Phosphorus-Containing Zeolites for Biofuel Production

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Phosphorus-Containing Zeolites for Biofuel Production

A Dissertation Presented

by

JASON GULBINSKI

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2023

Chemical Engineering
Phosphorus-Containing Zeolites for Biofuel Production

A Dissertation Presented

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JASON GULBINSKI

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ABSTRACT

PHOSPHORUS-CONTAINING ZEOLITES FOR BIOFUEL PRODUCTION

February 2023

JASON GULBINSKI, B.CH.E., UNIVERSITY OF DELAWARE

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Wei Fan

Fossil fuel consumption increases 2% a year due to transportation fuels and specialty chemicals for plastics and synthetic fibers such as p-xylene, a monomer of polyethylene terephthalate. p-Xylene demand was over 50 million tons in 2021 and will increase by 5% a year through 2026. Therefore, sustainable p-xylene production is desired. p-Xylene is produced renewably through Diels-Alder cycloaddition of biomass-derived 2,5-dimethylfuran (DMF) with ethylene from bio-ethanol and dehydration over an acid catalyst. Industrial aluminosilicate zeolite catalysts achieve a selectivity of 75%, with loss to side products and coking. A new class of catalysts, phosphoric acid-containing aluminum-free zeolites, P-zeosils, like dealuminated zeolite P-BEA show high selectivity to p-xylene over 95%. However, the active site structure and structure-property relationships leading to the high selectivity are unknown. Herein, the catalytic performance of homogeneous phosphoric acid in p-xylene production with and without adding siliceous zeolite in the reactions is investigated. Phosphoric acid is active for p-
xylene production, but phosphoric acid adsorbing on the siliceous zeolites during the reaction shows an improved selectivity. However, impregnation of phosphoric acid on the siliceous zeolite before the reaction forming the P-zeosil achieves the highest selectivity (>95%). Changing Si/P ratio and calcination temperature on the impregnated P-zeosils are investigated through X-ray diffraction (XRD), nitrogen adsorption and $^{31}$P solid state magic angle spinning nuclear magnetic resonance (MAS NMR). The P-zeosils exhibit Brønsted acid sites (BAS). Good agreement was found between DMF initial reaction rate and the BAS density. Low Si/P ratio (Si/P<3) and higher calcination temperatures lead to BEA crystal structure damage and formation of oligomerized polyphosphates and silicon phosphates, decreasing BAS density. The oligomerized polyphosphates and silicon phosphates can be hydrolyzed with water and cofed water/alkylamines, which can significantly increases the BAS density. Further understanding of the active site structure of P-BEA and other P-zeosils is crucial for their future industrial use in renewably relevant reactions.
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CHAPTER 1

INTRODUCTION

1.1 Renewable p-Xylene and Other Biofuels

Since the industrial revolution, man-made greenhouse gas emissions from fossil fuel consumption have caused an ever-growing threat of climate change. Current carbon dioxide levels in Earth’s atmosphere are greater than any point in the last 650,000 years, increasing of surface temperatures averaging 1 °C throughout the last century, melting the polar ice caps, and warming and acidifying the oceans. Exacerbated climate change can lead to disruptions in global ecosystems, potentially causing mass wildlife extinctions and global food and water shortages.\(^1\) The consumption of fossil fuels, such as oil and natural gas, are so ingrained in our economy that demand continues to grow despite the dangers of climate change. Global oil production typically increases about 2% a year, and although global oil production decreased by approximately 10% in Q1 2020 due to the coronavirus pandemic, the global oil production is nearing pre-pandemic levels and growth rates.\(^2\) Demand for oil continues to increase not only because of transportation fuels, including gasoline, diesel, and jet fuel, but also due to increased demand for the large variety of specialty petrochemicals. The specialty petrochemicals are indispensable for preparing everyday products in the form of synthetic fibers, plastics, asphalt, pharmaceuticals, and cosmetics.
The specialty chemicals derived from fossil fuels could become the largest fractional outputs per barrel of oil, as consumer electric and hybrid vehicle adoption can plateau demand for transportation fuels. Demand for one of the most popular specialty chemicals, \( p \)-xylene, reached over 50 million tons in 2021, and demand is expected to increase by a compounded annual growth rate of 5% through 2026. The largest demand for \( p \)-xylene comes from the production of polyethylene terephthalate (PET), used in synthetic fibers and plastics with a “1” inside the “recyclable triangle.” \( p \)-Xylene is typically produced through cracking of naphtha and gas oil byproduct streams, yielding benzene, toluene, and xylenes (BTX) of which \( p \)-xylene can be purified. Likewise, catalytic upgrading of petroleum reformate also produces BTX-rich feeds of which \( p \)-xylene can be separated. Crude oil-to-chemicals (COTC) have gained traction in recent years, which can generate specialty chemical conversion of over 45% of a barrel of oil, nearly 3 times greater yield of specialty chemicals than typical oil processing, and \( p \)-xylene could potentially account for over 50% of the COTC products. Therefore, a renewable process to produce \( p \)-xylene is highly desired to compete with \( p \)-xylene from fossil fuels.
Biomass feedstocks, containing lignocellulosic biomass, could provide a renewable carbon source to displace fossil fuel processes to produce \( p \)-xylene.\(^{13, 14}\) There are many proposed processes to produce \( p \)-xylene from biomass, such as: direct synthesis from ethylene derived from bio-ethanol by trimerization/cycloaddition and subsequent dehydrogenation to \( p \)-xylene.\(^ {15}\) methanol-to-aromatics (MTA) from bio-methanol,\(^ {16}\) fermentation of glucose to acetic acid or isobutanol followed by catalytic transformation to \( p \)-xylene,\(^ {17}\) and catalytic pyrolysis of biomass to BTX with \( p \)-xylene separated out.\(^ {18, 19}\) However, the drawbacks to these processes include limitations to fermentation, poor biomass yield, and low \( p \)-xylene selectivity requiring further separation steps.\(^ {20}\) A direct...
catalytic route from biomass to $p$-xylene can be achieved through the Diels-Alder cycloaddition of ethylene to 2,5-dimethylfuran (DMF), forming a cycloadduct intermediate which is dehydrated to $p$-xylene over a solid acid catalyst, which shows high atom economy and $p$-xylene selectivity.$^{21-27}$ Hydrolysis of lignocellulosic biomass produces glucose$^{28}$, which is then converted to hydroxymethylfurfural (HMF).$^{29}$ Further deoxygenation of HMF yields DMF,$^{30}$ which then undergoes the Diels-Alder cycloaddition with ethylene and dehydration over solid acid sites to produce $p$-xylene. Every sequential step has achieved over 80% selectivity toward the desired product (Scheme 1.1). It has previously been found phosphoric-acid containing aluminum-free or near-aluminum-free zeolites P-BEA and P-SPP can achieve over 95% selectivity to $p$-xylene in the final step with DMF and ethylene, an improvement over commercial standard Brønsted acid catalyst Al-BEA and Lewis acid catalysts like Zr-BEA and Sn-BEA$^{7,22}$ which only achieve 75% $p$-xylene selectivity with significant side product formation through alkylation and oligomerization side reactions.$^{31}$

The $p$-xylene reaction from DMF and ethylene proceeds through a tandem Diels-Alder cycloaddition of ethylene to DMF and subsequent dehydration over a solid acid catalyst. Considerable previous work has gone into understanding the energetics and reaction mechanism of the tandem reaction over both Lewis and Brønsted acid catalysts.$^{21,32-36}$ The first reaction step, the Diels-Alder cycloaddition, is more energetically favorable with an uncatalyzed activation energy of approximately 40 kcal/mol than the
second step, the dehydration of the cycloadduct with an uncatalyzed activation energy of approximately 60 kcal/mol, which would not proceed under previously studied reaction temperatures (200-300 °C) without catalyst present. The first cycloaddition step proceeds through symmetry-allowed HOMO-LUMO association of the ethylene with the DMF, where the smaller the HOMO-LUMO energy gap, the quicker the reaction.\textsuperscript{33} Lewis acids can further reduce the HOMO-LUMO energy gap by binding of the ethylene to further reduce the LUMO of the ethylene, decreasing the activation energy to approximately 20 kcal/mol with alkali substituted Zeolite Y, increasing the reaction rate.\textsuperscript{34} The Diels-Alder cycloaddition is not catalyzed by Brønsted acids, as the reaction activation energy of protonated ethylene with DMF is calculated to be 72 kcal/mol and protonated DMF with ethylene is calculated to be 55 kcal/mol, both higher than the uncatalyzed activation energy of 40 kcal/mol\textsuperscript{33}. The second step dehydration of the cycloadduct can effectively be catalyzed by both Brønsted and Lewis acids, but Brønsted acid sites associated with framework aluminum have a greater degree of enhancement. In Brønsted acids, the activation energy is decreased to approximately 15 kcal/mol, a decrease of 45 kcal/mol, for the C-O bond cleavage. The best Lewis acids studied in this mechanism show only a decrease to approximately 30 kcal/mol for C-O bond cleavage in alkali-substituted zeolite Y, with larger alkali substitutions showing less efficacy.\textsuperscript{34}

Energetics and mechanisms of side reactions, such as the hydrolysis ring-opening of DMF to form 2,5-hexanedione and oligomerization of the cycloadduct with additional
DMF have also previously been investigated. The hydrolysis ring-opening of DMF with water produced from the cycloaduct dehydration to form 2,5-hexanedione has a forward and backward activation energy of 28 and 20 kcal/mol, respectively. Because they are lower than the activation energy for the cycloaddition with ethylene and the small difference in energy between forward and reverse reactions, the formation of 2,5-hexanedione is expected to reach equilibrium with water and DMF. At high DMF conversion, 2,5-hexanedione will convert back to DMF which can react to \( p \)-xylene, thereby not causing a significant loss in \( p \)-xylene selectivity. However, 2,5-hexanedione could oligomerize or be alkylated, reducing the selectivity to the final product of \( p \)-xylene. The activation energy for the cycloaduct reacting with another DMF to form oligomeric products is 1.5 kcal/mol higher than the one for the dehydration of cycloaduct into \( p \)-xylene, and this can be further increased to 2.2 kcal/mol higher than the dehydration to \( p \)-xylene pathway when \( n \)-heptane is used as a solvent. The increased activation energy for side reactions can reduce the side reaction rate and increase \( p \)-xylene selectivity. Selectivity towards \( p \)-xylene could be improved with a weaker acid catalyst than typical aluminosilicate catalysts, as aluminosilicate catalysts are strong enough to catalyze both pathways. Weaker acid catalysts may not have as significant a reduction in activation energies of aluminosilicates to both the desired reaction to \( p \)-xylene as well as side reactions. Since the activation energies are so close for the pathway to \( p \)-xylene and the oligomerization reaction, a weaker acid site could reduce the \( p \)-xylene activation energy
pathway enough to still proceed, but not reduce the side reaction pathways as much such that the side reaction pathways are not favorable at the given temperature.\(^{35}\)

**1.2 P-Materials for Renewable \(p\)-Xylene Production**

Zeolites are crystalline materials, a class of aluminosilicates with tetrahedrally coordinated \(\text{TO}_4\) subunits, with \(T\) either Si or Al connected to each other through bonds with oxygen. The T-O-T bonds have a wide degree of possible bond angles, leading to many possible crystalline structures. In zeolites, the \(\text{TO}_4\) are arranged in such a way that leads to open channels throughout the structure called pores. The pores of zeolites are generally smaller than 2 nanometers called micropores. Shown in Figure 1.1, BEA* (3-letter code assigned by International Zeolite Association) structure has pores arranged in a 12 T atom ring, forming micropores with 7.6 angstrom diameter.\(^{37}\) Self-pillared pentasil (SPP) structure contains mixed layers of MFI 3-letter code assigned by International Zeolite Association) nanosheets orthogonally connected to in a house-of-cards structure.\(^{38,39}\) MFI structure has 10 T atom rings, with 5 angstrom diameter micropores. The layering of the zeolite nanosheets introduces mesopores 2-7 nanometers thick.\(^{37}\) P-BEA and P-SPP represent the phosphoric acid-impregnated zeolites.
Figure 1.1 Zeolite structures of BEA*, MFI, and MFI arrangement in SPP

P-BEA and P-SPP represent a new class of solid acid catalysts which can efficiently and selectively produce fuels and petrochemicals such as $p$-xylene from biomass-derived feeds. While aluminosilicate zeolite catalysts have shown important applications in the conversion of biomass, the significant presence of water and oxygenated compounds in biomass feeds can lead to low catalyst lifetime, low selectivity, and coking over the strong aluminum acid sites. Therefore, catalysts with tunable acid strength are necessary for biomass conversion in order to improve their catalytic performance including selectivity and catalyst life time. One previous solution to reduce acid site strength of aluminosilicate zeolites is to substitute the aluminum for other trivalent heteroatoms like Ga, Fe, and B, but they were found to significantly reduce the rate of reaction compared to the aluminosilicate zeolites. The impregnation of phosphoric acid onto Al-free zeolites has shown enhanced selectivity over Al-zeolites in not only $p$-
xylene production from DMF and ethylene, but also several other catalytic applications. P-containing zeosil P-SPP has shown a high selectivity in the formation of 1,3-butadiene and pentadienes from the dehydrodecyclization of tetrahydrofuran and methyltetrahydrofuran. 1,3-butadiene is an important monomer for rubber production. In addition, phosphoric-acid impregnated SiO$_2$ has shown high selectivity in production of furan-containing lubricants from biomass feeds.

P-BEA and P-SPP are chemically similar to industry standard solid phosphoric acid catalysts (SPA) which have been used for benzene alkylation with ethylene and propylene to ethylbenzene and cumene respectively, alkene isomerization and oligomerization for gasoline and diesel fuels, and in Fischer-Tropsch-derived product oligomerizations. They are made with phosphoric acid impregnated on kieselguhr silica with a low Si/P ratio (Si/P<3), and subject to high temperature calcination of at least 300 °C. The phosphorus species present on SPA catalysts are highly dependent on the moisture content and time and temperature of the calcination, with several crystalline silicon phosphate species listed in order of decreasing water content: Si(HPO$_4$)$_2$·H$_2$O silicon hydrogen phosphate monohydrate, Si$_5$O(PO$_4$)$_6$ silicon orthophosphate, SiHP$_3$O$_{10}$ silicon hydrogen tripolyphosphate, and SiP$_2$O$_7$ silicon pyrophosphate. Of free phosphoric acid species not bound to silica species, orthophosphoric acid (H$_3$PO$_4$), pyrophosphoric acid (H$_4$P$_2$O$_7$) and polyphosphate (P$_2$O$_5$) species are also present. Hydrolysis of silicon phosphate species can produce different free
phosphate species dependent on the reaction temperature. Different silicon phosphate species, degree of hydration, and reaction conditions affecting the ratios of free phosphate species present lead to different activity and selectivity within the commercially studied reactions.\textsuperscript{56} Under ultra-dry conditions (water content <200 ppm) benzene alkylation with propylene to cumene has higher activity compared to moderate hydration conditions (200-1000 ppm), where oligomerization of propylene to nonene and dodecene dominates over the benzene alkylation to cumene.\textsuperscript{50} At higher water content (>1000 ppm), the propylene oligomerization activity is reduced.\textsuperscript{57, 58} These results can be explained by the increase in hydrolysis of silicon phosphates which forms pyrophosphoric acid when the water content is above 200 ppm. The pyrophosphoric acid is more active for propene oligomerization. Above 1000 ppm of water, pyrophosphoric acid is hydrolyzed to orthophosphoric acid, a weaker acid and therefore less active in propene oligomerization.\textsuperscript{57} While not beneficial for cumene production, propene oligomerization is a commercial process to produce diesel fuels from Fischer-Tropsch processes, and therefore the optimization of the water content maximizing the pyrophosphoric acid species leads to higher diesel selectivity.\textsuperscript{57, 58}

The major difference between P-zeosils and SPA is that P-zeosils can be made with tunable Si/P ratio, and with dispersed P sites within the microporous structures. These features could lead to higher activity per P than SPA catalysts, as the microporous structure can induce confinement effects which could improve selectivity, lead to
significantly higher surface areas and active site accessibility, and diffusion limitations in BEA zeolite for the \( p \)-xylene reaction were previously ruled out.\textsuperscript{36} With a tunable Si/P ratio and microporous structures, it may be possible to preferentially generate certain P species and various distributions of these species on P-zeosils that would not be possible on SPA with high P content (Si/P<3).

While P-zeosils have been found as highly selective and active in \( p \)-xylene reaction, the reason for the high selectivity is not yet known. The active site structure or most active P species has not yet been identified. Understanding why P-zeosils can selectively catalyze the \( p \)-xylene reaction and their active site structure could facilitate application of P-zeosils in other renewably relevant reactions.

1.3 Thesis Scope

This thesis is broken down into 3 main chapters. First, in Chapter 2 the intrinsic activity of liquid phosphoric acid in the \( p \)-xylene reaction is studied and compared to the phosphoric acid-impregnated dealuminated BEA (P-BEA). The interaction between phosphoric acid and the dealuminated BEA zeolite support under reaction conditions is investigated, to help explain why the P-BEA is a superior catalyst to liquid phosphoric acid. In Chapter 3, the synthesis conditions of the P-BEA and other P-zeosil materials are altered to investigate the effect of Si/P ratio and calcination temperature on the phosphorus speciation and stability of the zeolite crystal structure, to establish the structure-property relationships for P-BEA in the \( p \)-xylene reaction. The catalytic performance of P-BEA and
other P-zeosils are further improved by the hydrolysis of condensed phosphate structures in the presence of water or water/amine which can greatly increase the observed Brønsted acid site density (Chapter 4). The discovery could show promise in helping further narrow down active site species and potentially improve activity in renewably relevant reactions. It is the objective of this thesis to unveil the nature of P-zeosils by developing structure-property relationships for phosphate species, their interactions with the silica support, and their efficacy in reactions. Chapter 5 and Chapter 6 draw conclusions from this work to be used in future efforts.
Chapter 2
PHOSPHORIC ACID AND P-BEA FOR P-XYLENE PRODUCTION

2.1 Introduction

To understand why P-BEA can achieve such high selectivity in p-xylene reaction, it is important to first understand the intrinsic activity of phosphoric acid in the absence of any zeolite support as a catalyst for p-xylene production, such that the effect of the zeolite support can be investigated and the association of phosphoric acid with the zeolite support can be studied.

