cracking requires relatively mild temperatures compared to most cracking reactions, which would help give an indication of how water affects catalysis at lower reaction temperatures [30]. Water effects have been studied in detail at high temperatures and pressures, like those common in most catalytic cracking units, but additional understanding of water at less severe conditions is necessary. The reason for such investigations is to determine whether water may be able to provide improvements to the kinetics of cracking reactions that can only be achieved at mild conditions.

The diluent effect of water has been already been studied on ZSM-5. Site competition between water and hydrocarbons allows water to prevent the oligomerization of coke precursors [9]. However, this effect occurs at high pressures of steam. Other studies have investigated the processes of zeolite steaming in order to prepare improved catalysts. Industrially, Y zeolites are steamed in order to promote the stability (stunted ability to coke) of the catalyst [3]. This process also takes place at severe reaction conditions. In both cases, water helps improve the overall state of the system by preventing coke formation, but this comes at the expense of fewer available active sites. The goal of this work is to consider the influence of water at mild conditions. This disallows water from its traditional role as a rate (and deactivation) inhibitor, and allows for the possibility to observe a new phenomenon.

In fact, rate enhancements for aromatic compounds at low water partial pressures have been studied in some detail [7, 11]. However, complete understanding of the overall effect of water on catalytic cracking requires additional investigation. If exposure to small amounts of water could enhance the reaction rate with minimal side effects, mostly involving deactivation or selectivity, industrial catalytic cracking would improve greatly with this information.

Experimental

Catalyst Preparation

ZSM-5 catalysts were purchased from Zeolyst International. Because the zeolite was in its ammonium form, the catalyst was calcined in dry air for 5 hours at

600 °C to make the catalyst acidic. A low temperature ramp (2 °C/min) was selected to avoid damaging the MFI framework. Only one SiO_2/Al_2O_3 ratio was used in the following experiments. The ratio for this catalyst (high acid site density sample) was $SiO_2/Al_2O_3 = 23$; it was expected that catalysts with too low of a Si/Al ratio would have no effect when exposed to water due to the absence of extraframework alumina. After calcination, the zeolite powders were pelletized, crushed, and sieved; the final particle diameter for these particles ranged from 90-250 microns.

Isopropylamine temperature-programmed desorption was used to find the number of acid sites per gram of catalyst. Approximately 40 mg of a zeolite sample was packed in a quartz reactor with a thermocouple attached near the sample on the outside of the reactor. Products from the reactor were measured with an MKS Cirrus 200 mass spectrometer. In order to remove any initially adsorbed water, the reactor was flushed with helium and preheated to 300 °C before cooling to 100 °C. Isopropylamine was injected into the reactor until constant peak heights for isopropylamine appeared on the mass spectrometer for subsequent pulses. Physisorbed isopropylamine was removed by maintaining the helium flow rate and temperature for 4 hours. Next, desorption of chemisorbed species took place as the temperature increased to 600 °C (10 °C/min temperature ramp). Desorbing propylene during the temperature ramp was tracked by mass spectrometry and quantified using calibration standards.

Reactions at Continuous Flow Conditions

Cumene cracking (Aldrich, 98% purity) on ZSM-5 was performed using each zeolite with differing Si/Al ratios. In the case of Si/Al = 11.5 zeolite, 5 mg of catalyst was mixed with 95 mg of glass beads. The mixture was loaded between two glass wool layers in a quartz reactor. Helium was chosen as an inert carrier gas for the reaction with a flow rate between 120 and 180 mL/min. The system pressure was nearly atmospheric, though there was a tendency for the product stream to form coke downstream of the reactor. This occasionally led to a higher system pressure (up to 5 psig) until lines were cleaned. Before reaction, the reactor temperature was raised to 300 °C while helium flowed over the catalyst in order to desorb water and other species. The reactor was then cooled to the desired temperature, which was between 200 and 300 °C.