Liquid phosphoric acid has been used as an industrial catalyst for nearly a century, being used as a direct catalyst for alkylation of aromatic hydrocarbons,\(^6\) polymerization of gaseous olefins,\(^6\) and the use of silica-supported phosphoric acid has been shown to dehydrate alcohols.\(^6\) Reactions typically involve higher temperatures which lead to oligomerization of phosphoric acid into polyphosphates and metaphosphates. In the last 2 decades, a new class of phosphoric acid catalysts emerged, named chiral phosphoric acids.\(^6\) These phosphoric acid catalysts consist of monophosphoric-derived esters such as 1,1’-bi-2-napthol(BINOL)-phosphoric acid, with functionality within the P-OH and P=O, and the organic template conferring steric and electronic influence from the ring system and preventing rotation introducing chirality. The organic substituents can be tailored to alter functionality and provide enantioselective products in a variety of organic and
biologically relevant reactions at relatively low temperatures (<100 °C). However, for many reactions relevant to renewable chemistries a higher temperature is required.

Association of silica supports with aqueous phosphoric acid *in-situ* in a non-polar \( n \)-heptane solvent could be classified as Pickering emulsion, in which an oil-and-water mixture is stabilized into an emulsion by the addition of solid particles, where the solid particles disperse at the oil-water interface.\(^6\) In the last decade, Pickering emulsions have gained popularity in catalytic processes,\(^6\) increasing conversion and selectivity. Zeolites with phosphoric acid in an organic phase are mentioned in literature to likely create a Pickering emulsion in the right environment.\(^7\)

Therefore, the purpose of Chapter 2 is to understand the activity of liquid phosphoric acid in the \( p \)-xylene reaction and how the interaction of phosphoric acid with the silica support can improve its activity. Unsupported liquid phosphoric acid is tested in \( p \)-xylene production. Both the reaction rate and selectivity are compared with the cases where silica supports are mixed with liquid phosphoric acid in the reaction solvent.\(^7\) The changes of \( p \)-xylene selectivity and reaction rate to the phosphoric acid concentration, with and without silica support, and with varying weights of silica support are observed. Evidence for liquid phosphoric acid adsorption on silica supports during the reaction called as *in-situ* adsorption is also tested. The stability of phosphoric acid on the silica support under reaction conditions is investigated, as the interaction between phosphoric acid and silica support is important to understand the stability of phosphoric acid on silica
supports under reaction conditions. Other types of support for phosphoric acid, such as carbons and metal oxides, are studied in comparison to silica supports, with silica supports typically showing the highest activity. Solvent effects are also studied, with comparisons between the typical solvents, \textit{n}-heptane, and other solvents, 1,4-dioxane and tetrahydrofuran. Attempts to further improve reaction rate with copper-based Lewis acid catalysts are also investigated.

\section*{2.2 Experimental Design}

\subsection*{2.2.1 Catalyst Preparation}

Phosphoric acid impregnated zeolite P-BEA was prepared with post-synthetic modification of commercial Al-BEA with Si/Al=12.5 (Zeolyst, CP814E). Al-BEA was subject to nitric acid treatment to remove aluminum, with 25 mL 70\% nitric acid added to 0.5 g Al-BEA in an autoclave and held for 90 °C for 1 day. The mixture was centrifuged at 3825 relative centrifugal force, the nitric acid supernatant discarded, and the cake redispersed in water, followed by washing with 1 L of DI water through vacuum filtration and drying at 70 °C for 1 day to make dealuminated BEA (deAl-BEA). Then, 0.4 g of deAl-BEA was mixed with 3.35 mL of dilute phosphoric acid, the concentration depending on desired Si/P ratio. For Si/P=27, the solution is 0.72 wt\% H$_3$PO$_4$, for Si/P=10 1.96 wt\% H$_3$PO$_4$, and Si/P=3 6.22 wt\% H$_3$PO$_4$. Mixtures of deAl-BEA and phosphoric acid were dried at 70 °C for 1 day, followed by calcination at 600 °C with 400 °C/hr ramp, 30-minute hold, and under 100 mL/min flowing dry air. Other supports were impregnated in similar fashion: Si-SPP
(537 m²/g 38, 39), fumed SiO₂ (CAB-O-SIL M5, 200 m²/g 72), and Si-BEA-HF (488 m²/g 73), a low-defect Si-BEA synthesized using HF⁷⁴ which is more hydrophobic than deAl-BEA, lacking the defects generated through removal of framework aluminum.

In preparation of Cu-BEA materials, 2 methods were attempted: direct impregnation of Cu(NO₃)₂ on deAl-BEA and ion-exchange of Cu(NO₃)₂ on calcined H-BEA (CP814E). With direct impregnation, 3.35 mL of 0.074 M Cu(NO₃)₂ solution was impregnated on 0.4 g deAl-BEA leading to a Si/Cu=27. For ion exchange, 1 L of 0.5 M Cu(NO₃)₂ was mixed with 0.5 g of H-BEA with stirring for 1 hour, filtered, and washed with 1 L of DI water, and the process repeated once more. Both samples were subject to 600 °C calcination in the same method as P-BEA. Attempts were then made to impregnate phosphoric acid on the Cu-BEA materials, with similar methods to P-BEA preparation.

Sodium-substituted phosphate impregnated deAl-BEA was prepared with similar methods to the preparation of P-BEA samples with Si/P=27. Sodium substituted phosphates were tested to see which proton on the phosphate may be the most active for the p-xylene reaction. As 3.35 mL of a 0.72 wt% H₃PO₄ was used for impregnation on 0.4 g of deAl-BEA to obtain P-BEA Si/P=27, 3.35 mL of 0.88 wt% NaH₂PO₄, 1.04 wt% Na₂HPO₄, and 1.20 wt% Na₃PO₄ were used to prepare NaH₂PO₄-BEA, Na₂HPO₄-BEA, and Na₃PO₄-BEA respectively all with Si/P=27. Materials were subject to the same calcination conditions as P-BEA.
2.2.2 Reaction Preparation

*p*-Xylene reactions were run under 3 different cases. Case 1; liquid 85 wt% phosphoric acid was added directly to the reaction mixture prior to sealing the reactor. Phosphoric acid concentration was varied from 1.7 mM to 45 mM by increasing the mass of 85 wt% phosphoric acid. Case 2; liquid 85 wt % phosphoric acid and solid silica support were separately added to the reaction mixture, with no impregnation of phosphoric acid on the support prior addition, allowing silica-phosphoric acid interactions in the reaction mixture (in-situ adsorption). In this case, 2 different phosphoric acid concentrations were used, 11 mM and 22 mM, in combination with 0.2 g, 0.5 g, and 0.8 g of deAl-BEA added separately to the reaction mixture. Additionally, 0.5 g of other silica supports including Si-SPP, Si-BEA (HF), and fumed SiO₂ were tested with 11 mM of phosphoric acid, to investigate the effects of different supports and their association with phosphoric acid. Case 1 and 2 are compared to case 3 where the reactions were catalyzed using P-BEA prepared by the impregnation of phosphoric acid on the deAl BEA before the reactions.

All reactions were run in a 160 mL Hastelloy Parr reactor charged with 50 mL of 1.35 M 2,5-dimethylfuran (DMF, >99.8%, Acros organics) in n-heptane (99%, Alfa Aesar) with 1.0 mL of n-tridecane (>98%, Alfa Aesar) internal standard. Catalysts were added directly to the reaction mixture before sealing. The sealed reactor was purged with nitrogen to test for leaks and remove atmospheric oxygen, then the temperature was increased to 250 °C, taking about 30 minutes to reach the set point. The gas entrainment
impeller was set to 550 rpm after sealing the reactor. After the temperature set point was reached, the reactor was then pressurized with 62 bar ethylene, beginning the reaction. Ethylene pressure was maintained at 62 bar over the course of the reaction. Most reactions were performed for 24 hours, with 1 mL of liquid samples taken through a double-block valve sampling system immediately after ethylene pressurization (t=0) and at designated sampling times.

Leaching studies, where solid silica support is removed after a designated time of reaction, was used to investigate the stability of phosphoric acid on the impregnated supports and *in-situ* adsorption of phosphoric acid with the solid supports. Leaching tests are performed on P-BEA and P-SPP catalysts. In addition, leaching tests were also performed for the case where liquid phosphoric acid and silica support were added in the reaction mixture separately. Typical reaction procedure was run for 3 hours, at which time the reactor was cooled. Reaction solution was centrifuged and filtered to remove the solids, then the reaction solution was re-added to the reactor, brought back reaction conditions, and reacted for 21 additional hours.
2.2.3 Reaction Analysis

Concentrations of reactants, product, and side products were analyzed using gas chromatography on an Agilent 6890A GC with RTX-VMS (Restek) capillary column and flame ionization detector (FID). Response factors and retention times for DMF, \( p \)-xylene (>98 %, Alfa Aesar) and 2,5-hexanedione (>98 %, Alfa Aesar) were calibrated with standard chemicals. Response factors and retention times for alkylated side products were estimated from representative species, 1-methyl-4-propyl benzene (>99%, TCI America) and response factor and retention time of oligomer products were estimated as the addition of DMF and \( p \)-xylene response factors and retention times. DMF conversion, \( X_{DMF} \), \( p \)-xylene selectivity, \( S_{px} \), and mass balances were calculated as shown:

\[
X_{DMF} = 100 \times \frac{C_{DMF,t=0} - C_{DMF,t}}{C_{DMF,t=0}} \quad (1)
\]

\[
S_{px} = 100 \times \frac{C_{px}}{C_{DMF,t=0} - C_{DMF,t}} \quad (2)
\]

\[
Mass \ Balance = \frac{\sum_i n C_i}{C_{DMF,t=0} - C_{DMF,t}} \quad (3)
\]

with \( t \) as the time after ethylene pressurization, \( C_i \) as the concentration of product \( i \), and mass balance calculated with \( n \) : 1 stoichiometric ratio of DMF in product \( i \): \( n=1 \) for \( p \)-xylene, 2,5-hexanedione, and alkylated product, with \( n=2 \) assumed for oligomeric products. Initial reaction rates were measured by mol of DMF reacted per hour, and per mol of phosphorus, measured at DMF conversions below 20%.
2.3 Results and Discussion

2.3.1 Role of Silica Support with Liquid Phosphoric Acid and P-BEA in \( p \)-Xylene Reaction

Initial reactions of the 3 cases mentioned above were first considered at constant P concentration of 11 mM: case 1, liquid phosphoric acid without silica support; case 2, liquid phosphoric acid with 0.5 g of deAl-BEA support; and case 3, with phosphoric acid impregnated on deAl-BEA to make P-BEA and used in reaction. Shown in Figure 2.1, liquid phosphoric acid displays the lowest selectivity to \( p \)-xylene, 60%, lowest initial reaction rate, and significant deviation in the mass balance indicating undetectable side products, which may be due to the coke formation. \( p \)-Xylene selectivity, mass balance, and initial DMF conversion rate all increase when liquid phosphoric acid and deAl-BEA are added together in the reaction mixture, yet the impregnated P-BEA shows even greater \( p \)-xylene selectivity, mass balance, and initial DMF conversion rate. The results of case 2, with addition of phosphoric acid and deAl-BEA in the reaction mixture, suggest phosphoric acid likely associates with the deAl-BEA support in the reaction mixture (in-situ adsorption), either through physisorption or P-O-Si bonds formed under reaction conditions, leading to an increase in selectivity, DMF conversion rate, and mass balance. DeAl-BEA in the absence of phosphoric acid shows negligible activity, therefore the improved activity is likely due to the association of phosphoric acid and deAl-BEA in the reaction mixture.
Figure 2.1: Catalytic activity of liquid phosphoric acid, with and without deAl-BEA, and P-BEA. The three cases: liquid phosphoric acid without silica support (case 1, red), liquid phosphoric acid added with deAl-BEA to reaction mixture (case 2, black), and P-BEA, deAl-BEA impregnated with phosphoric acid, dried, and calcined prior to reaction (case 3, green). $p$-Xylene selectivity (A), mass balance on DMF basis (B) and initial DMF conversion rate per mol of phosphorus at conversions below 20% of DMF (C). Reactions were performed using 11 mM liquid $\text{H}_3\text{PO}_4$ in case 1 and 2, 0.5 g of deAl-BEA support in case 2, and 1.0 g of P-BEA Si/P=27 in case 3. Reaction conditions: 250 °C and 62 bar of ethylene with 1.35 M DMF in $n$-heptane solvent. Error bars in (C) represent the repeated results of each reaction 3 times, which are used to access the reproducibility of the phosphoric acid catalysts in $p$-xylene production, with rates accurate within +/- 10% of the initial rate. Side product distributions are shown in Figure 2.16 of the appendix to Chapter 2.
While liquid phosphoric acid without silica support shows low selectivity compared to case 2 and case 3, the selectivity to \( p \)-xylene is dependent on the concentration of the liquid phosphoric acid without silica support, seen in Figure 2.2. At low concentration, such as at 1.7 mM phosphoric acid, the liquid phosphoric acid can achieve over 80% selectivity to \( p \)-xylene, but selectivity rapidly decreases with increasing phosphoric acid concentration from 1.7 mM to 45 mM. DMF conversion rate increases with increasing phosphoric acid concentration, but when normalized as a rate per mol of P in Figure 2.2 C, the rate per mol P decreases with increasing concentration. This may be due to poor solubility of phosphoric acid in \( n \)-heptane,\textsuperscript{75} resulting in poor dispersion of phosphoric acid. However, under the reaction conditions (250 °C), the solubility of phosphoric acid might be much higher than at room temperature. In addition, 85 wt% phosphoric acid will bring water into the reaction media, and water is also produced from the dehydration of the cycloadduct. At a complete conversion, approximately 1.0 g of water is produced. While poorly soluble in \( n \)-heptane at room temperature, at 250 °C, water mole fraction can be as high as 0.46\textsuperscript{76} in \( n \)-heptane. Although it is unknown how the water-\( n \)-heptane system, or other species in solution, could affect the solubility of phosphoric acid under reaction conditions, it is very likely water is miscible with \( n \)-heptane under the reaction conditions and phosphoric acid is dispersed within one phase.
The explanation for decreasing activity per mol P with increasing phosphoric acid concentration could be that phosphoric acid and water are fully soluble at reaction conditions, but phosphoric acid is not fully dissociated, and is in equilibrium with dissociated protons. To estimate the proton concentration, two extremes were considered: a pKa=4 of aqueous phosphoric acid estimated at 250 °C,⁷⁷,⁷⁸ and a pKa=35 estimated from computation calculations assuming phosphoric acid could dissolve and dissociate in n-heptane. Results of proton concentration with pKa=4 are given in Figure 2.2.
2.2 D, with the log of DMF conversion rate plotted against the log of proton concentration, generating a nearly linear trend with the slope=0.82, suggesting first-order kinetics with respect to proton concentration. Changing the pKa to the estimated \( n \)-heptane dissociation constant does not significantly alter the slope, but generates extremely small proton concentrations, and therefore turnover frequencies with many orders of magnitude above reasonable results. In the true system, pKa is likely changing with reaction progress as water is produced from the dehydration of the cycloadduct, changing the mole fraction of water, and possibly altering the pKa. At elevated temperature 250 °C, it is likely a single liquid phase as water content is below the extrapolated water solubility limit from literature, and the water content in the single phase greatly reduces the pKa from that of the pKa in \( n \)-heptane.

While the reaction outcome of liquid phosphoric acid without silica support could result from complex phase interactions with the reaction media, the effect of adding deAl-BEA is more obvious. As seen in Figure 2.3, with 11 mM liquid phosphoric acid, the addition of just 0.2 g of deAl-BEA improves the selectivity nearly to that of the impregnated P-BEA, and additional deAl-BEA does not further improve selectivity. At higher liquid phosphoric acid concentration, 22 mM, an increase in deAl-BEA mass does continue to show an increase in \( p \)-xylene selectivity. This result suggests at high phosphoric acid concentration, there may be partitioning of phosphoric acid between the reaction solution and adsorbing on the deAl-BEA. More deAl-BEA may uptake more liquid
phosphoric acid from the reaction solution, resulting in a higher selectivity. Despite not increasing the $p$-xylene selectivity at 11 mM, additional deAl-BEA greater than 0.2 g continues to increase the initial DMF conversion rate shown in Figure 2.3 C, up to a limit with diminishing increases for additional deAl-BEA. However, this plateau may be restrained by the limitations of the reaction kinetics. Previous research described a 2-kinetic regime for the 2-step cycloaddition of ethylene to DMF and subsequent dehydration to $p$-xylene.$^{32}$ Only the second step, the dehydration of the cycloadduct to $p$-xylene, is catalyzed by Brønsted acids. Therefore, when the Brønsted acid concentration is higher than certain value, the dehydration reaction becomes rate-limited to the rate of cycloaddition reaction, which is dependent on ethylene pressure and DMF concentration, therefore zeroth order in Brønsted acid site density. The plateaued rate observed in Figure 2.3 C is near the expected rate from literature in the cycloaddition-limiting regime, and any beneficial effect of excess deAl-BEA may not be observed. Elemental analysis of the catalyst recovered after reaction, shown later in Table 2.1 confirms that most of the
phosphorus associates with the deAl-BEA, although some phosphoric acid may remain in solution.

The transition from the dehydration-limiting regime to the cycloaddition limiting regime is observed for P-BEA Si/P=27 and Al-BEA Si/Al=12.5 by varying the catalyst mass and comparing the BAS density assuming 1:1 BAS density to P or Al plotted against the initial reaction rate in Figure 2.4. The transition into the cycloaddition regime occurs at approximately 3.0 mM of BAS sites, with the rate of P-BEA plateauning around 0.3 M DMF/hr. However, Al-BEA shows a higher cycloaddition-limiting rate nearing 0.4 M DMF/hr. This may be due to extra-framework aluminum in the Al-BEA acting as a Lewis acid and catalyzing the cycloaddition of ethylene and DMF but may also be due to non-

Figure 2.3 Reaction results with liquid phosphoric acid and deAl-BEA support added in the reaction mixture. p-Xylene selectivity shown with 11 mM (A) and 22 mM (B) of liquid phosphoric acid mixed with 0.2, 0.5, and 0.8 g of deAl-BEA (case 2). Initial DMF conversion rate observed at constant liquid phosphoric acid concentration of 11 mM with deAl-BEA mass increasing up to 1.5 g (C). Dashed line indicates DMF conversion rate before the reaction is rate-limited by the cycloaddition of DMF and ethylene. Side product distributions are given in Figure 2.18 in the appendix to Chapter 2.
selective reactions with 2,5-hexanedione over the acid sites which appear to increase DMF conversion but the rate of 2,5-hexanedione conversion may not restricted by the rate of cycloaddition, as Al-BEA is significantly less selective than P-BEA. This comparison between P-BEA and Al-BEA also confirms that no diffusion limitations are present in the P-BEA, as diffusion limitations were ruled out in a previous study\(^3\) in the p-xylene reaction with the same commercial Al-BEA CP814E from Zeolyst. Similar reaction rates found between the commercial Al-BEA and Al-BEA synthesized with less than 200 nm particle size, where no further improvement in rate was found with Al-BEA with smaller particle sizes, indicating that the commercial Al-BEA likewise did not experience diffusion limitations. With similar rates observed with the commercial Al-BEA and P-BEA, internal diffusion limitations can be ruled out in P-BEA.

**Figure 2.4 Initial reaction rate vs mMol solid acid site in P-BEA and Al-BEA.** A 1:1 ratio is assumed for 1 mol BAS: 1 mol P or Al, for P-BEA Si/P=27 and Al-BEA Si/Al=12.5 (CP814E). Dashed line indicates the kinetic regime where the initial reaction rate scales linearly with increasing acid site density, or dehydration-limited regime, while the solid line indicates where the rate-limiting step switches to the cycloaddition of ethylene with DMF, or cycloaddition-limiting regime, which is not catalyzed by Brønsted acid sites.
Other siliceous supports (Si-SPP, Si-BEA (HF) and fumed SiO₂) were tested with 11 mM of liquid phosphoric acid to compare to deAl-BEA, seen in Figure 2.5. For each support, 0.5 g were used. Fumed SiO₂ and Si-SPP show similar reaction results to deAl-BEA, with higher DMF conversion rate and \( p \)-xylene selectivity compared to liquid phosphoric acid without support. Interestingly, Si-BEA (HF) shows similar selectivity to the other siliceous supports, yet the reaction rate was similar to that of the liquid phosphoric acid without silica support. Elemental analysis of the recovered supports after reaction shows association of the liquid phosphoric acid in the reaction media, though the recovered Si-BEA (HF) showed less phosphorus than the other recovered supports, suggesting the surface chemistry of the support could influence the \textit{in-situ} adsorption of liquid phosphoric acid (Shown later in Table 2.1). The low reaction rate with the Si-BEA (HF) also suggest that the surface chemistry of the support could influence the activity of the adsorbed phosphoric acid, with the lack of Si-OH defects\(^{74}\) on the Si-BEA (HF) reducing the activity of the adsorbed phosphoric acid, but association with the Si-BEA (HF) still increasing selectivity. Curiously, the fumed SiO₂ also showed high selectivity despite the lack of micropore structure. Therefore the phosphoric acid on silica may be intrinsically selective to \( p \)-xylene and micropores need not be required for a high selectivity.

The transition in the 2-kinetic regime is also observed for the other siliceous supports studied shown in Figure 2.6. Interestingly, fumed SiO₂ and Si-SPP show higher
initial rates at low loadings of P below 3 mM, while deAl-BEA does show low initial rates at low P loading, similar to the liquid phosphoric acid without silica support.

Figure 2.5 The effect of other silica supports on p-xylene reaction (A), p-xylene selectivity (B) and initial reaction rate (C) with 0.5 g of each support and 11 mM of liquid H₃PO₄. Side product distributions are given in Figure 2.19 in the appendix of Chapter 2.

Figure 2.6 Initial reaction rate vs mMol acid site P for liquid phosphoric acid and silica supports. 1:1 ratio is assumed for mol P: mol acid site, with 0.5 g of deAl-BEA, Si-SPP, and fumed SiO₂ in each reaction.
Due to the lower selectivity and activity of liquid phosphoric acid in the presence of the silica support compared to the prepared P-zeosil catalysts, it is possible that liquid phosphoric acid may remain in the liquid solution phase. Therefore, stability of the phosphoric acid on P-zeosils and the extent of the partition of liquid phosphoric acid in the reaction solution versus the adsorption on the silica support must be addressed.

Stability of liquid phosphoric acid on deAl-BEA and Si-SPP support, as well as impregnated P-BEA and P-SPP, was assessed with a leaching test, shown in Figure 2.7. The P-zeosils P-BEA and P-SPP with Si/P=27 show negligible DMF conversion after the removal of the solid catalysts, and elemental analysis confirmed near identical Si/P ratio of the P-zeosils prior and after the reaction. While this suggests stability of the impregnated phosphorus on the P-BEA and P-SPP, it could be also possible that the P desorbs under high temperature reaction conditions but the *in-situ* interaction with the silica support leads to improved selectivity and DMF conversion rate. The P re-adsorbs during the reactor cools down. Hot filtration may be necessary to determine if P remains adsorbed under reaction conditions. However, in the case with liquid phosphoric acid and deAl-BEA and Si-SPP added together, at the same Si/P ratio of the P-zeosil leaching tests, the reaction medium shows additional 15% conversion after removal of the solid silica supports. This further supports the hypothesis that a fraction of the liquid phosphoric acid could remain in the reaction solution and not adsorb on the silica supports. When the concentration of liquid phosphoric acid is increased to 45 mM, with Si/P=3, over 30% conversion is observed after
the removal of solid silica support, suggesting at high P concentration, more P could be found in the reaction solution.

Figure 2.7 Leaching tests with P-BEA and P-SPP, and liquid phosphoric acid with deAl-BEA. 0.5 g of P-BEA and P-SPP Si/P=27 (A) and for 0.5 g of deAl-BEA with 6 mM $\text{H}_3\text{PO}_4$ (Si/P=27) and 45 mM $\text{H}_3\text{PO}_4$ (Si/P=3) (B). The dashed line at 3 hours indicates the time at which the reactor was cooled, the solids filtered out, and the liquid reaction media added back to the reactor and further reacted for 21 hours. P-BEA Si/P=27 without solid catalyst removal is shown for comparison. Side product distributions are given in Figure 2.20 in the appendix of Chapter 2.

With the leaching test demonstrating that phosphoric acid may remain in the solution after the removal of solid catalyst attempts were made to quantify the amount of phosphoric acid remaining in the solution by recovering the spent catalysts after reaction and observing the Si/P ratio by elemental analysis. Three scenarios were used to determine the leaching of phosphoric acid: P-BEA Si/P=27 before and after reaction, in-situ-impregnated (ISI) P-BEA, P-SPP, P-fumed SiO$_2$ and P-Si-BEA (HF), where the silica supports and phosphoric acid were added to $n$-heptane without DMF and brought to reaction conditions, then the solid supports were recovered, and the reactions with liquid phosphoric acid and deAl-BEA at Si/P= 45 and 13.5. Results are summarized in Table 2.1.
P-BEA Si/P=27 shows negligible difference in Si/P ratio before and after reaction, which is consistent with the results from the leaching test in Figure 2.7 where no additional DMF conversion was observed after P-BEA Si/P=27 removal. In the in-situ-impregnated (ISI) samples, the Si/P ratio of the recovered P-BEA-ISI shows negligible difference compared to the expected Si/P ratio with 13.3 compared to the expected value of 13.5. P-SPP-ISI shows slightly less P than expected with a higher Si/P ratio of 14.7 compared to P-BEA-ISI, while P-fumed-SiO$_2$-ISI shows a higher Si/P ratio of 16.9. P-Si-BEA-HF-ISI shows the highest Si/P ratio of 19.5, with nearly 30% of the P not observed by elemental analysis of the Si-BEA-HF-ISI. These results are expected based on the hydrophilicity of the support: deAl-BEA is very hydrophilic with its Si-OH nests generated from dealumination and Si-SPP also contains significant defects based on the layering of the single layers of MFI structure. Fumed SiO$_2$ is more hydrophobic, only containing isolated defects$^{72}$ and no micropore structure, and Si-BEA-HF is very hydrophobic containing low defects and large particle size.$^{74}$ Interestingly the elemental analysis of the deAl-BEA with liquid phosphoric acid after reaction shows less P than expected, which is consistent with the residual activity of reaction solution in the leaching test after the solid catalyst removal. The deAl-BEA with phosphoric acid after reaction samples also show less P than on the BEA than after the P-BEA-ISI impregnation, therefore the presence of DMF in the reaction solution may influence the partition of phosphoric acid in the reaction solution and on the silica support.
The three different catalytic cases with phosphoric acid are summarized in Scheme 2.1. (1) Phosphoric acid was added in the liquid reaction mixture in the absence of any solid support, (2) phosphoric acid was added in the liquid reaction mixture along with inert silica support including siliceous zeolite (i.e., allowing for phosphoric acid–support assembly to proceed in the reaction mixture), and (3) phosphoric acid was first impregnated on the siliceous zeolite support and then the preassembled supported phosphoric acid catalyst was added in the liquid reaction mixture. It was found that the reaction rate and selectivity to p-xylene are different in the above cases reflecting the effect of the solid support on the catalytic performance of phosphoric acid. In case 1, a low concentration of phosphoric acid (1.7 mM) in the absence of any solid support
exhibited high selectivity to p-xylene (80% selectivity to p-xylene at 60% conversion of DMF), which decreased with increasing acid concentration. The selectivity to p-xylene and activity of phosphoric acid significantly increased by adding a silica support into the reaction system (case 2). This improvement was attributed to phosphoric acid partial association with the surface of the silica support under the reaction conditions (in situ catalyst assembly). Phosphoric acid predeposited on siliceous zeolite supports (e.g., P-BEA, P-SPP) synthesized via impregnation prior to the reaction (case 3) catalyzed the reaction heterogeneously without noticeable leaching and exhibited the highest activity and selectivity to p-xylene, suggesting an important role of the silica support and the need to ensure that phosphoric acid acts as a heterogeneous catalyst in order to accomplish selective conversion of DMF to p-xylene.

**Scheme 2.1 The three cases of phosphoric acid addition studied in the p-xylene reaction.** Liquid $\text{H}_3\text{PO}_4$ (case 1) can catalyze the reaction selectively only at low concentration of $\text{H}_3\text{PO}_4$. $\text{H}_3\text{PO}_4$ with silica support (case 2): $\text{H}_3\text{PO}_4$ will associate with the silica supports during the reaction, which significantly improves the reaction rate and p-xylene selectivity. $\text{H}_3\text{PO}_4$ impregnated on silica support (case 3) such as P-BEA and P-SPP catalyzes the reaction heterogeneously with the highest selectivity and activity.
2.3.2 P-Impregnation on Other Silica, Carbon, and Metal Oxide Supports

$p$-Xylene reactions with phosphoric acid impregnated on other types of supports are also shown in Figure 2.8. A comparison between multiple other P-impregnated silica supports, P-SBA-15, P-35nm silica nanoparticle (SNP), P-silica gel, and P-MCM-41; P-impregnated metal oxides, P-Al$_2$O$_3$, P-P25 (TiO$_2$), P-MnO$_2$, P-MgO, and P-ZrO$_2$; and P-impregnated carbons P-active carbon and P-BP2000 are also displayed. All supports were impregnated to 1.8 wt% P, which is equivalent to Si/P=27 used for silica supports, and 0.25 g of each sample was used in the reaction. Silica supports include P-SBA-15, P-MCM-41 (sodium free), P-fumed SiO$_2$ (Cab-o-sil M5), P-35 nm silica (Lysine silica), and P-silica gel (Davisil grade 636, 35-60 mesh, Sigma Aldrich). Carbon supports include P-BP-2000, P-active carbon (Norit SX ultra). Metal oxide supports include P-MgO (99% MgO, Alfa Aesar), P-MnO$_2$, P-SnO$_2$ (99%, SnO$_2$, Sigma Aldrich), P-ZrO$_2$ (99%, Alfa Aesar), P-TiO$_2$ (P25 TiO2) and P-Al$_2$O$_3$. P-Silica supports show the highest reaction rates and selectivity, except for P-MCM-41 which showed low initial reaction rate. All other supports except P-ZrO$_2$ showed high yield of $p$-xylene but displayed lower rates than the siliceous supports. It is interesting many supports show high yield to $p$-xylene; therefore, the selectivity of the P-catalysts may be due to the presence of the P and less important is the type of support, except in the case of P-ZrO$_2$. However, silica supports show the highest reaction rate with high selectivity and therefore are the best support.
Figure 2.8 *p*-Xylene reaction data with P-silicas, P-metal oxides, and P-carbons (Top left) DMF conversion vs time and (top right) *p*-xylene yield vs DMF conversion. P-silica impregnated species show the highest DMF conversion in 24 hours, >70%, except for P-MCM-41. P-carbon materials show >30 % conversion in 24 hours. P-metal oxides show low DMF conversion <30%, except for P-ZrO₂, but P-ZrO₂ shows lower *p*-xylene yield. Initial rates are shown in the bottom figure.
2.3.3 Solvent Comparison between \textit{n-Heptane}, \textit{1,4-Dioxane}, and Tetrahydrofuran

In considering the activity of P-zeosils and their leaching behavior, the effect of the solvent becomes increasingly important. Previous research has found the \textit{p-xylene} reaction to be dependent on the solvent when \textit{n-heptane}, \textit{1,4-dioxane}, tetrahydrofuran (THF) and isopropanol (IPA) are considered.\textsuperscript{79} The previous research indicated polar aprotic solvent, \textit{1,4-dioxane}, showed the highest reaction rate with silica-alumina aerogels and H-BEA zeolite, due to the stability of charged intermediates using polar aprotic solvents. However, the polar protic solvent, IPA, exhibited decreased efficacy. Therefore, the two additional solvents 1,4-dioxane and THF were considered for their activity with P-zeosils and liquid phosphoric acid, shown in Figure 2.9. P-BEA and liquid phosphoric acid show the highest selectivity to \textit{p-xylene} in \textit{n-heptane} compared to 1,4-dioxane and THF. The selectivity with H-BEA is within 10\% of the selectivity observed in literature for THF and 1,4-dioxane at full conversion of DMF. For P-BEA and liquid phosphoric acid, the selectivity in \textit{n-heptane} and dioxane are similar, but the reaction rate in \textit{n-heptane} is significantly greater than in 1,4-dioxane, shown in Figure 2.10.
Figure 2.9 Solvent effect in reaction with P-BEA, liquid phosphoric acid, with and without additional deAl-BEA, and H-BEA. (A) n-heptane (B) 1,4-dioxane, (C) THF. Reactions in n-heptane and 1,4-dioxane have the highest selectivity, though P-BEA may be more selective in n-heptane while liquid phosphoric acid without support may be more selective in 1,4-dioxane. Reactions in THF show lowest selectivity. Reactions using H-BEA in 1,4-dioxane and THF are shown for comparison.

Figure 2.10 Solvent effect on initial reaction rates for Figure 2.9. 0.5 g P-BEA Si/P=27 and 11 mM liquid phosphoric acid, with and without deAl-BEA support, and 0.5 g H-BEA in (A) n-heptane (B) 1,4-dioxane, (C) THF. H-BEA reactions are plotted with the rate of M p-xylene yield/hr. Reactions in n-heptane have the highest rate of DMF conversion with P-BEA and liquid phosphoric acid, but 1,4-dioxane has the highest rate of p-xylene production with H-BEA, consistent with literature.
2.3.4 Using Copper Catalysts for \(p\)-Xylene Reaction and Comparison to P-Catalysts

An additional copper containing catalyst, bulk crystalline CuCl\(_2\), was found to be highly active and selective in the \(p\)-xylene reaction using 1,4-dioxane solvent\(^{80}\) in literature, and tested experimentally with selectivity as high as P-BEA in \(n\)-heptane solvent. CuCl\(_2\) also shows a high initial reaction rate as shown in Figure 2.11 with varying catalyst mass, able to achieve over 0.5 M DMF/hr, 60% greater than the initial rate observed for P-BEA Si/P=27 in the cycloaddition-limiting regime. CuCl\(_2\) is a Lewis acid catalyst, which can catalyze the cycloaddition of ethylene and DMF, which is why it is able to see much higher initial reaction rate than P-BEA.

![Figure 2.11 Reaction results with CuCl\(_2\). (A) \(p\)-Xylene selectivity vs initial reaction rate and (B) initial reaction rate for 0.35 g, 0.7, and 1.4 g CuCl\(_2\) in 1,4-dioxane solvent. Selectivity is as high as P-BEA Si/P=27, with initial DMF conversion rate able to achieve 60% higher than the initial reaction rate with P-BEA.](image)

Because of the high activity of the CuCl\(_2\), attempts were made at synthesizing Cu-BEA catalysts, with the goal of improving the reaction rate using Lewis acid sites over that of P-BEA while retaining selectivity, and to eventually incorporate P and Cu together to...
possibly achieve a superior catalyst. As shown in Figure 2.12, Cu-impregnated H-BEA showed high reaction rate in dioxane, higher than P-BEA in dioxane, but the selectivity was not as high as P-BEA. In \textit{n}-heptane, P-BEA still had a higher initial reaction rate than the Cu-exchanged H-BEA. The P-Cu-BEA catalysts did not show as high activity as Cu-exchanged BEA or P-BEA in dioxane or \textit{n}-heptane, respectively. These results are reflected in that CuCl$_2$ has high reaction rates in dioxane but low rates in \textit{n}-heptane, while P-BEA has high reaction rates in \textit{n}-heptane but not dioxane. All selectivity to \textit{p}-xylene were over 80\%, therefore major differences are only seen in the initial reaction rates. A boron containing catalyst, B-BEA was also synthesized with boric acid and tested and compared to P-BEA but was found to have a lower selectivity, therefore was not used to make a bifunctional catalyst with Cu. Boric Acid itself did not show activity, shown in Figure 2.23 of the appendix to Chapter 2.
Figure 2.12 $p$-Xylene reaction results with Cu-impregnated and Cu-exchanged BEA compared to P-BEA (top left) Initial reaction rate with Cu-exchanged H-BEA, P-BEA Si/P=27, and P-Cu-exchanged-BEA in 1,4-dioxane and $n$-heptane. Cu-ex-BEA has higher activity than P-BEA in 1,4-dioxane, but P-BEA has higher activity in $n$-heptane. P-Cu-ex-BEA is not as good as Cu-ex-BEA in dioxane or P-BEA in $n$-heptane. (top right) Initial reaction rate between CuCl$_2$ and P-BEA Si/P=27. CuCl$_2$ shows higher initial rate in dioxane, but P-BEA Si/P=27 shows higher rate in $n$-heptane. (middle left) Selectivity of Cu-impregnated-deAl-BEA in dioxane compared with CuCl$_2$ and P-BEA. The Cu-impregnated-deAl-BEA shows high selectivity, comparable to P-BEA. (middle right) P-BEA Si/P=27 and Cu-impregnated-deAl-BEA in $n$-heptane and dioxane. P-BEA shows highest selectivity. (bottom left) $p$-Xylene selectivity vs DMF conversion, showing the CuCl$_2$ shows higher selectivity than Cu-ex-H-BEA. (bottom right) Initial rate of DMF conversion.
2.3.5 Using Sodium-Substituted Phosphates to Prepare P-Catalysts

Sodium-substituted phosphates, NaH₂PO₄, Na₂HPO₄, and Na₃PO₄ were tested in p-xylene reaction to determine which acidic proton within phosphoric acid is most active in the p-xylene reaction. Reactions with both sodium-substituted phosphate BEA and bulk crystalline sodium-substituted phosphate salts were tested in p-xylene reaction. In Figure 2.13, the sodium-substituted phosphate BEA shows that with a single sodium substitution, the DMF conversion significantly decreased, and with 2 or more sodium substitutions, there was negligible conversion. Similar results are seen with increased catalyst mass in Figure 2.14. Therefore, it is likely the first acidic proton which is most active for the p-xylene reaction.