A pair of syringe pumps were used to flow cumene and water into the helium carrier gas. In order to remove impurities from the cumene stream before reaction, the cumene was first distilled. Next, the distillate was exposed to a γ-alumina adsorbent and stored under nitrogen until required for reaction. After the pretreatment of the catalyst, reactants were injected into the system. The cumene partial pressure was between 2.06 and 8.19 torr, and water partial pressure was held between 13.77 and 61.60 torr, if water was present. Products were analyzed by a Hewlett Packard 6890 gas chromatograph connected to the system. A wall coated open tubular (WCOT) column separated product components before a flame ionization detector (FID) measured responses. Since the hydrocarbons in the produce contained no

heteroatoms, response factors were assumed to be 1. As a result, concentrations could be reliably found by comparing the peak areas to those of known standards.

Results and Discussion

Cumene reactions were performed on CBV 2314 at a variety of conditions, but in almost every case without water, coking of the catalyst was severe. Attempts were made to extrapolate rate data to 0 time on stream (when cumene was introduced to the reaction system) by assuming an exponential decay for reaction rate. Unfortunately, such attempts to extrapolate led to significant error during repeated experiments for reactions without water, though comparing points at the same time on stream showed much less error in repeatability. Reported results will be for data points collected 30 minutes after any changes were made to the system conditions.

The carbon balance for these reactions was usually within 10% error. Most of the time, the carbon balance was low due to propylene oligomerizing in the catalyst to form coke precursors and not appearing in GC analysis. Occasionally, coke would form in the lines downstream of the reactor and form a plug leading to a pressure drop. This would lead to higher FID responses in the GC, which would be then recorded as a net positive carbon balance until lines were cleaned again. Results that deviated too strongly with regards to carbon balance were rejected from analysis.

Reaction products for cumene cracking are known to yield only propylene and benzene in stoichiometric ratios. Aside from feed impurities that were recognized during direct injection of the feed into the GC, these were the only products.

However, due to coking, these products were not detected in stoichiometric ratios, and the moles of propylene were consistently less than the moles of benzene. The measured selectivity for propylene was between 48.5% and 49.5% (propylene to benzene ratio: 0.94:1 to 0.98:1) across a wide variety of conditions. Conversions were sometimes very high in order to get results comparable to other results in the literature.

Water Enhancement on ZSM-5

In all cases where water was present, a rate enhancement was observed. Additionally, catalyst deactivation would cease or slow down for as long as water was flowing into the reactor. In some cases, rate would even increase slightly while in the presence of water. As soon as water was removed, rate decreased, though not always back to (projected) baseline conditions.

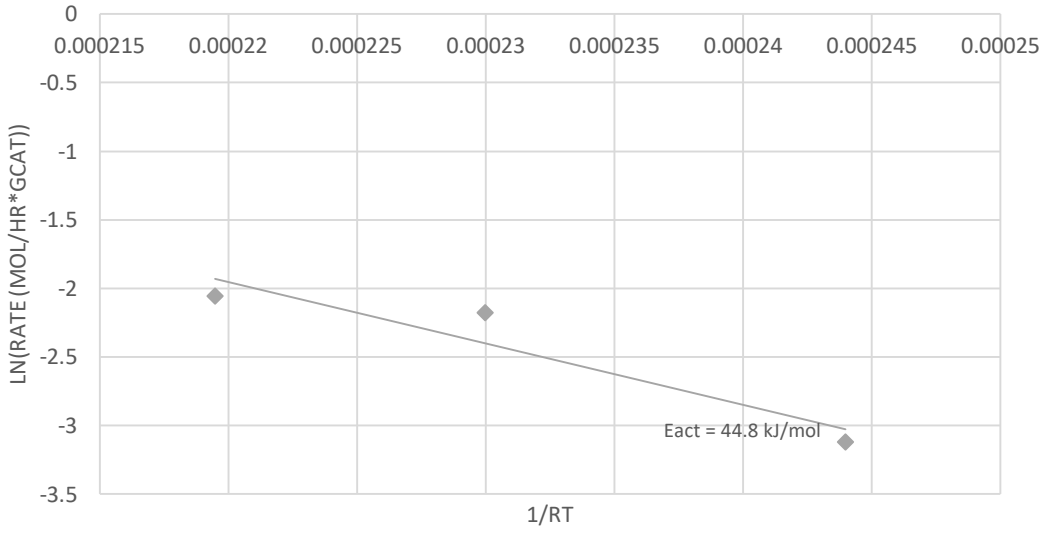

Figure 15. Arrhenius plot for cumene (3.6 torr, 2.0 mL/hr) cracking on ZSM-5 (Si/Al = 11.5, 5 mg) without water