![Figure 2.13](image)

**Figure 2.13:** Reaction results for the reactions with NaH₂PO₄-BEA, Na₂HPO₄-BEA, and Na₃PO₄-BEA compared to P-BEA. All catalysts contain Si/P=27. (A) DMF conversion vs time is shown, with only NaH₂PO₄-BEA and P-BEA showing activity in the reaction, although the initial rate of NaH₂PO₄-BEA is less than 10% of the initial rate with P-BEA Si/P=27. (B) In p-xylene selectivity vs DMF conversion, the NaH₂PO₄-BEA shows similar selectivity to P-BEA Si/P=27.
In Figure 2.15, the \( p \)-xylene reaction results with \( \text{H}_3\text{PO}_4 \) and \( \text{NaH}_2\text{PO}_4 \) at 11 mM and 45 mM are shown. \( \text{Na}_2\text{HPO}_4 \) and \( \text{Na}_3\text{PO}_4 \) were not tested due to negligible activity after impregnation on deAl-BEA. Although \( \text{NaH}_2\text{PO}_4 \) after impregnation on BEA shows activity for the reaction, negligible activity was observed with the bulk crystalline \( \text{NaH}_2\text{PO}_4 \). It is interesting the \( \text{NaH}_2\text{PO}_4 \) is not active except when impregnated on deAl-BEA. It is possible the zeolite support aids in 2nd proton dissociation, or the Na ion-exchanges with Si-OH to form \( \text{H}_3\text{PO}_4 \) which is active. Still the result is consistent with the sodium-substituted impregnated deAl-BEA, where the \( \text{H}_3\text{PO}_4 \) is most active.

Figure 2.14 Reaction comparison between P-BEA and \( \text{NaH}_2\text{PO}_4 \)-BEA. Both catalysts contain Si/P=27 and 1.0 g of catalyst used in reaction. (A) DMF conversion vs time show P-BEA Si/P=27 shows higher reaction rate, as consistent with results seen in Figure 2.13. (B) \( p \)-xylene selectivity shows P-BEA Si/P=27 and \( \text{NaH}_2\text{PO}_4 \)-BEA Si/P=27 show similar selectivity. (C) 2,5-Hexanediol selectivity shows \( \text{NaH}_2\text{PO}_4 \)-BEA shows lower 2,5-hexanediol selectivity than P-BEA Si/P=27.
2.4. Conclusions

The method of introducing phosphoric acid into the reaction mixture was found to significantly alter the catalytic performance in the reaction for producing $p$-xylene from DMF and ethylene. Without any silica support, phosphoric acid in $n$-heptane solvent was selective for $p$-xylene production only when the concentration was lower than 1.7 mM phosphoric acid (80% selectivity to $p$-xylene). Increasing the phosphoric acid concentration decreased the selectivity to $p$-xylene (40% with 45 mM phosphoric acid) and initial reaction rate per phosphorus. Addition of various silica based supports

Figure 2.15 DMF conversion vs time with $\text{H}_3\text{PO}_4$ and $\text{NaH}_2\text{PO}_4$ at 45 mM P and 11 mM P. Interestingly $\text{NaH}_2\text{PO}_4$ does not show activity in the $p$-xylene reaction, although $\text{NaH}_2\text{PO}_4$-BEA is active for the reaction as shown in Figure 2.13 above.
including fumed silica and Si-SPP into the reaction mixture in the presence of phosphoric acid significantly improved the selectivity and reaction rate, which was due to the association of phosphoric acid on the surface of the supports. The reaction was catalyzed by both homogeneous phosphoric acid and heterogeneously stabilized acid sites. It was found that silica supports are necessary to stabilize phosphoric acid and improve their catalytic activity and selectivity. However, the ordered microporous structure of zeolite is not required for the high activity and selectivity of phosphoric acid associated on solid support, which is consistent with previous literature. The extent of the association of phosphoric acid on the surface of the solid supports depended on the surface characteristics of the supports; Si–OH groups favored the association of phosphoric acid with the solid supports under reaction conditions. P-BEA and P-SPP catalysts made by impregnation of phosphoric acid on the siliceous zeolite supports prior to the reaction catalyzed the reaction heterogeneously without noticeable leaching under reaction conditions; these catalysts were also the most active and selective to p-xylene. Other supports also provide beneficial activity to phosphoric acid such as metal oxide supports (except ZrO₂) and carbon supports, which show higher selectivity than liquid phosphoric acid. However, silica supports show significantly higher reaction rate. Despite Al-BEA showing increased activity in 1,4-dioxane, n-heptane solvent showed highest activity with P-BEA. Copper catalysts CuCl₂ and Cu-impregnated and ion-exchanged BEA showed high activity and selectivity in 1,4-dioxane, but not in n-heptane solvent. However, because of
the low activity of seen with P-BEA in dioxane, the impregnation of phosphoric acid on Cu-catalysts did not improve the reaction rate in an attempt to create a bifunctional catalyst containing both Lewis and Brønsted acid sites.
2.5 Appendix to Chapter 2

Figure 2.16 Side product yields from Figure 2.1. (left) 2,5-Hexanidine yield consistent with all reactions, begins to decrease at higher DMF conversion. (center) Phosphoric acid without support shows highest alkylated product formation. (right) Small oligomer product yield in all reactions (<1% yield).

Figure 2.17 Side product yields from Figure 2.2. Green: 45 mM (260 mg) H₃PO₄; black: 130 mg (22 mM); red: 11 mM (65 mg); orange: 6.0 mM (35 mg); pink: 3.5 mM (20 mg); blue: 1.7 mM (10 mg). (top left) DMF % Conversion vs time, used for initial rate calculation. (top right) 2,5-Hexanidine % yield similar in all reactions. (bottom left) Alkylated product yield, with lowest concentration showing highest alkylated yield (bottom right) Oligomer product yield low in all reactions (<1%).
Figure 2.18 Side product yields for Figure 2.3. (top left) DMF % conversion vs time, used to calculate initial rates. (top right) 2,5-Hexanedione % yield, similar in all reactions. (bottom left) Alkylated product % yield, decreases with increasing deAl-BEA mass. (bottom right) Oligomer product yield.

Figure 2.19 Side product yields from Figure 2.5 (top left) DMF % conversion vs time, used in initial rate calculation. (top center) p-Xylene % Selectivity. (top right) 2,5-Hexanedione % yield. (bottom left) Alkylated product % yield, highest without support. (bottom center) Oligomer product yield. (bottom right) Mass balance, lowest with no support.
Figure 2.20 Side product yields for Figure 2.7. p-Xylene selectivity data for (top left) 0.5 g P-SPP Si/P=27 (top right) 0.5 g P-BEA Si/P=27 (middle top left) 0.5 g deAl-BEA + 6mM H$_3$PO$_4$ Si/P=27 (middle top right) 0.5 g deAl-BEA + 45 mM H$_3$PO$_4$ Si/P=3 (middle bottom left) 2,5-hexanedione yield (middle bottom right) alkylated product yield (bottom left) oligomer product yield (bottom right) mass balance.
Correlations from literature\textsuperscript{77, 78} for the first dissociation constant of phosphoric acid. The calculated equilibrium between \([\text{H}_3\text{PO}_4]\) and the first dissociation to \([\text{H}_2\text{PO}_4^-]\) and \([\text{H}^+]\) provides estimates to \([\text{H}^+]\) with varying phosphoric acid concentration. The dissociation constant at 25 °C, \(\text{pK}_a = 2.14\), was used in the empirical correlation between temperature and first dissociation constant, given in the \(-\log K_a \text{ vs } T\) equation below. Although the data in the correlation was limited to 60 °C, \(\text{pK}_a = 4.02\) was calculated. This lies between the literature values of \(\text{pK}_a = 3.692\) at 236 °C and \(\text{pK}_a = 4.368\) at 301 °C, and therefore the calculated value from the correlation is acceptable.

\[
-\log K_a = \frac{799.31}{T} - 4.5535 + .013486T
\]

\[
K_a = \frac{[\text{H}_2\text{PO}_4^-][\text{H}^+]}{[\text{H}_3\text{PO}_4]}
\]

\[
[\text{H}^+] = -K_a + \sqrt{K_a^2 + 4K_a[H_3\text{PO}_4]/1000}
\]

**Figure 2.21** \(p\)-Xylene selectivity of deAl-BEA, fumed SiO\(_2\) and Si-SPP with variable phosphoric acid concentration. (A) deAl-BEA (B) fumed SiO\(_2\) and (C) Si-SPP with phosphoric acid concentration ranging from 3.5 mM to 22 mM phosphoric acid. deAl-BEA shows the highest selectivity at all phosphoric acid concentrations, while fumed SiO\(_2\) and Si-SPP show decreasing \(p\)-xylene selectivity with increasing phosphoric acid concentration.
Figure 2.22 \( p \)-Xylene reaction data for \( \text{ZrO}_2 \) (left) DMF conversion vs time and (right) \( p \)-xylene selectivity vs DMF conversion for \( \text{ZrO}_2 \) without P impregnation. P-BEA, P-SPP and \( \text{ZrO}_2 \) (without P) all show high activity and selectivity for the dehydra-decyclization of tetrahydrofuran to 1,3-butadiene in literature\(^4\), therefore \( \text{ZrO}_2 \) was tested in \( p \)-xylene reaction as well. It was found to have poor activity.

Figure 2.23 \( p \)-Xylene reaction results with other liquid mineral acids, \( \text{HNO}_3 \) and \( \text{H}_3\text{BO}_3 \), which do not show activity in the \( p \)-xylene reaction. Interestingly, \( \text{H}_3\text{BO}_3 \) does not show activity, however \( \text{H}_3\text{BO}_3 \)-impregnated deAl-BEA (B-BEA, Figure 2.12) does show activity.
CHAPTER 3

EFFECTS OF SI/P RATIO AND CALCINATION TEMPERATURE ON P-BEA CATALYSTS

3.1 Introduction

P-zeosils recently reported in literature are distinctly different from commercially available solid phosphoric acid (SPA). For nearly a century, SPA catalysts have been used in the petrochemical industry for olefin oligomerization and benzene alkylation to cumene. SPA catalysts are made by impregnation of concentrated phosphoric acid on mesoporous silica or kieselguhr with a low Si/P ratio (Si/P ≤ 3) followed by specific calcination conditions. The synthesis method and low Si/P ratio lead to a mixture of different crystalline silicon phosphate phases: silicon hydrogen tripolyphosphate SiHP₃O₁₀, silicon orthophosphate Si₅O(PO₄)₆, hexagonal silicon pyrophosphate SiP₂O₇, and various hydrates such as SiH(PO₄)₂·H₂O. P-zeosil syntheses differ from SPA synthesis by using dilute phosphoric acid solutions impregnated on crystalline microporous or hierarchical zeolites, with higher Si/P ratios (Si/P > 10). Higher Si/P ratios lead to preservation of the microporous structure within zeolites, allowing high surface area and shape selectivity from the confined micropore environment possibly improving selectivity in reactions (though it is not necessary for the production of p-xylene from DMF and ethylene). Despite a century of use and decades of research, it remains unclear if the active sites in SPA and likewise P-zeosils are uncoordinated free phosphoric acid, a certain
polyphosphate, crystalline silicon phosphate, or phosphates covalently linked to the silica support.

It is also important to note P-zeosils are distinguishable from phosphoric acid-doped aluminosilicate zeolites and silicoaluminophosphate (SAPO) materials. Aluminum site modification by phosphoric acid in zeolites is well understood to modulate the acidity of zeolite catalysts.\textsuperscript{84, 85} Phosphoric acid modification of zeolites improves the framework stability under harsh reaction conditions, such as hydrothermal conditions with water and steam.\textsuperscript{86-90} Meanwhile, P-zeosil Brønsted acidity exhibited by P-OH groups associated with distinct phosphate structures is weaker than the Brønsted acid sites associated with the aluminum in aluminosilicate zeolites,\textsuperscript{91, 92} though it is unknown which P-OH groups from a given phosphate species are active sites for a particular reaction. While P-zeosils have been found to be active and selective in a variety of relevant renewable reactions, the structure of the active sites and mechanisms for high selectivity are currently not understood.

After understanding the interactions between phosphoric acid and silica supports when they are mixed in the reaction medium separately in Chapter 2, it is the purpose of Chapter 3 to understand the different types of phosphate species present on P-BEA due to variations Si/P ratio and synthesis conditions. It was found that with more phosphorus and a lower Si/P ratio, calcination results in oligomeric phosphate species on P-BEA, forming polyphosphates and Si-O-P bonds from silicon phosphate phases. Calcination of
P-BEA with Si/P=3 results in substantial damages to the BEA crystal structure and the formation of a silicon phosphate impurity phase. It was also found that condensed oligomeric phosphate species can be hydrolyzed in the presence of water.

Changes in phosphate species from varied Si/P ratio, calcination temperature, and humidity treatment were characterized using $^{31}$P solid-state magic angle spinning nuclear magnetic resonance (MAS NMR). The effects of Si/P ratio and calcination conditions on the stability of the BEA structure were investigated using X-ray diffraction (XRD) and quantified using quartz internal standards. Changes in surface area of P-BEA and BEA structure due to Si/P ratio and calcination temperature were observed with nitrogen adsorption. Effect of defects within the BEA structure on stability the BEA structure during P-BEA Si/P=3 synthesis was investigated, where healing of Si-OH defects after deAl-BEA calcination were studied. A new proposed technique for identifying P structures was investigated using X-ray adsorption near edge structure (XANES). The effects of Si/P ratio and calcination temperature on acid site density were measured by temperature-programmed desorption-reaction of a basic probe molecule, t-butyamine (TBA) over Brønsted acid sites. From the measurement, a good agreement between the measured Brønsted acid site (BAS) density and initial reaction rate of DMF conversion in the $p$-xylene reaction was observed.
3.2 Experimental Design

3.2.1 Catalyst Preparation

P-BEA Si/P=27, 10, and 3 were prepared according to the methods described in the materials and methods session of Chapter 2. In addition, a step in P-BEA synthesis was added, where the deAl-BEA was first calcined after drying but prior to phosphoric acid impregnation, to generate a P-BEA variant material labeled cl-P-BEA. Calcination of deAl-BEA was performed at 600 °C for 12 hr, with a 1 °C/minute ramp from room temperature with 100 mL/min dry air flowing.

Additional P-zeosil, P-Silicalite-1 was synthesized from a commercial Silicalite-1 sample. Silicalite-1 is first calcined at 600 °C for 8 hr with a ramping rate of 1 °C/min from room temperature under 100 mL/min of dry flowing air. Afterward, P-Silicalite-1 is obtained through the impregnation of the Silicalite-1 sample using dilute phosphoric acid to make Si/P=27 and Si/P=3 following typical phosphoric acid impregnation and calcination procedure for P-BEA given in Chapter 2.

Aluminum-containing zeolites Al-BEA Si/Al=12.5 (Zeolyst, CP814E) and ZSM-5 Si/Al=11.5 (Zeolyst, CBV2314) are impregnated with dilute phosphoric acid without dealumination. Aluminosilicate zeolites are first calcined at 600 °C for 12 hr with a ramping rate of 1 °C/min to 600 °C from room temperature and 100 mL/min of dry flowing air. Phosphoric acid impregnation followed the similar procedure as in P-BEA Si/P=3,
where 3.5 mL of a 6.19 wt% aqueous phosphoric acid solution was added to 0.4 g of the calcined aluminosilicate zeolites. This followed the same impregnation method and zeolite mass for deAl-BEA to obtain an Si/P=3 of P-BEA-3, which corresponds to approximately 11 wt% P in the P-impregnated zeolites H-BEA and ZSM-5.

Impregnation of deAl-BEA was also performed with other mineral acids, $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ instead of $\text{H}_3\text{PO}_4$. Solution of 0.63 M $\text{H}_2\text{SO}_4$ was prepared from a stock $\text{H}_2\text{SO}_4$ (1.0 M, Thermo Fisher Scientific) solution. 3.5 mL of the 0.63 M solution was added to 0.4 g of dried deAl-BEA. Stock $\text{HNO}_3$ (70%, Thermo Fisher Scientific) solution was diluted to 0.62 M, then 3.5 mL of the 0.62 M solution was added to 0.4 g of dried deAl-BEA.

Bulk crystalline silicon phosphate $\text{Si}_5\text{O(PO}_4)_6$ standard material was synthesized from readily available silicic acid, phosphoric acid, and DI water. First, 1.49 g of silicic acid (99%, Sigma Aldrich, #60780, 100 mesh) and 0.31 g of DI water were mixed in a 100 mL Nalgene beaker with a Teflon spatula. Then 3.39 g of phosphoric acid (85 wt%, Alfa Aesar) was added dropwise while stirring with the Teflon spatula. The resultant wet cake was left at room temperature for aging of 1 day, then placed in a 90 °C convection oven for 1 day, then further dried at 90 °C in a vacuum oven for 1 day. Finally, 0.5 g of the vacuum-dried precursor material was heated under flowing $\text{N}_2$ at 100 mL/min, to 800 °C with a ramping rate of 400 °C/hr, then to 900 °C with a ramping rate of 100 °C/hr. After reaching to 900 °C, the sample was ambient cooled down to room temperature. Silicon phosphate $\text{Si}_5\text{O(PO}_4)_6$ crystal structure was virialized using Visualization for Electronic and Structural
Analysis (VESTA) software. The XRD pattern of Si₅O(PO₄)₆ crystal structure was calculated to confirm its crystalline structure using VESTA.⁹⁴

### 3.2.2 Catalyst Characterization

Crystal structures and relative crystallinity of P-BEA, P-silicalite-1, P-Al-BEA and P-ZSM-5 samples were characterized by X-ray diffraction (XRD) with Rigaku SmartLab diffractometer. Cu-Kα radiation was used as the X-ray source, produced at 40 mA and 45 kV with a step size of 0.016°. Diffraction patterns were obtained between 5° and 40° 2-θ angle. Relative crystallinity measurements were taken with an internal quartz standard (Silicon (IV) oxide, 99.5 %, 325 mesh, Alfa Aesar) mixed with the samples, with 25 mg of sample ground with 25 mg of the internal quartz standard, of which all 50 mg was placed and flattened onto the glass slide for XRD measurement. Peak area integration was performed with Origin Peak Analyzer Pro. The area of the largest peak in quartz at 26.5° was used for reference comparison to the area of the 22.5° peak for BEA materials and the area of the 23° peak for MFI materials. The commercial Al-BEA and ZSM-5 samples were taken as 100% crystalline standards, with the relative crystallinity of the other samples scaled to the Al-BEA and ZSM-5 100% crystallinity.

Nitrogen adsorption isotherms were taken on automated gas sorption analyzer (Autosorb, iQ2, Quantachrome) after degassing of the samples at 300 °C under vacuum for 12 hours. For the adsorption branch, 52 data points were obtained, and 41 data points were obtained for the desorption branch. Multi-point BET⁹⁵ surface area was calculated
using adsorption branch data within the linear region of $V(1-P/P_0)$ and with positive C constant, indicating physical realizability, using Quantachrome ASiQwin software.

Phosphorus species identification of the P-BEA and silicon phosphate materials was studied using $^{31}$P direct polarization NMR performed with solid-state magic-angle-spinning (MAS) Bruker 600 MHz spectrometer, tuned to 600 MHz for $^1$H and 242.93 MHz for $^{31}$P. About 20-30 mg of each sample was packed in a 4 mm ZrO$_2$ rotor with Kel-F cap, with spinning speed 6 kHz. Two pulse phase modulation and $^1$H decoupling were employed to obtain the spectrum, with initial $^1$H $\pi/2$ pulse followed with 5 ms radiofrequency pulse to both $^1$H and $^{31}$P and 100 s recycle delay. Typically, 64 scans were run to obtain sufficient signal-to-noise and peak and spinning sideband resolution. Chemical shifts were calibrated using 2 ppm for H$_3$PO$_4$ and peak assignments were taken from literature.$^{61}$

$^{29}$Si direct polarization NMR were also taken on P-BEA, silicon phosphate, and deAl-BEA materials in the solid-state 600 MHz MAS Bruker spectrometer using 4 mm ZrO$_2$ rotor. $^{29}$Si NMR spectra was obtained at 5 kHz of rotor spinning speed. 119.2 MHz operating frequency was used. 200 s recycle delay with 256 scans is able to provide sufficient resolution.

Different P materials, including P-BEA Si/P=3 and 27, silicon phosphate, P-zeolites P-Al-BEA and P-ZSM-5, as well as Na$_3$PO$_4$-, Na$_2$HPO$_4$-, and NaH$_2$PO$_4$-BEA zeolites were characterized using X-ray absorption near-edge spectra (XANES) with synchrotron
radiation at the TES beamline in NSLS-II at Brookhaven National Laboratory. The energy of the X-ray radiation was accurately adjusted in energy range from 2140 eV to 2200 eV, encompassing the K-α edge of phosphorus at 2150 eV. Samples were prepared using approximately 50 mg sandwiched between polypropylene thin film for X-ray fluorescence (Spex SamplePrep 3520 Polypropylene Window Film 5 µm thick) and fluorescence detector in inert helium environment. When the incident X-ray has sufficient energy to eject K-α electrons from phosphorus atoms, other electrons fill the hole and generate characteristic radiation, detected by the fluorescence detector. Post-edge intensity is normalized to 1, while the intensity of the fluorescence at the edge, colloquially called the white line intensity, varies depending on the electron delocalization around the central P atom, with higher delocalization leading to higher white line intensity. The P-XANES was used to determine if differentiation of P species with varying proton substitution (P-OH vs P-O-P or P-O-Si) is possible.

3.2.3 Catalyst Reaction and Analysis

$p$-Xylene reactions were run with P-BEA Si/P=3, 10, and 27 and results were analyzed according to the same procedure as in Chapter 2. Catalyst mass of each P-BEA sample was chosen such that there was a constant concentration of P in the reactor across all samples of 2.7 mM of P. This is achieved with catalyst masses of 0.23 g of P-BEA Si/P=27, 0.09 g of P-BEA Si/P=10, and 0.038 g of P-BEA Si/P=3.
Initial DMF conversion rates are compared to the Brønsted acid site (BAS) density through temperature-programmed reaction of the probe molecule t-butylamine (TBA, 98%, Alfa Aesar) on the Brønsted acid site. The reaction of TBA over Brønsted acid site produces isobutene and NH₃, of which the isobutene is detected and quantified by flame ionization detector (FID) in a modified Gas Chromatography unit, referred to in literature as Reactive Gas Chromatography (RGC). The quartz inlet liner serves as micro-catalytic reactor, HP-PLOT Q column (Agilent19091P-QO4) and FID for signal acquisition and analysis, with a 6-port valve for column bypass. The commercial quartz inlet liner (5188-5365) is packed with 20-30 mg of pelletized and sieved catalyst to obtain a particle size of 250-1000 μm to prevent over-pressurization of the inlet and stacked between 2 quartz wool plugs. Accurate mass of catalyst was obtained by weighing the quartz liner with the bottom quartz wool plug before and after sample addition, as well as the total mass of the fully packed liner, with sample and 2 quartz wool plugs, before and after the experiment. The packed liner was pre-treated at 400 °C for 1 hour in the inlet under helium, then the inlet temperature set to 150 °C until equilibrated for surface saturation. At inlet temperature of 150 °C, the TBA was injected using the automated liquid sampler (ALS) with 1 μL of TBA injected at 1-minute intervals, with 15 total injections deemed sufficient to saturate the catalyst surface. Inlet temperature 150 °C is held for 2 hours, purging the surface of the catalyst of any physio adsorbed TBA, so that only BAS-associated TBA remained. The 6-port valve was set such that the column was bypassed
for catalyst pre-treatment, TBA surface saturation, and purge, so TBA injected in the inlet would flow directly to the FID. Oven temperature was set at 100 °C and column flow maintained with helium to not damage the column through oxidation. After the 2-hour inlet purge at 150 °C, oven temperature was cooled to 30 °C, the 6-port valve pneumatically activated to bring the column online with the inlet. The inlet temperature was ramped to 400 °C, reactively desorbing the TBA producing isobutene and ammonia. Isobutene was trapped in the column at the oven temperature of 30 °C. After the inlet reached 400 °C, the oven temperature was increased by 10 °C/min to 200 °C, eluting the isobutene to be detected by FID. FID was calibrated with standard isobutene gas and ZSM-5 of Si/Al=11.5, 40, and 140, and split ratio verified manually with bubble flow meter. The calculation of BAS density from isobutene peak area is shown Section 3.4.

Calibration gas propylene with 1010 ppm and 937000 ppm were used to determine the calibration factor for the FID in RGC. BAS density was determined with the following equation,\(^{59}\) where \(PA_{\text{alkene}}\) refers to the peak area of the alkene, \(CF\) refers to the calibration factor, and with \(SR\) refers to the split ratio, which was set at 100 and was occasionally experimentally verified with bubble flow meter, and with catalyst mass in grams:

\[
\text{BAS density} = \frac{PA_{\text{alkene}} \times CF \times (SR + 1)}{\text{Catalyst mass}}
\]

Calibration results are given in the appendix of Chapter 3, Figure 3.35.
3.3 Results and Discussion

3.3.1 Effect of Si/P Ratio on Catalyst Structure and Acid Site Density

P-BEA with Si/P=27, 10, and 3 were used as catalysts in the p-xylene reaction from DMF and ethylene, with the results shown in Figure 3.1. The DMF conversion vs reaction time, shown in Figure 3.1 A, and initial DMF conversion rate, shown in Figure 3.1 C, show P-BEA Si/P=27 has the highest initial rate of DMF conversion of 0.36 M DMF/hr, and achieves full conversion in 24 hours. P-BEA Si/P=10 shows an initial DMF conversion rate of 0.22 M DMF/hr, and P-BEA Si/P shows the lowest initial DMF conversion rate of 0.08 M DMF/hr, requiring 48 hours to achieve a full conversion. The three reactions were run with constant P concentration in the reactor with 2.7 mM P and DMF/P ratio of 498, therefore suggesting higher Si/P ratio leads to higher activity on a per-phosphorus basis. The selectivity to p-xylene is shown in Figure 3.1 B, with all samples showing roughly similar selectivity, increasing from 70% to over 90% at a near full conversion. The similar selectivity may suggest that all samples have the same type of active site despite different Si/P ratios. The difference in initial DMF conversion rate may be due to the active site being more populated on a P-BEA with a higher Si/P ratio.
The active sites of the P materials catalyzing the \( p \)-xylene reaction are likely Brønsted acid sites\(^{91} \) and RGC is used with \( t \)-butylamine (TBA) probe molecule to determine the BAS density, displayed in Table 3.1. P-BEA Si/P=27 showed 104 \( \mu \text{mol/g cat} \) BAS density, nearly 50% higher than P-BEA Si/P=3, showing a BAS density of 70 \( \mu \text{mol/g cat} \) cat. P-BEA Si/P=27 and Si/P=3 were tested many times across multiple batches of catalyst and consistently showed +/- 5% of the given BAS density. P-BEA Si/P=10 showed 124 \( \mu \text{mol/g cat} \) BAS density, higher than that of P-BEA Si/P=27. The trend of BAS density in \( \mu \text{mol/g cat} \) may not at first glance match the trend observed in the initial DMF conversion rate, but the \( p \)-xylene reactions were run with equal mol of P in reaction, not equal mass of catalyst. When the BAS density is converted from per-gram-catalyst to per-mol-phosphorus, the trend matches the observations of initial DMF conversion rate from

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**Figure 3.1** \( p \)-Xylene reaction results for P-BEA Si/P=27, 10, and 3 with equal amount of P in reactor. Reactions using 0.23 g of P-BEA Si/P=27, 0.09 g of P-BEA Si/P=10, and 0.038 g of P-BEA Si/P=3. Time vs DMF conversion (A), \( p \)-xylene selectivity vs DMF conversion (B), and Initial DMF conversion rate (C).
Figure 3.1: P-BEA Si/P=27 shows 0.184 mol BAS/mol P, P-BEA Si/P=10 0.085 mol BAS/mol P, and P-BEA Si/P=3 shows 0.019 mol BAS/mol P. Interestingly, the BAS density of P-BEA Si/P=3 is improved when first calcining the deAl-BEA prior to P impregnation. The cl-P-BEA Si/P=3 shows improved BAS density of 122 μmol/g cat, an increase of 75%. However, when calcined-deAl-BEA is used to prepare cl-P-BEA Si/P=27, the BAS density does not improve, instead showing a small decrease to 95 μmol/g cat from 104 μmol/g cat. The increase in BAS density observed due to calcination of the deAl-BEA prior to P impregnation for Si/P=3 may be due to preservation of the BEA crystalline structure, where the first calcination prevents the collapse of the BEA structure during the second calcination after P impregnation to Si/P=3, as shown later in Figure 3.2. BEA structure could facilitate access to P within the sample or more available surface area, increasing

<table>
<thead>
<tr>
<th>Material</th>
<th>BAS Density (μmol/g cat)</th>
<th>BAS Density (mol BAS/mol P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-BEA Si/P=27</td>
<td>104</td>
<td>0.184</td>
</tr>
<tr>
<td>P-BEA Si/P=10</td>
<td>124</td>
<td>0.085</td>
</tr>
<tr>
<td>P-BEA Si/P=3</td>
<td>70</td>
<td>0.019</td>
</tr>
<tr>
<td>cl-P-BEA Si/P=3</td>
<td>122</td>
<td>0.034</td>
</tr>
<tr>
<td>cl-P-BEA Si/P=27</td>
<td>95</td>
<td>0.168</td>
</tr>
<tr>
<td>H$_2$SO$_4$-deAl-BEA Si/S=3</td>
<td>36</td>
<td>--</td>
</tr>
<tr>
<td>HNO$_3$-deAl-BEA Si/N=3</td>
<td>39</td>
<td>--</td>
</tr>
<tr>
<td>deAl-BEA</td>
<td>36</td>
<td>--</td>
</tr>
<tr>
<td>P-Silicalite-1 Si/P=27</td>
<td>203</td>
<td>0.359</td>
</tr>
<tr>
<td>P-Silicalite-1 Si/P=3</td>
<td>37</td>
<td>0.010</td>
</tr>
</tbody>
</table>
BAS density. Calcination with Si/P=27 does not significantly damage the BEA structure, leading to more similar results between the P-BEA Si/P=27 and cl-P-BEA Si/P=27 samples.

BAS density of P-BEA is unique to the impregnation with phosphoric acid. The impregnation with other mineral acids, H$_2$SO$_4$ and HNO$_3$, did not lead to an increase in BAS density above that of the parent deAl-BEA sample. DeAl-BEA shows a BAS density of 36 μmol/g cat, likely due to residual Al after dealumination. The H$_2$SO$_4$ and HNO$_3$ impregnated deAl-BEA samples with Si/S=3 and Si/N=3 show 36 and 39 μmol/g cat, respectively, with no significant difference compared to deAl-BEA. The novelty of the increase in BAS density with phosphoric acid impregnation, but not other mineral acids, may be due to the tendency of phosphoric acid to remain on the deAl-BEA after 600 °C calcination. At high temperatures, phosphoric acid can oligomerize to higher-coordinated and complex phosphate species, with P-O-P bonds from other phosphoric acid, or P-O-Si bonds with the silica support.$^{61,97}$ However, sulfuric acid and nitric acid do not oligomerize like phosphoric acid, but instead thermally decompose to H$_2$O and SO$_3$$^{98}$ and NO$_2$, H$_2$O, and O$_2$$^{99}$ respectively, at the calcination temperature of 600 °C. The condensation of phosphoric acid allows it to stay in a solid phase at 600 °C calcination, well below the minimum temperature of 950 °C needed for volatilization of phosphorus in the P$_2$O$_5$-SiO$_2$ system.$^{100}$

XRD of P-BEA with Si/P =3, 10, and 27 with comparison to the parent deAl-BEA are shown in Figure 3.2 A. While P-BEA Si/P=27 and 10 maintain their BEA crystallinity, P-BEA
Si/P=3 shows a complete collapse of BEA structure and shows the emergence of a new impurity phase. Comparison with the synthesized standard silicon phosphate Si$_5$O(PO$_4$)$_6$ material XRD$^{101}$ and its simulated XRD shows the impurity phase matches the largest peak at 25° 2-θ, and smaller peaks at 10-15° and 32° 2-θ, displayed in Figure 3.2 B. The Si$_5$O(PO$_4$)$_6$ impurity is also the expected structure from the SiO$_2$-P$_2$O$_5$ phase diagram provided from literature$^{100, 102}$ given the 600 °C calcination temperature and Si/P ratio of 3. The collapse of the BEA structure of the P-BEA Si/P=3 material therefore results in the formation of this identifiable silicon phosphate. Crystallinity of the P-BEA samples can be quantified through the analysis with the quartz internal standard, as shown in Figure 3.2 C. DeAl-BEA and P-BEA Si/P=27 keep high crystallinity of over 95% when compared to the parent Al-BEA. Relative crystallinity of P-BEA Si/P=10 decreases to 75%. In P-BEA Si/P=3, no BEA structure peaks are present for comparison thereby having a 0% relative crystallinity, showing complete collapse of BEA structure.
The collapse of the BEA crystal structure after phosphoric acid impregnation and calcination at Si/P=3 and 600 °C may be unique to deAl-BEA. Weight equivalent of phosphoric acid impregnated on parent material, Al-BEA, and ZSM-5, does not fully collapse their BEA and MFI structure after calcination. P-Al-BEA retained 60% relative crystallinity and P-ZSM-5 retained 42% relative crystallinity when impregnated with 11 wt% phosphoric acid and calcined at 600 °C, compared in Figure 3.2 D. Zeolite

**Figure 3.2: XRD of P-BEA Si/P=3, 10, 27, deAl-BEA, and silicon phosphate with relative crystallinity.** XRD of P-BEA Si/P=3, 10, 27 compared with deAl-BEA (A) with comparison of P-BEA Si/P=3 to the synthesized silicon phosphate Si₅O(PO₄)₆ standard material and simulated XRD in black (B). Unit cell structure of Si₅O(PO₄)₆ shown in the (100) projection (C) showing both tetrahedrally and octahedrally coordinated silicon. Relative crystallinity of Al-BEA, deAl-BEA, P-BEA Si/P=3, 10, 27, P-silicalite-1 Si/P=3, cl-P-BEA Si/P=3, and P-ZSM-5 and P-Al-BEA (D). Relative XRD measurements with quartz internal standard are given in Figure 3.22 and 3.23 in the appendix of Chapter 3.
modification with phosphoric acid is studied extensively in literature, with Al and P likely associating,\textsuperscript{88-90, 103, 104} possibly preventing degradation of the zeolite crystal structure.\textsuperscript{89} Dealumination with nitric acid leads to the removal of framework aluminum and generation of Si-OH silanol nest sites at the aluminum vacancy site.\textsuperscript{105} Phosphoric acid could associate with the silanol nest sites, in similar fashion to Sn associating with silanol nests in Sn-impregnation of dealuminated zeolites.\textsuperscript{106-109} Then during 600 °C calcination, the defective nature of the silanol nest sites may be susceptible to further damage in the presence of phosphoric acid, damaging the crystal structure. Testing if the presence of defect silanol nest sites affects the stability of the silica crystal structures during calcination with phosphoric acid at 600 °C, siliceous MFI type, Silicalite-1, was impregnated with phosphoric acid to Si/P=3 and subject to 600 °C calcination. The P-Silicalite-1 Si/P=3 experienced minimal damage to the crystal structure after 600 °C calcination, maintaining over 90% relative crystallinity. Similarly, calcination of deAl-BEA prior to phosphoric acid impregnation healed the defect sites (displayed later in Figure 3.5 D and F), and after phosphoric impregnation to Si/P=3 of the calcined deAl-BEA to make cl-P-BEA Si/P=3, the cl-P-BEA Si/P=3 maintained 50% relative crystallinity after calcination at 600 °C. Therefore, the absence of silanol nest defect sites in the parent Silicalite-1 sample and the healing of the defects in deAl-BEA with calcination prior to impregnation to phosphoric acid may have kept the crystal structures from completely collapsing during 600 °C calcination at Si/P=3.
3.3.2 Effect of Calcination Temperature on Catalyst Structure

The effect of calcination temperature on the BEA crystallinity of P-BEA Si/P=3, ranging from calcination temperature of 300 °C to 600 °C in 100 °C increments is shown in Figure 3.3. In Figure 3.3 A, the XRD of the P-BEA Si/P=3 samples after calcination are shown, while Figure 3.3 B shows the same samples after washing with water to remove the P and silicon phosphate to characterize the residual BEA structure more clearly. Intensity of all BEA diffraction peaks decreases with increasing the calcination temperature. At 600 °C of calcination temperature, BEA peaks are no longer observed, suggesting that the BEA crystal structure is completely damaged. Relative crystallinity of the BEA structure of these P-BEA Si/P=3 materials after washing is quantified in Figure 3.3 C. When the calcination temperature is 300 °C, the relative BEA crystallinity already decreases to 50%. The relative crystallinity further decreases to 36% at 400 °C. By 500 °C, only 15% relative BEA crystallinity remains, and at 600 °C no BEA peaks are observed therefore the relative crystallinity is 0%. The decrease in BEA crystallinity affects the surface area as micropores collapse and the zeolite structure is damaged. The surface area of the samples was measured using N₂ adsorption and calculated with the BET method tabulated in Table 3.2 and isotherms displayed in Figure 3.3 D and E. The N₂ adsorption isotherms of the P-BEA Si/P=3 with calcination temperature 300 °C, 500 °C, and 600 °C prior to washing with water are shown in Figure 3.3 D, with no significant differences in surface area with all samples between 25 and 30 m²/g. The low surface area
and minimal difference observed are likely due to phosphoric acid filling pores within the BEA crystal, but after washing with water the effect of calcination temperature on the BEA surface area is more obvious, displayed in Figure 3.3 E. After washing with water, P-BEA Si/P=3 calcined at 300 °C shows 370 m²/g while P-BEA Si/P=3 calcined at 600 °C only has 67 m²/g, nearly 80% decrease. The large drop in surface area corresponds with the collapse of BEA structure observed in the XRD measurements Figure 3.3 B.