Arrhenius plots were used to estimate the activation energy barriers. In the dry case, activation energy was determined to be 44.8 kJ/mol (Fig. 15). If water partial pressure was set to 13.77 torr, the energy barrier was 40.2 kJ/mol (Fig. 16). However, the energy barrier rose to 72.4 kJ/mol when the water partial pressure was doubled (Fig. 17). Reaction orders were also determined at two different temperatures. At 275 °C and 220 °C, reaction orders were found to be around 0.5 and 0, respectively. This indicates why the points on Figures 15 and 16 do not follow very precise lines; observed activation energy is shifting from true activation energy to apparent activation energy as the temperature decreases. With this in mind, the approximate activation energies for the dry data set on the left and right part of the curve is 11.8 and 67.3 kJ/mol respectively.

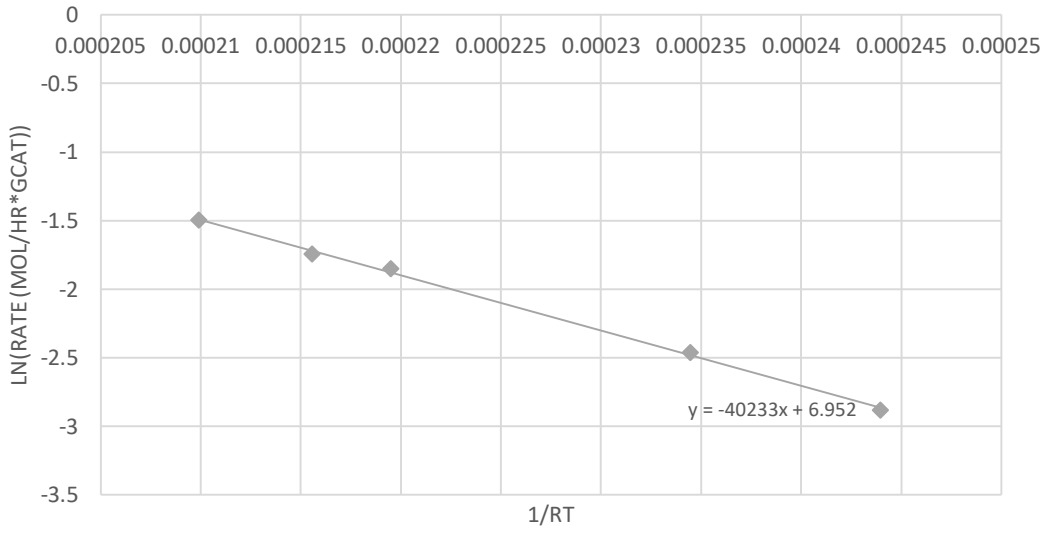

Figure 16. Arrhenius plot for cumene (3.6 torr, 2.0 mL/hr) cracking on ZSM-5 (Si/Al = 11.5, 5 mg) with water (13.8 torr, 2.0 mL/hr)