Table 3.2: Calculated BET surface area of P-BEA Si/P=3 with 300 °C and 600 °C calcination before and after wash with H₂O.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area m²/g (not washed)</th>
<th>BET surface area m²/g (washed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-BEA Si/P=3 300 °C</td>
<td>29</td>
<td>370</td>
</tr>
<tr>
<td>P-BEA Si/P=3 600 °C</td>
<td>25</td>
<td>67</td>
</tr>
</tbody>
</table>
Figure 3.3: XRD and N\textsubscript{2} adsorption of P-BEA Si/P=3 with variable calcination temperature. Calcination temperature varied from 300 °C, 400 °C, 500 °C, and 600 °C (A) and XRD of the same P-BEA Si/P=3 samples after washing with water, with comparison to deAl-BEA (B). Relative crystallinity of P-BEA Si/P=3 with calcination temperature from 300-600 °C (C) Measurements with quartz internal standard are given in Figure 3.22 in the appendix of Chapter 3. N\textsubscript{2} adsorption of P-BEA Si/P=3 300, 500, and 600 °C (D) and N\textsubscript{2} adsorption of the same P-BEA Si/P=3 samples after washing with water (E).
3.3.3 Effect of Other Mineral Acids on Acid Site Density and Catalyst Structure

Other mineral acids, H$_2$SO$_4$ and HNO$_3$, were also tested for their effect on BEA crystal structure stability during calcination, with XRD shown in Figure 3.4 A and relative crystallinity calculated in Figure 3.4 B. The H$_2$SO$_4$-deAl-BEA and HNO$_3$-deAl-BEA show only small damages to the BEA crystal structure, with a relative crystallinity of 82% for H$_2$SO$_4$-deAl-BEA and over 95% for HNO$_3$-deAl-BEA, unlike the P-BEA Si/P=3 which has fully lost its BEA crystalline structure after calcination. The other mineral acids, H$_2$SO$_4$ and HNO$_3$, do not damage the crystal structure like phosphoric acid, likely due to their decomposition at higher temperatures before sufficient damages to the BEA structure can occur. This is also the reason for minimal difference in BAS density between deAl-BEA and H$_2$SO$_4$- and HNO$_3$-deAl-BEA as seen in Table 3.1.

![Figure 3.4 XRD of HNO$_3$-deAl-BEA, H$_2$SO$_4$-deAl-BEA, and deAl-BEA. XRD after 600 °C calcination (A) and quantified relative crystallinity of HNO$_3$-deAl-BEA, H$_2$SO$_4$-deAl-BEA and P-BEA Si/P=3 to deAl-BEA (B). Measurements with quartz internal standard used for calculation are given in Figure 3.24 in the appendix of Chapter 3.](image)
3.3.4 Characterization of P-BEA with $^{31}$P NMR and $^{29}$Si NMR

With stability of the BEA crystal structure and formation of silicon phosphate established, the presence of different phosphorus species is determined with $^{31}$P and $^{29}$Si NMR. Silicon phosphates and polyphosphate species are present on SPA, it remains unknown whether Si-O-P covalent bonds are present on SPA yet they have been studied on P-SPP. After impregnation, interactions of phosphoric acid with itself and the zeolite can undergo a wide range of coordination and possible species. A $Q_n$ naming system is used to describe the coordination of different phosphate, with $n$ representing the number of other oxygen-linked species to the central phosphorus atom. $Q_0$ is uncoordinated free phosphoric acid, with $Q_1$ representing phosphoric acid dimers, a terminal phosphate species on a polyphosphate chain, or also a terminal surface-Si bound phosphate. $Q_2$ is designated as phosphorus with 2 oxygen-bound neighbors, either P-O-P and/or P-O-Si, with $Q_3$ representing near-fully coordinated phosphate with 3 P-O-P and/or P-O-Si bonds, yet the central phosphate retains the P=O. $Q_4$ species are designated as fully bound P-O-Si with no P=O, such as in the silicon phosphate $\text{Si}_3\text{O(PO}_4\text{)}_6$. A $Q_n$ naming system is also used for Si coordination, with $Q_4$ referring to fully tetrahedrally coordinated silica with 4 Si-O-Si and/or Si-O-Al bonds. $Q_3$ sites refer to defect sites with Si-OH terminal silanol group.

$^{31}$P and $^{29}$Si NMR of P-BEA Si/P=3 and 27 and deAl-BEA are displayed in Figure 3.5. The $^{31}$P NMR of P-BEA Si/P=27 and 3 in Figure 3.5 A and B, respectively, show the
difference in phosphorus species present after 600 °C calcination due to the variation in Si/P ratio. P-BEA Si/P=27 only shows $Q_0$, free phosphoric acid, at 0 to -3 ppm, and $Q_1$ either phosphoric acid dimers with P-O-P or surface-bound Si-O-P species between -10 and -20 ppm. P-BEA Si/P=3 shows more complex oligomeric P species as well as $Q_0$ and $Q_1$ species, but the largest fraction of P species are seen between -45 and -55 ppm, the highly condensed and oligomeric $Q_3$ and $Q_4$ structures with multiple P-O-P or P-O-Si bonds. The silicon phosphate and complex polyphosphates overlap in this region. Highly complex phosphate oligomers present in P-BEA Si/P=3 lack available P-OH acid sites, and therefore could additionally explain the lower BAS density observed in P-BEA Si/P=3 compared to P-BEA Si/P=27 which has mostly free phosphoric acid with available P-OH acid sites. $^{29}$Si NMR spectra shown in Figure 3.5 C and D show defect Si-OH site, $Q_3$, at -100 ppm, and $Q_4$ full tetrahedrally coordinated Si from -110 to -120 ppm for both Si/P=27 and Si/P=3. However, for P-BEA Si/P=3, the $^{29}$Si NMR shows broader and less intense peaks than the P-BEA Si/P=27, which could be due to the collapsed BEA structure preventing full relaxation of internal Si.

The effect of 600 °C calcination on the $^{29}$Si NMR of deAl-BEA without P impregnation is shown in Figure 3.5 E and F. In Figure 3.5 E, the deAl-BEA prior to calcination contains significant $Q_3$ Si-OH defect sites from the silanol nests formed after the removal of aluminum through nitric acid dealumination. After 600 °C calcination, the $Q_3$ defects are greatly reduced. In the absence of defect sites, the subsequent calcination
after P impregnation to Si/P=3 maintains BEA crystal structure as in cl-P-BEA Si/P=3, therefore phosphoric acid may interact with the defect sites during the calcination leading to the damages in its crystal structure. In addition, $Q_3$ sites are not fully healed after calcination with Si/P=27 and Si/P=3 in the typical P-BEA samples as shown in Figure 3.5 C and F, and so association of phosphoric acid with the defect sites may prevent healing the defective $Q_3$ sites, as happens when deAl-BEA is calcined without prior phosphoric acid impregnation.
Figure 3.5 $^{31}$P and $^{29}$Si MAS NMR of P-BEA Si/P=27, 3 and deAl-BEA. P-BEA Si/P=27 (A, C) and P-BEA Si/P=3 (B, D) and deAl-BEA (E, F) before calcination and after calcination at 600 °C.
Scheme 3.1 Diagram of humidity treatment of samples where samples are placed in a vial within an autoclave, with liquid water in the autoclave surrounding the vial but without direct contact with the sample.

Figure 3.6 $^{31}$P NMR of P-BEA Si/P=27 and 3 with humidity treatment and ambient exposure. (A) P-BEA Si/P=3 with humidity treatment showing decrease in $Q_3/Q_4$ P structures. (B) P-BEA Si/P=27 humidity treatment showing hydrolysis of $Q_1$ P structures. (C) P-BEA Si/P=3 exposed to ambient instead of in humidity treatment. (D) P-BEA Si/P=27 exposed to ambient conditions, showing decrease in $Q_1$ but not full hydrolysis as with humidity treatment.
The sensitivity of P-BEA with respect to moisture conditions was also investigated with $^{31}$P NMR. The $^{31}$P NMR spectra of P-BEA taken immediately after calcination at 600 °C was compared to the ones collected from the same P-BEA Si/P=27 and Si/P=3 samples after humidity treatment and treating under ambient conditions. For humidity treatment, P-BEA samples were placed in a vial within a second larger container like an autoclave, with liquid water outside the inner vial containing the P-BEA without direct contact of the liquid water and P-BEA. When the second larger container is closed, humidity in the container will rise and water vapor will interact with the P-BEA, shown in Scheme 3.1. For ambient treatment, samples were left out on a lab bench without a lid. Both treatments were conducted at room temperature for 1 day. Comparison of the treatment to post-calcined samples is given in Figure 3.6. After calcination, P-BEA Si/P=3 shows a $Q_0/(Q_3+Q_4)$ ratio of about 0.35, with an increase to 0.57 with ambient exposure and 0.72 with humidity treatment, showing hydrolysis of oligomerized P species. For P-BEA Si/P=27 after calcination the $Q_0/Q_1$ ratio is approximately 3, and after ambient exposure the ratio increases to 4. With humid treatment, the $Q_1$ species are fully hydrolyzed.
3.3.5. Characterization of P-BEA and other P-Materials using Phosphorus X-ray Absorption Near Edge Structure (P-XANES)

In conjunction with $^{31}$P NMR, P-XANES of P-BEA Si/P=27 and Si/P=3 were run to determine if any distinguishable features in X-ray fluorescence could help understand the differences in the P structures of P-BEA.\textsuperscript{112, 113} In Figure 3.7 A, P-BEA Si/P=27 and Si/P=3 after 600 °C calcination show the same position of the white line at 2150 eV, indicating the oxidation states of the phosphorus are the same. However, P-BEA Si/P=27 has a higher peak, or white-line intensity, than P-BEA Si/P=3. The intensity of the white line is determined by the delocalization of electrons around the central P atom, with higher white line intensity resulting from more delocalization of electrons\textsuperscript{96}. Delocalization can be conceptually understood as the degree of resonance structures present in a compound around the central P atom. But fully protonated phosphoric acid, as the dominant P structure in P-BEA Si/P=27, lacks significant resonance, with only 1 dominant Lewis electron structure. However, if the phosphoric acid has 1 deprotonation, with a P-OH

Figure 3.7 Phosphorus XANES of P-BEA Si/P=27 compared to Si/P=3 (A), the effect of humidity treatment on Si/P=3 (B), and a theoretically calculated XANES for representative species from $Q_0$ ($H_3PO_4$) and $Q_3$ ($P_4O_{10}$) from collaborators.

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becoming P-O\(^-\) due to solvation effects in the zeolite pore, there are 3 degenerate resonance structures because it is ambiguous which of the 3 equivalent P-OH groups in phosphoric acid are deprotonated. In P-BEA Si/P=3, the dominant P structures are highly condensed phosphates, such as P\(_4\)O\(_{10}\) or branched polyphosphates with terminal P-OH. If the terminal P-OH in a polyphosphate chain is deprotonated, there may be less degenerate resonance structures, as the deprotonation would be localized to the terminal P-O\(^-\). This can explain why P-BEA Si/P=27 has a higher white line intensity than Si/P=3. In Figure 3.7 B, the white line intensity of Si/P=3 can be increased with humidity treatment, possibly due to the hydrolysis of oligomerized P-structures as shown in the \(^{31}\text{P}\) NMR of P-BEA Si/P=3 (Figure 3.6). In collaboration with Stony Brook University, the P-XANES of representative P structures of P-BEA Si/P=27 and Si/P=3, phosphoric acid and P\(_4\)O\(_{10}\) respectively, were theoretically simulated in Figure 3.7 C, with white line intensity consistent with observations in Figure 3.7 A and B.

**Figure 3.8 P-XANES of P-BEA and standard P-materials.** (A) P-XANES of P-BEA Si/P=27 and 3, Na\(_3\)PO\(_4\), NH\(_3\)H\(_2\)PO\(_4\) standard materials, compared with PPh\(_3\), OPPh\(_3\), TPP, and OPOPh\(_3\). PPh\(_3\): Triphenylphosphine, OPPh\(_3\): triphenylphosphine oxide, TPP: Triphenylphosphite, OPOPh\(_3\): Triphenylphosphate. (B) Plot of K-edge location vs the expected oxidation state of each material.
As P-XANES are a new technique to study P-zeolites, P-XANES of standard phosphate species were run, shown in Figure 3.8, with standard materials triphenylphosphine (PPh₃), triphenylphosphine oxide (OPPh₃), triphenylphosphite (TPP) triphenylphosphate (OPOPh₃), ammonium dihydrogen phosphate (NH₄H₂PO₄) and trisodium phosphate (Na₃PO₄). Figure 3.8 B shows the trend of higher oxidation state leading to higher K-edge energy, as K-shell electrons are more tightly bound to the central P atom in a more oxidized material. Interestingly, OPOPh₃, Na₃PO₄, NH₄H₂PO₄, and the P-BEA Si/P=27 and 3 all have an expected oxidation state of +5 based on standard oxidation state rules, yet the P in the P-BEA samples show the highest K-edge location energy, indicating a possible oxidizing environment within a zeolite pore.

P-XANES of P-BEA Si/P=27 and 3 are compared to the silicon phosphate bulk crystalline material and 99% phosphoric acid gel in Figure 3.9. Consistent with the trends seen edge intensity with phosphorus concentration, the silicon phosphate has a lower edge intensity than P-BEA Si/P=3. When P-BEA Si/P=27 is compared to the 99% phosphoric acid gel, the edge intensity of the phosphoric acid gel is significantly lower, despite most of the P species in both samples being Q₀. Therefore, it is not just the type of P species which may affect the white line intensity, but the concentration of that type of P species as well as dispersion within the zeolite pores will also affect the white line intensity.
Figure 3.9 P-XANES with P-BEA Si/P=27, Si/P=3, silicon phosphate, and 99.9% phosphoric acid gel. P-BEA Si/P=27, 3 and silicon phosphate (A) Consistent with previous trends, the higher concentration of P leads to a lower edge intensity. (B) P-BEA Si/P=27 compared with a 99.9% phosphoric acid gel. The phosphoric acid gel has considerably lower white line intensity than P-BEA Si/P=27, therefore the dispersion of phosphoric acid within the zeolite may be responsible for an edge intensity increase.

Of interest are the P-XANES of the P-BEA and P-SPP Si/P=27 and P-BEA Si/P=3 when subject to ultra-dry conditions, shown in Figure 3.10. Little difference is seen between samples prepared within the air-free environment and those prepared with 600 °C calcination within 24 hours prior, but exposed to atmospheric conditions, suggesting
ambient exposure may not have an instant direct effect on P structural sites as does more thorough humidity treatment seen in Figure 3.7.

Figure 3.10 P-XANES on P-BEA Si/P= 27 and 3 and P-SPP Si/P= 27 with atmosphere control. Samples were heated to 400 °C in ultra-high vacuum, sealed in an ampoule, opened on-site and the slide prepared with the SPEX polypropylene film within an air- and oxygen-free glovebox of (A) P-SPP Si/P= 27 (B) P-BEA Si/P= 27, and (C) P-BEA Si/P= 3.
When other types of supports were used for P-impregnation, such as TiO$_2$, Al$_2$O$_3$, and active carbon, and H-BEA and H-ZSM-5 lower edge intensity is observed than when silica supports are used, shown in Figure 3.11 for Si/P=27 (or 1.8 wt% P) and Figure 3.12 for Si/P=3 (or 11 wt% P) and Figure 3.13 for H-BEA and H-ZSM-5 at 1.8 and 11 wt% P. All silica supports show very similar edge intensity. The edge intensity may be due to the ability of the phosphate proton to dissociate on the surface of the supports, indicating the phosphate protons on the silica support may be more labile. With all supports, the edge intensity is higher with lower P concentration, as seen in the P-BEA samples. Interestingly, the TiO$_2$ support shows an edge shift of 1 eV higher in both 1.8 wt% P and 11 wt% P, indicating a more oxidized environment. Additionally, pre- and post-edge features are observed, indicating bound state transitions and variable coordination of the phosphorus.$^{113}$ The single post-edge hump seen in the siliceous and other non-siliceous supports is associated with polyphosphates, yet the post-edge feature in TiO$_2$ could indicate an apatite-like structure when associated with TiO$_2$.\textsuperscript{112} γ-Al$_2$O$_3$ also may show a post-edge feature at 1.8 wt% P. P-active C with 1.8 wt % P also shows a pre-edge shoulder not seen in 11 wt% P on P-active C. The differences in pre- and post-edge features seen between 1.8 wt% P and 11 wt % P indicate further differences in P arrangement at different concentrations. In the Al-zeolite containing supports H-BEA and H-ZSM-5, a peak shift is observed at 1.8 wt% P. But at 11 wt% P, no peak shift is observed, indicating at
higher P concentrations the interactions between P may play more important role than the interaction between the P with the aluminosilicate zeolite surface.

Figure 3.11 P-XANES with Si/P=3 on silica supports and 11 wt% P on other supports. (A) siliceous supports and (B) 11 wt% P on other supports. All silica supports show very similar white line intensity, although P-BEA HF may be slightly larger. The type of metal oxide has significant impact on the white line intensity, lower in intensity than P-BEA Si/P=3.

Figure 3.12 P-XANES with Si/P=27 on silica supports and other supports with 1.8 wt% P. (A) Silica supports with Si/P=27 and (B) other supports with 1.8 wt% P, silica supports showing similar edge intensity, and higher edge intensity than the Si/P=3 shown in Figure 3.11 A. All edge intensities are also higher than shown in Figure 3.11 B with 11 wt % P, with γ-Al₂O₃ edge significantly higher.
Effect of P concentration from the P impregnated samples using the supports including fumed SiO$_2$, TiO$_2$, active carbon, γ-Al$_2$O$_3$ and the aluminum-containing H-BEA and H-ZSM-5 is directly compared in Figures 3.14, 3.15, 3.16, 3.17, 3.18, respectively, with Si/P=3 (11 wt% P), Si/P=27 (1.8 wt% P) and Si/P=100 (0.5 wt% P). In consistent with the BEA supports, decreasing the P content on the supports leads to a higher edge intensity, with TiO$_2$ showing pre- and post-edge features at 1.8 wt% and 11 wt% P in Figure 3.15.