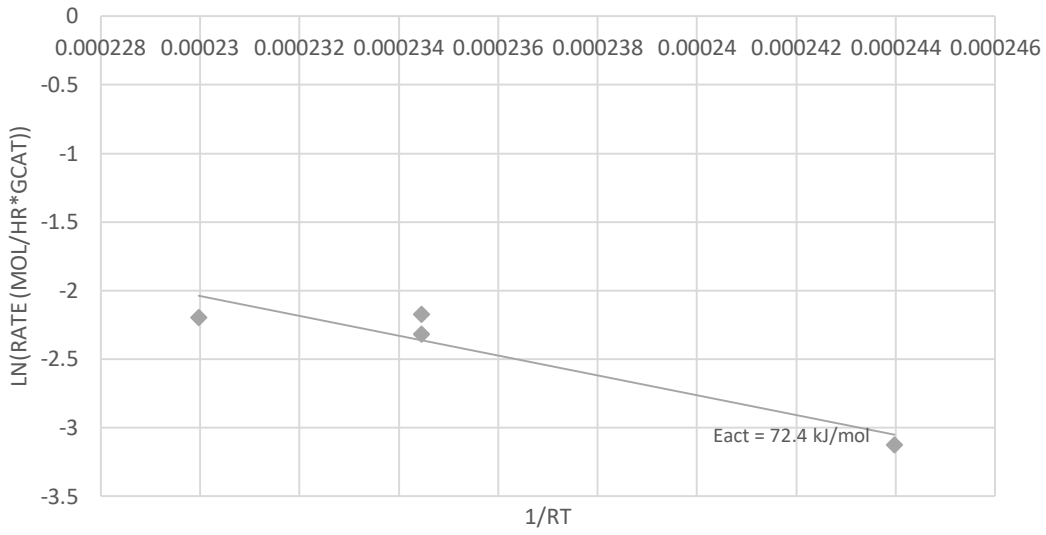

Figure 17. Arrhenius plot for cumene (3.6 torr, 2.0 mL/hr) cracking on ZSM-5 (Si/Al = 11.5, 5 mg) with water (27.5 torr, 2.0 mL/hr)

From the different activation energies for the cases with different partial pressures of water, it could be concluded that there is a certain amount of water that is ideal for the catalyst. Beyond that point, water becomes increasingly inhibitive of cracking rates. This is expected from literature sources because at some point water must behave as a diluent and competitively adsorb on the catalyst. However, the point where water begins to shift from a strictly positive role seems to be at a very low partial pressure. More investigation into how water partial pressure affects rate enhancement for zeolites is necessary.

It is interesting that activation energy would change little or even increase when it is easily observed that rate increases with water. However, observed rates for cumene cracking without water are not truly representative of the actual kinetics due to deactivation whereas cracking rates with water are more straightforward [31]. In fact, the main role of water in cumene cracking seemingly is to be a cleaning agent.

As a strictly qualitative assessment, water apparently has the ability to undo a certain degree of coking and to prevent any additional buildup of coke precursors while it is present. This is slightly different from a diluent since a diluent by nature only is able to adsorb on the catalyst surface, not react with coke as water seems to do in cumene cracking. Additional investigations with the use of a differential reactor setup would be more likely to yield results unfettered by deactivation phenomena.

ANSYS Simulations

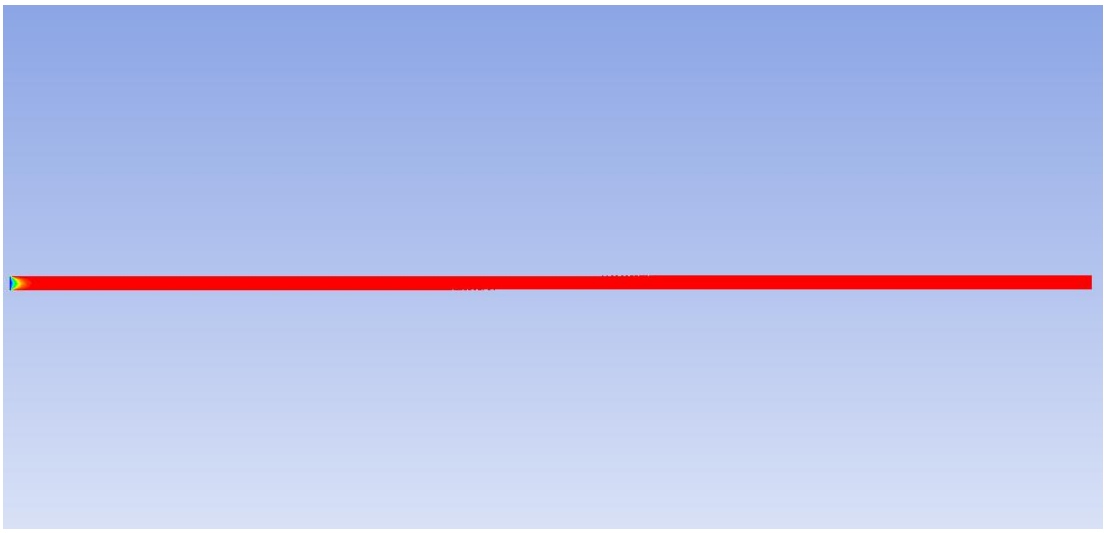

Figure 18. Temperature contour plot of the first 13 cm into the flow reactor before reaching the catalyst bed; blue represents room temperature and red shows the reactor at 300 °C

A model was developed using ANSYS Fluent for the pre-bed region of the flow reactor in order to map reaction temperature. This model could identify how soon after entering the reactor gases were heated to reaction temperature; from the simulation results (Fig. 18), it is apparent that reactants are able to reach reaction temperature rapidly. Another temperature difference worthy of consideration is the

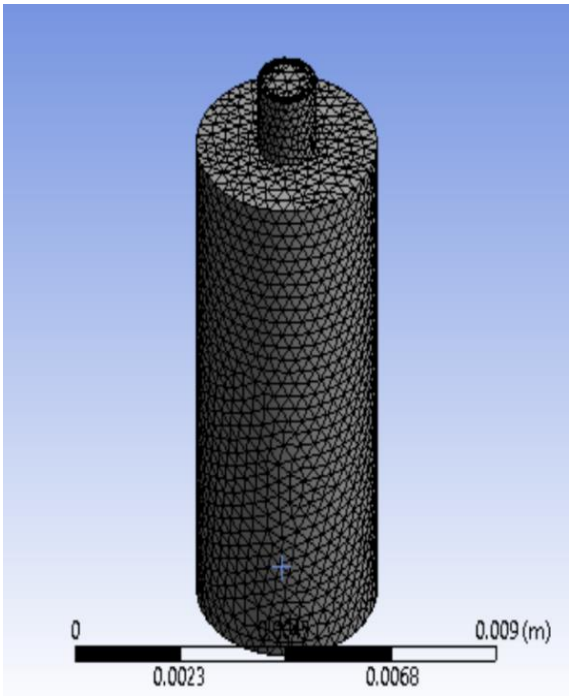

Figure 169. ANSYS mesh model of flow reactor bed

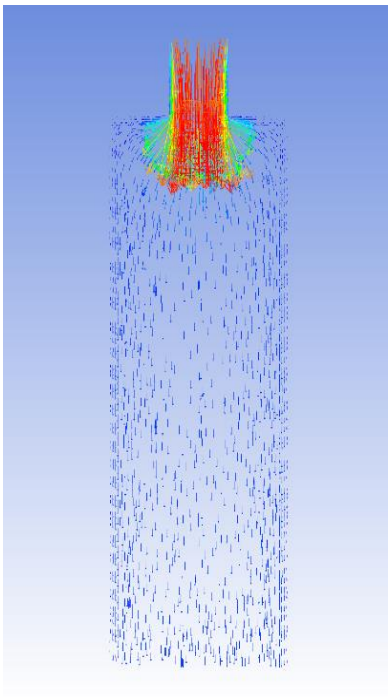

Figure 20. ANSYS velocity profile for determining dispersion of reactants through the catalyst bed; blue indicates the reactants are well-dispersed

possibility that there may be a temperature differential within the zeolite, but the reactant is too dilute for this to occur.

In order to demonstrate that 5 mg of catalyst was a sufficient mass for catalytic cracking experiments, a simulation was made for the catalyst bed to show how easily reactants disperse in a porous medium (Fig. 19). A velocity profile for reactants coming through a small cross-sectional area demonstrates how cumene is expected to disperse within the catalyst (Fig. 20). Since 5 mg is a small amount of catalyst for the system, there were concerns over the likelihood of reactants channeling past the catalyst and lowering the rate. However, the velocity profile gives a nice demonstration of how cumene channeling is avoidable for this system. Reactant flows were nearly uniform about 15% through the bed.

Conclusions

Water is capable of rate enhancement at all conditions studied; this rate enhancement occurs as a result of increased catalyst stability (less coking). However, this stability lasts only while water continues to be present in the reaction system. This is unlike the steaming of Y zeolites to form more stable USY catalysts, which has a much longer longevity than the studied case. Different partial pressures of water were investigated, and results indicated that water may have a positive effect on activation energy for a very small range of pressures. Outside of this range, water may still have an overall positive effect as it thwarts coke formation, but its effect on activation energy may in fact be negative.