Figure 3.13 P-XANES with P-H-BEA, P-H-ZSM-5, and P-BEA. (A) 1.8 wt% P compared with P-BEA Si/P=27. Similar intensities are observed, but a 1 eV peak shift is observed with the Al-containing zeolites, indicating a more oxidizing environment than within P-BEA Si/P=27. (B) 11 wt% P compared with P-BEA Si/P=3, all with similar intensity and a decrease in intensity from 1.8 wt% P.

Figure 3.14 P-XANES of P-fumed SiO$_2$ with Si/P=3, 27, and 100. Edge intensity grows with Si/P=3 to 27 but does not further increase with Si/P=100.
Figure 3.15 P-XANES of TiO$_2$ with 11 wt% P, 1.8 wt% P, and 0.5 wt% P. 11 wt% P shows the lowest edge intensity, with little difference between 0.5 wt% P and 1.8 wt% P. Pre-edge features grows from 0.5 wt% P to 1.8 wt% P, with no increase from 1.8 wt% P to 11 wt% P, yet post-edge feature grows from 1.8 wt% to 11 wt% P.

Figure 3.16 P-XANES of P-active C with 0.5 wt% P, 1.8 wt% P, and 11 wt% P. Peak intensity decreases with increasing wt% P. Interestingly, a pre-edge shoulder is observed in 1.8 wt% P and may be small in 0.5 wt% P, yet is not observed in 11 wt% P.

Figure 3.17 P-XANES of P-y-Al$_2$O$_3$ with 0.5 wt% P, 1.8 wt% P, and 11 wt% P. Peak intensity is similar between 0.5 wt% P and 1.8 wt% P, but decreases with 11 wt% P.
Sodium-substituted phosphate impregnated deAl-BEA samples are also compared in P-XANES, shown in Figure 3.19. For Si/P=27 in 3.19 A, no peak shift was observed, but the decrease in peak intensity with increasing sodium substitution is consistent with the Si/P=3 shown in 3.19 B. From literature, increasing K-substitution on solid phosphate salts led to higher edge intensity, and in aqueous solution, increasing K-substitution led to decrease in edge intensity. Interestingly, the Na-substituted phosphates within the zeolite follow the trend for decreasing edge intensity with increasing substitution as seen in aqueous phosphate solutions, with the edge intensity trend more pronounced at lower concentration of Si/P=27 than Si/P=3. This may indicate the adsorption on the zeolite surface and within zeolite pores mimics an aqueous environment which could lead to proton dissociation from the phosphates.

Figure 3.18 Additional P-XANES of P-ZSM-5 and P-H-BEA with 0.5 wt% P, 1.8 wt% P, and 11 wt% P for (A) P-H-BEA Si/Al=12.5 and (B) P-H-ZSM-5 Si/Al=11.5. Both show similar intensity for 0.5 wt% P and 1.8 wt% P, with a decrease in intensity for 11 wt% P.
3.4 Conclusion

Study on the effects of P concentration of P-BEA catalyst in the p-xylene reaction and BAS density measurement suggests that a higher P loading results in a lower initial DMF conversion rate and lower BAS density on a per phosphorus basis. The BEA structure is also not stable with high P loading. At Si/P=3, the BEA crystalline structure is completely damaged after calcination at 600°C, which significantly reduces the available surface area and/or accessibility to the active P sites. At Si/P=3, the phosphoric acid has also significantly oligomerized into complex P-O-P structures and silicon phosphate by condensing P-OH sites which may serve as Brønsted acid sites. The combination of complex P-O-P structures and loss of crystallinity in P-BEA Si/P=3 could be responsible for the reduction in its activity when compared to P-BEA Si/P=27. The lack of defect Si-OH sites or presence of Al in zeolites may inhibit crystal structure damage during calcination with phosphoric acid impregnation to Si/P=3. By removing the defect sites, such as

\[ \text{Figure 3.19 P-XANES with phosphates of varying sodium-proton substitution. } H_3PO_4, \text{ NaH}_2\text{PO}_4, \text{ Na}_2\text{HPO}_4, \text{ and Na}_3\text{PO}_4 \text{ with (A) Si/P=3 and (B) Si/P=27. For Si/P=27, a peak shift may be observed for NaH}_2\text{PO}_4. \text{ Peak intensity decreases with increasing sodium substitution.} \]
through calcination of deAl-BEA prior to P impregnation, or with pure siliceous material like Silicalite-1, damage to the crystal structure can be minimized, which could increase the BAS density of P BEA catalysts. P-XANES also showed a distinct difference in edge intensity with variation in Si/P ratio not only on P-BEA, but on other P-silica supports and P-metal oxides and carbons, where higher Si/P ratio led to higher white line intensity. Interestingly the edge intensity at low Si/P ratio increased with humidity treatment, suggesting the edge intensity could be related to the P structure within the P-material.
3.5 Appendix to Chapter 3

The appendix of Chapter 3 includes the thermogravimetric analysis of P-BEA Si/P=27, 3 and deAl-BEA, as well as P-BEA Si/P=3 after humidity treatment in Figure 3.20, which can help understand the condensation temperature of P-OH sites. XRD of P-BEA with Si/P=3, 4, 5, 6.5, and 8 are included to show the effects from Si/P ratios on stability of BEA structure during P impregnation and calcination (Figure 3.21). XRD for quantitative analysis of relative crystallinity with quartz internal standard are shown for deAl-BEA, P-BEA Si/P=27, 10, and 3, and P-BEA Si/P=3 with varying calcination temperature in Figure 3.22. Relative crystallinity XRD with quartz internal standard of P-H-BEA and P-ZSM-5 was studied to quantify the effect Al on zeolite stability during P impregnation, given in Figure 3.23 and 3.24. P-silicalite-1, and HNO$_3^-$ and H$_2$SO$_4^-$-deAl-BEA XRD are given in Figure 3.25. Stability of silicon phosphate during humidity treatment, in liquid water and $n$-heptane at elevated temperatures, and under reaction conditions is shown in Figure 3.26, 3.27, and 3.28 respectively. $p$-Xylene reactions with higher mass of P-BEA Si/P=3 and silicon phosphate are shown in Figure 3.29, and initial rates are compared in Figure 3.30. $^{31}$P and $^{29}$Si NMR are given for the silicon phosphate material in Figure 3.31, and SEM images in Figure 3.32-3.34. Calibration results for the FID in RGC measurement and BAS density of H-ZSM-5 standards are given in Figure 3.35. P impregnated supports P-fumed SiO$_2$, P-Si-SPP, and P-BEA (HF), are tested with TBA in RGC to obtain BAS density in comparison to reaction results in Chapter 2 in Figure 3.36.
Figure 3.20 Thermogravimetric analysis of P-BEA Si/P=3, 27 and deAl-BEA (A) Derivative of weight with respect to temperature and (B) weight loss in thermogravimetric analysis of P-Bea Si/P=3 after humidity treatment and air exposure, showing humidity treatment leading to quicker water adsorption after 1 day. An additional peak between 100 °C and 150 °C, which may be due to self-condensation of P-OH groups or with Si-OH groups. (C) Derivative weight and (D) weight % loss of P-EA Si/P=3, 27, and deAl-BEA, with only P-BEA Si/P=3 showing the extra peak between 100 °C and 150 °C.

Figure 3.21: XRD of P-BEA Si/P=3 to 8 (A) XRD of P-BEA Si/P=3 to 8, after impregnation, after washing after impregnation, after calcination, then after washing after calcination. BEA crystal structure is lost after calcination. (C) XRD of P-BEA Si/P=3 to 8 after calcination at 600 °C, showing BEA structure is lost by Si/P=5, and silicon phosphate forms after Si/P=3.
Figure 3.22 XRD of P-BEA with quartz internal standard used in relative crystallinity calculation in Figure 3.2 and 3.3 of (A) deAl-BEA, P-BEA Si/P=27, and P-BEA Si/P=3 after washing and (B) P-BEA Si/P=3 with calcination temperature from 300 °C to 600 °C compared to deAl-BEA.

Figure 3.23 XRD of P-H-BEA and P-ZSM-5 with quartz internal standard used in relative crystallinity calculation in Figure 3.2 and 3.3 of (A) H-BEA Si/Al=12.5 with comparison to P-impregnated H-BEA with 11 wt% P at 600 °C calcination and (B) H-ZSM-5 with Si/Al=11.5 with comparison to P-impregnated H-ZSM-5 after 600 °C calcination.
Figure 3.24 XRD of P-silicalite-1 and HNO$_3$- and H$_2$SO$_4$-deAl-BEA with quartz internal standard used in relative crystallinity calculation in Figure 3.2 and 3.4. (A) XRD of Silicalite-1 with comparison to P-Silicalite-1 Si/P=3 and (B) XRD of HNO$_3$-deAl-BEA Si/N=3 and H$_2$SO$_4$-deAl-BEA after calcination with comparison to deAl-BEA.

Figure 3.25 XRD of H-ZSM-5, P-H-ZSM-5 with 11 wt% P, and with washed sample, compared to the silicon phosphate bulk crystalline standard. The silicon phosphate is formed in 11 wt% P P-H-ZSM-5, but is able to be washed out during washing with 1 L water.
Figure 3.26 XRD of Humidity treated silicon phosphate for 2 days and 2 weeks, showing little change in crystal structure when compared to directly after heating at 900 °C in N₂.

Figure 3.27 XRD of Silicon phosphate in water treatment and heptane treatment at elevated temperatures (A) Stability of silicon phosphate during direct water treatment (WT) at room temperature, 50 °C and 100 °C for 1 day with comparison to after heating at 900 °C under N₂ and the simulated XRD. The main peaks decrease with increasing temperature and the impurity peak at 24.2° grows with higher temperature water treatment. (B) Stability of silicon phosphate in n-heptane treatment (HT) from room temperature to 250 °C. Silicon phosphate shows stability at high temperatures in n-heptane.
Figure 3.28 XRD of Silicon phosphate material before and after p-xylene reaction. The crystal structure has collapsed during the reaction and resulted in an amorphous hump at 20° 2θ. The peak at 38° 2θ is from the XRD plate holder. This result is interesting given the stability of the silicon phosphate in n-heptane at 250°C given in Figure 3.27. It may be possible water formed from the dehydration of the cycloadduct resulted in the structural damage.

Figure 3.29 p-Xylene selectivity vs DMF conversion for (A) silicon phosphate with mass varying from 0.05 g to 0.5 g and (B) P-BEA Si/P=3 with mass varying from 0.2 g to 1.0 g, with 1.0 g of P-BEA shown for comparison. Silicon phosphate and P-BEA Si/P=3 see similar trends, where higher mass of catalyst leads to lower p-xylene selectivity.
Figure 3.30 **Initial reaction rate data for Figure 3.29** (A) in M DMF conversion per hour and (B) M DMF conversion per hour per mmol P. Lower Si/P and higher mass of catalyst ratio leads to less activity per phosphorus.

Figure 3.31: **$^{31}$P and $^{29}$Si NMR of silicon phosphate crystalline standard** (A) $^{31}$P MAS NMR of the silicon phosphate crystalline standard, showing significant Q$_4$ structures with a small Q$_1$ peak. Asterisks indicate spinning sidebands of the Q$_4$ peak. (B) $^{29}$Si MAS NMR of the silicon phosphate crystal standard, showing tetrahedral silicon, Q$_4$, as well as the octahedral silicon, Q$_6$, indicative of the Si$_5$O(PO$_4$)$_6$ silicon phosphate structure.
Figure 3.32 SEM images of the silicon phosphate material with scale at (A) 30 μm and (B) 10 μm.

Figure 3.33 Additional SEM images of silicon phosphate with scale at (A) 50 μm and (B) and (C) at 5 μm.
Figure 3.34 Additional SEM images of silicon phosphate with scale at (A) 20 μm (B) 4 μm (C) 10 μm (D) 40 μm (E) 10 μm (F) 10 μm (G) 20 μm (H) 5 μm
Figure 3.35 Calibration of GC FID with propylene and H-ZSM-5 standards (A) Calibration of the FID in the reactive gas chromatograph with propylene gas, with trendline shown in red with an $R^2=.98$. Calibration factor for propylene was determined as $2.66 \times 10^{-6}$ μmol propylene per Peak Area. Calibration factor for butylene was calculated as 75% the calibration factor for propylene, $1.99 \times 10^{-6}$ μmol butylene per Peak Area. (B) Standard calculation with H-ZSM-5 Si/Al=25 using $t$-butylamine (TBA), sec-butylamine (SBA), and isopropylamine (IPA), with the red line shown as 100% observed Al as a BAS site. (C) Standard calculation with H-ZSM-5 with varying Si/Al ratio using TBA as a probe molecule, with the red line shown as 100% observed Al as BAS site.

Figure 3.36 Additional RGC data using P-fumed SiO$_2$, P-SPP, and P-BEA-HF made with low defect Si-BEA, all with Si/P=27. P-fumed SiO$_2$ and P-SPP show 30-40% higher BAS density than P-BEA, while the P-BEA-HF shows less than 50% P-BEA Si/P=27 BAS density.
CHAPTER 4

INCREASE IN ACID SITE DENSITY OF P-BEA BY HYDROLYSIS OF OLIGOMERIC PHOSPHORUS STRUCTURES

4.1 Introduction

The lower Si/P on P-BEA leads to more oligomerized P-structures, which could be a reason for the relatively low acid site density and low activity of P-BEA with a higher loading of phosphorus. It was also observed that water can hydrolyze highly oligomerized P species. The resulting hydrolysis of condensed phosphate species is free orthophosphoric acid, consistent with literature. However, the orthophosphoric acid may not be the acid site for p-xylene production, for example, water treatment on SPA catalysts resulted in an increase in propylene oligomerization, but a decrease in benzene alkylation to cumene and a decrease in catalyst lifetime. Therefore, it is possible different P species have a substantially different catalytic activity, and if the types of P species can be preferentially produced on the surface of the P-zeolites, they could be tailor-made to increase rates in a particular reaction.

Another method in literature of altering the P species is through controlled heating of solid phosphoric acid (SPA) at given times and temperatures between 200 and 300 °C to preferentially produce the pyrophosphoric acid, which was identified as the most active species in the propylene oligomerization reaction. Too high temperature
 (>300 °C) resulted in the formation of metaphosphoric acid, which shows poor activity in the propylene oligomerization reaction.

Here in Chapter 4, the purpose is to increase the Brønsted acid site density of P-zeolites and silicon phosphate by treating the catalysts with water or cofed water/TBA, referred to as “activation”. These activation procedures are hypothesized to hydrolyze the silicon phosphate phase and complex oligomeric P species in P-BEA Si/P=3, providing more acid sites. It was found that the temperatures of activation is crucial in order to avoiding reversible condensation of the hydrolyzed sites. The association of TBA with the hydrolyzed acid sites could prevent the opened sites from closing at elevated temperatures. Water/TBA activation procedures were also attempted on other P containing catalysts made by impregnation of phosphoric acid on other supports such as Si-SPP and fumed SiO₂ with Si/P=3, as well as bulk crystalline silicon phosphate, to investigate susceptibility to increases the Brønsted acid site density. In order to further increase the acid site density, crystalline silicon phosphate with a higher surface area was synthesized using a hard templating method. The ability to increase the Brønsted acid site density of P containing catalysts by activation and higher surface area may help deduce the structure of the active site, as well as potentially improve reaction rate in relevant renewable reactions.
4.2 Experimental Design

4.2.1 Reaction Preparation and Analysis

P-BEA Si/P=3 samples were activated under flow conditions according to the following procedure reported in literature\textsuperscript{117}. Before the experiments, the P-zeosil catalyst was pretreated at 400 °C in He for 4 hours. Under flow conditions dry TBA (10 torr) was first injected into the quartz reactor at 240 °C in a He flow of 100 sccm (WHSV = 2.2 g TBA/g cat-hr) to establish the rate under dry condition using an online GC. An immediate switch to the TBA/water mixture was achieved by using a 6-port valve, yielding the same partial pressure of TBA but with 180 torr water cofed. The injection of TBA/water lasted for at least 2 hours until the rate stabilized, and it was then switched back to the dry TBA flow again.

Standard RGC procedure from Chapter 3 was modified to inject liquid water and a solution of water and TBA using the GC automatic liquid sampler, in attempts to hydrolyze the condensed P structures that may form at elevated temperatures. The process is called as activation. This process was performed after the \textit{in-situ} heating at 400 °C and before the TBA saturation at 150 °C. The partial pressure of water in the inlet was 180 torr and the partial pressure of TBA was 10 torr, and these partial pressures were achieved using a 1.8 psig and 18 mL/min helium with an injection rate of 3 uL/min and a 16:1 mol ratio of water to TBA. Pulse Injections were performed with 5 µL of sample (water or water/TBA) for each injection, with 45 total injections and 1 minute between injections,
to sufficiently hydrolyze the complex P structures. When only water was, 140 °C was used for the activation, while 240 °C was used for the liquid mixture of water and TBA during activation. RGC procedure was also tested to run multiple trials without removal of the catalyst bed in the inlet, with in-situ heating the samples in helium at 400 °C between trials. Activation was attempted for P-BEA Si/P=27, 10, and 3. The effect of calcination temperature on BAS site density before and after activation was studied on P-BEA Si/P=3, P-fumed SiO₂ Si/P=3, as well as the silicon phosphate crystalline material.

While activation with water/TBA at 240 °C is thought to hydrolyze the complex P structures to increase BAS density, the newly opened BAS sites may be associated with TBA. To use these activated catalysts in reactions, it is necessary to remove the TBA without condensing the active sites opened with the activation process. Attempts were made to remove the adsorbed TBA by heating the activated samples to 400 °C under helium, as well as purging at 240 °C under helium. Activated P-BEA was purged at 240 °C for 1 hour, 6 hours, and 12 hours after water/TBA activation, then measuring the amount of TBA remained on the surface without additional surface saturation with TBA. Additional experiments with surface saturation of TBA were also performed after purging to determine the number of BAS sites which remained open after TBA had been purged off.
4.2.2 Catalyst Characterization

XRD and $^{31}$P NMR were used to characterize the activated P-BEA Si/P=3 in similar methods described in Chapter 2. XRD was run on P-BEA Si/P=3, P-fumed SiO$_2$ Si/P=3, and silicon phosphate crystalline bulk material to determine the effect of activation on the silicon phosphate structure. $^{31}$P NMR was run on P-BEA Si/P=3 before and after activation to determine the changes in P species present due to the activation. Prior to $^{31}$P NMR, the activated material was purged at 240 °C for 1 hour.