Chapter 4: Heptane Hydrocracking

Introduction

As olefins, heptenes are extremely active compounds for catalytic cracking on zeolites. After adsorption to the surface heptenes are able to isomerize and form a tertiary carbocation. When this species cracks to form isobutylene, the species left behind on the acid site is a secondary carbocation (propylene). Reactions with C6 or smaller olefins do not allow for such a stable adsorbed species to get left behind after β-scission, so the activity of heptenes as model compounds is notably very high [32].

However, industrial cracking of olefins first requires their formation since these species are not stable enough to be found naturally. To form these species, hydrocracking methods were developed to take advantage of the equilibrium that arises when metals are in contact with hydrocarbons. Hydrogen is also added to the feed in order to prevent olefin concentrations from becoming too high. Although olefins are very reactive for catalytic cracking, they are also prone to various other kinds of reactions. The addition of hydrogen allows for greater control over the concentration of olefins to prevent undesirable secondary reactions [33-38].

Due to the highly active nature of olefins, and heptenes in particular, it is a difficult task to run experiments where the conversion of olefins is not 100%. One solution to this problem is to create a small, but constant, partial pressure of heptenes inside the reactor by means of the hydrocracking methods discussed above. As heptene is consumed, it is regenerated by dehydrogenation of heptane on a metal

catalyst; the equilibrium between heptane and heptene helps keep the partial pressure of heptene constant. This important because it allows for kinetics at extremely small partial pressures of reactant.

Catalytic cracking of heptene first proceeds by isomerization to branched heptenes. This step is not strictly necessary, but it is the most likely outcome due to the relative stability of tertiary carbocations over secondary. These intermediates are capable of desorbing and leaving the catalyst to show up in the products. However, it can be difficult for branched hydrocarbons of such size to do so because internal diffusion limitations apply to these species. Instead, these branched olefins would readsorb to the catalyst until they undergo β-scission to smaller molecules. Propylene and isobutylene are not hindered nearly as much by internal diffusion and diffuse from the zeolite pores. These products subsequently interact with the metal catalysts in the bed, which are abundant, and are converted to isobutane and propane [35-37].

These two species, and possibly branched heptanes, will be the major products of heptane cracking reactions. Their relative abundances will give an indication of how strongly branched C7 hydrocarbons are able to diffuse through the zeolite structure. Water will not be present in this reaction system due to concerns with the oxidation of the metal, but its effects on zeolite activity can still be determined. In order to investigate the possible role of water for zeolites during hydrocracking reactions, zeolites can be pretreated with water at 500 °C before they are mixed with the platinum cocatalyst. If water pretreatment leads to a stable change in zeolite

activity, then it is possible that zeolite rate enhancements will also show improved rates for hydrocracking.

Experimental

Catalyst Preparation

ZSM-5 catalysts in the ammonium form were purchased from Zeolyst International. Catalysts were given acid functionality by calcination at 600 °C for 5 hours. The temperature ramp was set to 2 °C/min in order to prevent vaporizing water from damaging the zeolite. Three zeolites with different Si/Al ratios were used in experiments: CBV 2314 (SiO_2/Al_2O_3 = 23, 425 m^2/g), CBV 3024E (SiO_2/Al_2O_3 = 15, 405 m^2/g), and CBV 8014 (SiO_2/Al_2O_3 = 80, 425 m^2/g).

Two platinum cocatalysts with different loadings of metal (1 wt% and 2 wt%) were used in these experiments. In both cases, silica was used as a support. The 1 wt% platinum catalyst was obtained from Sigma Aldrich and used with minimum preparation whereas the 2 wt% platinum catalyst was prepared by incipient wetness impregnation. Silica gel (Aldrich, Davisil grade 635; 480 m^2/g; 0.75 cm^3/g pore volume) was impregnated with an aqueous solution of chloroplatinic acid; the acid solution was added dropwise to the support and mixed thoroughly with the support powder until the entire powder was a uniform yellow-brown. Afterwards, one gram at a time of impregnated sample was treated in dry air (2.5 cm^3/s) at 550 °C for 2 hours, then at 650 °C for 3 hours. The temperature ramp was kept to 2 °C/min to ensure the

integrity of the silica framework. At the end of this treatment step, the silica had a color change to black, as expected.

Zeolite and impregnated silica samples were combined in such proportions that the number of platinum atoms was greater than the number of acid sites by at least a factor of 8 [36]. This would disallow local concentration gradients between olefins and paraffins from forming. Instead, the concentration of heptenes in the gas phase could be kept nearly constant throughout the catalyst bed despite the highly reactive nature of olefins on zeolites.

For zeolites where Si/Al = 11.5, around 4 mg of zeolite powder was mixed with approximately a gram of 1% platinum on silica. Likewise, about 20 mg of zeolite powder with Si/Al = 40 was mixed with just over a gram of 1% platinum. Zeolites with Si/Al = 15 were mixed with 2% platinum catalyst at an approximate mass ratio of 4:600. To investigate how water might affect the zeolite, samples of zeolites with Si/Al = 11.5 and Si/Al = 40 were steam treated at 500 °C for 1.5 hours before addition to the platinum catalyst. Zeolite and silica powders were mixed thoroughly to improve cocatalyst homogeneity. Cocatalyst samples were pelletized, crushed, and sieved to diameters between 90 and 25 microns.

Hydrocracking at Continuous Flow Conditions

Heptane hydrocracking (Aldrich, 99% purity) on ZSM-5 and platinum cocatalyst was performed with each catalyst. Catalysts were loaded into a quartz reactor between glass wool. Hydrogen is necessary for the hydrogenation and

dehydrogenation of paraffins and olefins; the flow rate for this carrier gas was 105 mL/min. The pressure of the system was kept near atmospheric pressure.

Before the reaction, the metal catalyst was reduced by raising the reactor temperature to 300 °C (5 °C/min) while hydrogen flowed. Afterwards, the final temperature was set and reactor temperature was allowed to cool to the desired temperature, somewhere between 190 and 300 °C. A syringe pump was used to flow heptane into the reactor at a rate of 0.25 mL/hr after the catalyst was pretreated. The controlled variables for the reactor system were held constant for 30 minutes before data collection. A Hewlett Packard 6890 gas chromatograph was used to analyze the reaction products for the hydrocracking reaction. Products were separated by a porous layer open tubular column and were quantified by a flame ionization detector. Response factors for hydrocarbons were assumed to be equal to 1, and concentrations could be determined by comparing peak areas to known standards.

Results and Discussion

Hydrocracking Rates

Conversions for heptane hydrocracking were consistently below 30% for all runs in order to provide accurate rate data. Reported data implicitly have carbon balances within 10% error. Despite holding control variables constant for 30 minutes in order to allow the system to reach steady state, rate data was determined to be transient for all reactions. Rates would continue to increase, peak after about an hour, and steadily decrease for the rest of the experiment. Moreover, no correlation was

observed between reaction temperature and conversion. Pretreatment of zeolites with water also appeared to have no effect. The ratio of Si/Al for the zeolite also did not appear to affect results; platinum on silica, with no zeolite at all, also gave similar results to data that had acid functionality.

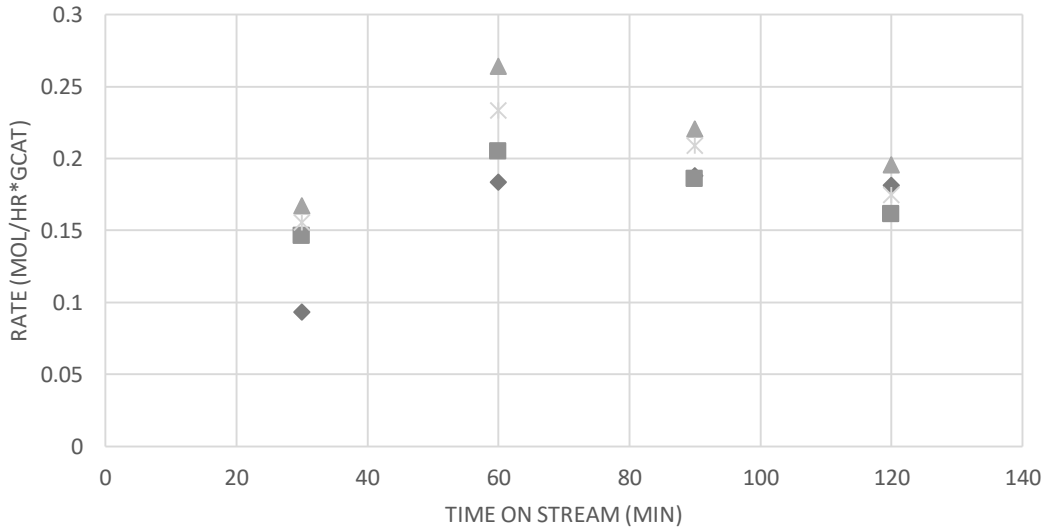

Figure 21. Rates of heptane (3.6 torr, 2.5 mL/hr) consumption as a function of time on stream; Pt with no zeolite: diamond: 250 °C; ZSM-5 with Si/Al = 15: square: 250 °C, triangle: 210 °C, star: 190 °C

Rather than hydrocracking, the results suggest the buildup of a hydrocarbon pool on the surface of the catalyst. The rate seems to increase at first because the hydrocarbon pools are not yet well-developed on the surface of the catalyst. However, this does not explain the observed reaction rate of platinum on silica without zeolite; this may be caused by a small degree of acid functionality that was present in the silica before impregnation. Continuous adsorption of heptenes, which quickly isomerize to methylhexenes and dimethylpentenes, lends to the steady growth of these hydrocarbon pools as the adsorbed molecules bond with each other. Eventually,

the pools will start to form coke on the zeolite surface, which will lead to steady deactivation of the catalyst, as observed.

Selectivity

Reactions were observed to have a selectivity of around 90% for isobutane. Aside from propane, very few other species were present. These results are very contrary to what would be expected for heptane hydrocracking. Although high selectivity for isobutane and propane is expected, these species should exist with near equimolar ratios.

As hydrocarbon pools develop, β-scission occurs around acid sites; these acid sites are associated with tertiary carbocations, so isobutylene is the only molecule synthesized. After isobutylene exits the zeolite, it reacts with hydrogen on the platinum surface to form isobutane, which is the major observed product. The overwhelming presence of isobutane in the products also suggests a hydrocarbon pool mechanism over hydrocracking.

Conclusions

For the reaction conditions set forth, hydrocracking was not the dominant mechanism for the results obtained. Instead, it seems that a hydrocarbon pool developed on the surface of the zeolite and interfered with data collection. At this time, it is unknown how water affects hydrocracking reactions at the conditions studied. Further investigation is required; improvements for the methodology include

using a smaller flow rate of heptane in order to reduce the probability of reactions of adjacent adsorbed compounds.

CHAPTER 5: CONCLUSIONS

For a variety of reaction conditions, water has been shown to provide a rate enhancement. For hexane cracking, water was shown to increase reaction rates and decrease activation energy to the point that internal diffusion started to become rate limiting. Despite higher rates, selectivity was not observed to change greatly over the conditions studied, and most importantly, propylene selectivity remained high. More interesting was that the rate enhancements continued even after the subsequent removal of water from the reaction system. Rate enhancements were connected to zeolites with low Si/Al ratios. Although the underlying cause of this connection is still unknown, it is believed that at these temperatures, water is able to react with extraframework alumina (EFAL) to create synergistic sites that interact with molecules adsorbed on acid sites.

In the case of cumene cracking, water acts as a cleaning agent that is able to reduce coke formation. However, this cleaning effect lasts only as long as water partial pressure is maintained in the reaction system; no permanent effects for water are known for these conditions. The amount of water partial pressure was also investigated to link partial pressure to activation energy, and it was determined that the range of pressure for water to decrease activation energy is extremely small. Assuming that water and EFAL can potentially react, these observations suggest that water does not react with EFAL at low temperatures like those seen in cumene cracking, but it will react at higher temperatures. This may imply some sort of activation energy barrier for a water-EFAL interaction.

Further investigation of water enhancement is still required. Future work would involve determining how exactly water enhancements are made possible by low Si/Al ratios. Removal of EFAL in order to discover if water enhancements cease would be one way to determine what the connection is between enhancements and low Si/Al ratios. Additional experiments at intermediate temperatures to determine the activation energy barrier for a water-EFAL interaction, should any exist, would also prove useful for determining the necessary steps required to treat zeolite catalysts. Additional studies on heptane hydrocracking would also be informative. Improvements for these studies would include smaller partial pressures of heptane in order to eliminate the hydrocarbon pool.

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