4.2.3 Catalyst Preparation

To improve catalytic performance of the silicon phosphate bulk crystalline material, the synthesis procedure of the silicon phosphate described in Chapter 2 was modified. Black-Pearls-2000 (CABOT, BP-2000 lot #1366211) carbon black was used as a hard template to introduce mesoporosity within the crystalline silicon phosphate material. It has to be mentioned that methods to increase silicon phosphate surface area have been reported in literature with more complex synthesis conditions,$^{118,119}$ but the addition of BP-2000 to the original procedure is a simple modification to the existing procedure similar to carbon-templating of mesopores in zeolites.$^{120}$ 2.16 g of solid BP-2000 were first physically mixed and grounded with solid silicic acid until homogenous prior to the dropwise addition of phosphoric acid. Similar drying procedures and heating under N$_2$ to 900 °C were followed as with original silicon phosphate synthesis recipe. However, with the addition of BP-2000, the sample was additionally calcined at 600 °C for
12 hours under 100 mL/min of dry air to oxidize the BP-2000, leaving accessible mesopores in the sample. A scheme of the synthesis is shown in Scheme 4.2 in the appendix of Chapter 4.

4.3 Results and Discussion

4.3.1 Activation of P-BEA Si/P=3 with Cofed Water/TBA

Figure 4.1 A shows the BAS density of P-BEA Si/P=3, before and after activation with water/TBA at 240 °C \textit{ex-situ}, under constant flow conditions with 180 torr H$_2$O and 10 torr TBA in collaboration with Han Chen in Abdelrahman lab. TBA reaction under flow conditions is given in Figure 4.2, showing over 10 times increase in isobutene formation. \textit{In-situ} activation described in the materials and methods session above reproduces the activation conditions using the automated liquid sampler in the RGC, resulting in over a 5-times increase in observed BAS density, consistent with the BAS density from the P-BEA Si/P=3 activated under flow conditions and measured in RGC. In Figure 4.1 B, the BAS densities were collected on the same bed of P-BEA Si/P=3, showing the initial BAS density without activation, the BAS density after the \textit{in-situ} activation, and the result after subsequent 400 °C heating in helium after activation. The activation has been reversed after 400 °C heating in helium, suggesting that the high temperature of 400 °C are closing any open sites which were generated using the \textit{in-situ} activation. Figure 4.1 C shows the modification of inlet temperature conditions during the 3 BAS measurements on the same bed of P-BEA Si/P=3. Figure 4.3 shows the injections with 15 times, 30 times, 45 times,
and 60 times with water at 140 °C and water/TBA cofeed at 240 C. No additional benefit is seen from more than 45 times injections with water or with water/TBA cofeed, indicating that the material is fully activated after 45 injections with water or water/TBA cofeed.

Figure 4.1 BAS density of the parent P-BEA Si/P=3, and P-BEA Si/P=3 activated with 180 torr TBA and 10 torr water. Flow condition activated by Han Chen in Abdelrahman lab and in-situ activation in RGC using liquid water/TBA mixture injected through autosampler (A). 3 trials run on the same bed of P-BEA Si/P=3, showing the initial BAS density, the BAS density after 45 water/TBA injections, and after heating at 400 °C (B). Inlet conditions for the 3 trials on P-BEA Si/P=3 (C) with the 2-hour purge at 150 °C after every TBA saturation omitted for brevity. P-BEA Si/P=3 BAS density was tested multiple times across different batches and showed +/- 5% change in BAS density. BAS density of the samples after activation was also tested multiple times across different batches, with BAS showing +/- 10% after activation.
Figure 4.2 Results of isobutene formation under flow conditions after cofeeding 180 torr H₂O and 10 torr TBA. Data provided by Han Chen, showing over 10 times increase in isobutene formation with water/TBA cofeed.

Figure 4.3 Number of 5 μL of injections required for activation. (A) only water at 140 °C and (B) water/TBA cofeed at 240 °C to the point where additional injections no longer have a positive effect on BAS density.
4.3.2 Characterization of Activated P-BEA Si/P=3 with XRD and $^{31}$P NMR

XRD and $^{31}$P NMR of the activated P-BEA Si/P=3 are shown in Figure 4.4. Figure 4.4A shows the XRD patterns of the samples activated with water/TBA at 240 °C, only water at 240 °C, and the parent P-BEA Si/P=3. The activation with water does not show any change in XRD structure with the silicon phosphate phase remaining. However, activation with the cofed water/TBA at 240 °C shows the collapse of the silicon phosphate phase, indicating the water/TBA cofeed can hydrolyze the silicon phosphate, which may indicate a possible reason for the large increase in BAS density observed due to the water/TBA cofeed activation at 240 °C, as the silicon phosphate is hydrolyzed to produce more active sites. $^{31}$P NMR spectra in Figure 4.4B also show a similar result as the XRD, where the highly condensed $Q_3$ and $Q_4$ in P-BEA Si/P=3 species are significantly decreased with the water/TBA cofed activation, but activation with only water at 240 °C does not significantly decrease the $Q_3$ and $Q_4$ species. Interestingly, the water/TBA treatment at 240 °C leads to an increase in not only $Q_0$ but also $Q_1$ species, suggesting one of these two species may be the active site. However, it is important to remember the NMR spectra are taken at room temperature after exposure to ambient moisture. It is possible that the $Q_0$ and $Q_1$ species condense to another type of P species under reaction conditions, which is the true active site. This current result would suggest that the $Q_0$ and $Q_1$ species present on P-BEA Si/P=3 at room temperature are necessary for active site generation under reaction conditions. It is also possible that the large fraction of $Q_1$ species seen in the $^{31}$P NMR
remain associated with the TBA, as the sample was only purged for 1 hour at 240 °C. If the $Q_1$ species seen is still associated with TBA, it is possible the $Q_0$ species are the active site, as association of the $Q_0$ species with a TBA may result in a chemical shift to appear as a $Q_1$ species.

Figure 4.4 XRD and $^{31}$P NMR of activated P-BEA Si/P=3. XRD (A) and $^{31}$P MAS NMR (B) of P-BEA Si/P=3 activated with 180 torr of water and 10 torr of TBA at 240 °C, compared with Si/P=3 after 600°C calcination and P-BEA Si/P=3 treated with 180 torr of water at 240 °C without TBA. Asterix in NMR denote spinning sidebands.

4.3.3 Effect of Calcination Temperature on Cofed Water/TBA Activation of P-Catalysts

XRD patterns were also taken for the silicon phosphate bulk crystalline material as well as P-fumed SiO$_2$ Si/P=3, from temperature of 300 °C to 600 °C in 100 °C increments as well as 900 °C, and after activation with water/TBA shown in Figure 4.5. In Figure 4.5 A, the XRD patterns show the silicon phosphate formation begins at 300 °C, with an impurity phase present at 300 °C and 400 °C. The characteristic peaks increase in intensity up to 500 °C with the impurity phase no longer present, and temperature up to 900 °C
does not show any additional change in the characteristic XRD peaks. When the silicon phosphate was activated with the water/TBA cofeed at 240 °C, there were no distinct changes in the XRD patterns, unlike the P-BEA Si/P=3 which shows collapse of the silicon phosphate crystal structure after water/TBA cofeed. However, P-fumed SiO\textsubscript{2} Si/P=3 in Figure 4.5 B shows similar results to P-BEA Si/P=3, with silicon phosphate formation as low as 300 °C, and shows significant damage to the silicon phosphate crystal structure after water/TBA cofeed activation at 240 °C. P-BEA Si/P=3 and P-fumed SiO\textsubscript{2} Si/P=3 may show the effect of water/TBA cofeed in the XRD because the silicon phosphate has formed on the surface of the silica supports, which could be more susceptible to the water/TBA cofeed treatment. Meanwhile, in the bulk silicon phosphate crystalline material, the surface of the silicon phosphate crystals may have been subject to the water/TBA treatment, but the interior of the crystal was unaffected, and therefore the long-range order seen in the XRD diffractogram was unchanged from the parent materials. Therefore, it is possible the water/TBA cofeed treatment is a surface-active treatment and does not penetrate within the crystal structure.
The effect of calcination temperature and water/TBA cofeed activation of P-BEA Si/P=3, P-fumed SiO\(_2\) Si/P=3, and silicon phosphate bulk crystalline material on their BAS density are shown in Figure 4.6. Materials in Figure 4.6 were not subject to the typical 600 °C calcination in air in the tube furnace after impregnation of phosphoric acid. Instead, the samples were heated in-situ in the RGC between 250 and 400 °C. Since the highest temperature that RGC setup can reach to is 400 °C, the samples were heated in the tube furnace at temperatures greater than 400 °C for comparison. After the given in-situ heating temperature, materials were treated with the water/TBA cofeed for activation, followed by typical BAS measurement. For P-BEA Si/P=3, in Figure 4.6 A, activation with water/TBA after in-situ heating temperatures between 250 °C to 400 °C led to a BAS density of approximately 900 μmol/g. However, 500 °C heating only resulted in approximately 500 μmol/g, nearly a 50% decrease, with 600 °C heating resulting in
approximately 400 μmol/g, and 900 °C leading to a significant reduction in BAS density, less than the standard non-activated P-BEA Si/P=3. This drop in BAS density after water/TBA treatment above 400 °C heating may coincide with the decrease in BEA structure observed in the XRD in Figure 3.3, therefore the loss of BAS density may be due to loss in BEA structure and damage to the silica support. A similar trend is observed in P-fumed SiO$_2$ Si/P=3 in Figure 4.6 B, with heating temperature from 250-500 °C leading to approximately 1200 μmol/g after water/TBA activation, with over 90% decrease with heating over 600 °C. Therefore, the damage to the silica structure at high temperatures as happens in BEA may also be occurring within the fumed SiO$_2$. In Figure 4.6 C, BAS density of the activated bulk silicon phosphate crystalline material is shown. Interestingly, the BAS density increases from 250 °C to 400 °C after activation, from approximately 375 μmol/g at 250 °C heating to over 900 μmol/g at 400 °C. As seen in the XRD in Figure 4.6 A, the silicon phosphate crystal structure is still forming up to 500 °C, and therefore the partially crystalline material with impurity may not be as susceptible to activation. However, like P-BEA Si/P=3 and P-fumed SiO$_2$ Si/P=3, the BAS density begins to decrease at high enough temperature, although the silicon phosphate shows the highest activated BAS density at 600 °C, but like P-BEA Si/P=3 and P-fumed SiO$_2$ Si/P=3, by 900 °C the BAS density is severely reduced, even with activation. At high temperatures of 900 °C, there may be additional structural changes or particle coalescence, reducing formation of BAS sites and susceptibility to activation with water/TBA.
Because of the high activity observed with P-BEA Si/P=3 with cofed water and TBA, P-BEA with higher Si/P ratio were also tested to improve activity with water/TBA cofeed shown in Figure 4.7. P-BEA Si/P=27 shows approximately 2-times increase with water/TBA activation, and P-BEA Si/P=10 shows approximately 3-times increase with water/TBA activation.

Figure 4.6 RGC results of P-BEA, P-fumed SiO₂, and silicon phosphate after activation. P-BEA Si/P=3 (A), P-fumed SiO₂ Si/P=3 (B), and Silicon phosphate (C) of samples which were previously uncalcined prior to RGC in-situ heating, from 250-400 °C. Heating higher than 400 °C were performed ex-situ. Each group of 2 reactions represents results obtained on the same bed of catalyst.
activation after calcination of the samples at both 400 °C and 600 °C. However, P-BEA Si/P=3 shows nearly 10-times increase at 400 °C calcination, but only a 5-times increase at 600 °C, which may be due to the decrease in BEA crystallinity observed in Figure 3.3 at higher temperature calcination at Si/P=3, but Si/P=27 and 10 retain BEA crystallinity at 600 °C, and likewise do not show difference in activated BAS density between 400 °C and 600 °C.

![Graph showing BAS density measurements](image)

**Figure 4.7 RGC result of P-BEA Si/P=27, 10 and 3 after activation.** P-BEA with water/TBA at 240 °C after 400 °C and 600 °C calcination of (A) P-BEA Si/P=27 (B) P-BEA Si/P=10 and (C) P-BEA Si/P=3. P-BEA Si/P=27 shows a 2x increase in BAS density, Si/P=10 shows a 3x increase in BAS density, and P-BEA Si/P=3 shows a 10x increase after 400 °C calcination, but only a 5x increase after 600 °C calcination

### 4.3.4 Synthesis of Silicon Phosphate with Improved Surface Area and Activation with Cofed Water/TBA

In attempts to improve the activity of the bulk crystalline silicon phosphate, BP-2000 was added to the synthesis trying to increase the surface area by creating mesoporosity in the crystalline materials. The XRD patterns, N₂ adsorption isotherms, and BAS density measurements of the synthesized crystalline silicon phosphate with and without water/TBA activation are shown in Figure 4.8. The XRD of the BP-2000 silicon phosphate in Figure 4.8 A shows the characteristic XRD peaks of the standard Si₅O(PO₄)₆
material, but in addition to significant extra peaks at 15° (possibly overlapping with existing peak from $\text{Si}_5\text{O(PO}_4\text{)}_6$), 23°, 24°, and 28° 2-θ. These peaks could correspond to silicon pyrophosphate $\text{SiP}_2\text{O}_7$ from literature\textsuperscript{121}. The N\textsubscript{2} adsorption isotherm in Figure 4.8 B show the standard silicon phosphate $\text{Si}_5\text{O(PO}_4\text{)}_6$ crystalline material has a low BET surface area, unable to be accurately measured below 1 m\textsuperscript{2}/g. However, the BP-2000 silicon phosphate shows an order-of-magnitude increase in surface area to 12 m\textsuperscript{2}/g, indicating the success of the addition of BP-2000 to increase the surface area. While this surface area is lower than the P-BEA materials and zeolites in general, it is a significant improvement over the standard bulk crystalline silicon phosphate. The BP-2000 silicon phosphate also shows an improved BAS density above the silicon phosphate material, shown in Figure 4.8 D and compared to the standard silicon phosphate in Figure 4.8 C. The BP-2000 silicon phosphate shows 3 to 5 times higher BAS density than the standard silicon phosphate without activation with water/TBA, depending on the heating temperature. With additional water/TBA activation, the BP-2000 silicon phosphate shows almost double BAS density with 600 °C heating, and over 10 times the BAS density with 900 °C heating. The BP-2000 silicon phosphate material shows the significantly greater BAS density after water/TBA cofeed activation after 900 °C heating than any other materials in this study after 900 °C heating. It is likely that the mesopores created by the BP-2000 carbon black and increased surface area are responsible for the increase in the
BAS density, both with and without water/TBA activation, but it is also possible the SiP$_2$O$_7$ material could be more susceptible to hydrolysis during the water/TBA treatment.

Figure 4.8 XRD, N$_2$ adsorption, and BAS density of BP-2000 silicon phosphate. XRD (A) and N$_2$ adsorption of the standard silicon phosphate Si$_5$O(PO$_4$)$_6$ and the BP-2000 silicon phosphate. BET surface areas are provided in the legend (B). BAS density measurements at 600 °C and 900 °C for the standard silicon phosphate (C) and BP-2000 silicon phosphate (D) both with and without water/TBA cofeed activation treatment at 240 °C.
4.3.5 Activation of P-Catalysts with Only Water Compared to Cofed Water/TBA

In addition to activation using water/TBA cofeed at 240 °C, it was found that water alone can improve the BAS density similarly to the water/TBA cofeed, albeit at a significantly lower temperature of 140 °C. The comparison between the water/TBA cofeed activation at 240 °C and the only water activation at 140 °C is shown in Figure 4.9A for P-BEA Si/P=3. Water at 240 °C does not increase the BAS density, possibly causing a slight decrease. The increase is apparent for the sample activated at 240 °C using water/TBA cofeed first. However, when only water is fed at 140 °C with a similar partial pressure of 180 torr and the same number of water injections, a large increase in BAS density is observed increasing the BAS density from approximately 70 μmol/g to 300 μmol/g, though the activation with water/TBA at 240 °C can achieve nearly 400 μmol/g of BAS. When the sample is first treated with water/TBA at 240 °C, and then subsequently treated with only water at 140 °C, the water can re-activate the P-BEA Si/P=3 to the BAS density observed with the water/TBA treatment at 240 °C. Water alone cannot activate the P-BEA Si/P=3 at temperatures higher than 140 °C, but cofed water/TBA can activate at 240 °C. It is possible that at elevated temperature of 240 °C, water opens the condensed phosphates, but they are near-instantaneously closed at 240 °C after switching the gas flow from water to N₂. In the case of activation with water/TBA, the association of the TBA with the opened acid sites at 240 °C may prevent the condensation of the created
BAS sites. The associated TBA can be reactively desorbed, which may be a higher temperature than 240 °C\textsuperscript{22}.

![Chart showing BAS density of P-BEA Si/P=3 after activation with water and water/TBA.](chart1.png)

**Figure 4.9** BAS density of P-BEA Si/P=3 after activation with water and water/TBA. Water activation at 140 °C leads to increase in BAS density, but not at 240 °C.

![Chart showing activation with water injections at varied temperatures.](chart2.png)

**Figure 4.10** Activation with water injections at varied temperatures. Water was injected 45 times at 140 °C, 170 °C, 200 °C, and 240 °C. At higher temperatures than 140 °C water activation does not show additional benefit, and at higher temperature may potentially show a decrease in BAS density.
The activation with water is only seen at low temperatures, such as 140 °C. Higher temperature in-situ water treatment at 170 °C, 200 °C, and 240 °C do not lead to an increase in BAS density, shown in Figure 4.10. It is possible the association of the TBA with opened P-OH sites prevent their closure, as shown later in Scheme 4.1.

4.3.6 Removal of TBA and IPA of Activated P-BEA Si/P=3 by Purging

To test how much adsorbed TBA remains on the surface after 240 °C activation with cofed water/TBA, the P-BEA Si/P=3 was activated with water/TBA at 240 °C, and then purged at 240 °C under helium for different time periods shown in Figure 4.11 B. This sample was not saturated with TBA at 150 °C after activation, and therefore the BAS measured is the TBA associated with the active sites during the activation. With 1 hour of purging time, the TBA associated with the opened BAS sites has dropped by 50%, and with 12 hour of purging time the BAS-associated TBA has decreased by 90%. The TBA is associating with the opened BAS sites and preventing their closure until the TBA has reactively desorbed.
Figure 4.11 P-BEA Si/P=3 BAS measurement after activation with IPA and TBA with purging. Water/IPA activation and purge (A) and water/TBA activation and purge, in which a 12-hour purge does not remove the IPA after water/IPA activation at 240 °C, but removed 90% of the adsorbed TBA after water/TBA activation at 240 °C.

Activation with 45 times of 5 μL injection of water/isopropylamine (IPA) at 240 °C was performed with the same mole ratio of water to IPA as in the water/TBA activations. After the activation with water/IPA at 240 °C, the sample was purged with helium at 240 °C for 12 hours. With regular BAS measurement using IPA instead of TBA, the observed BAS density is less than 50% of the observed value with TBA. The reduction of measured BAS density is consistent with previous literature using different amines to titrate BAS sites in P-materials, where it was found that the observed BAS density scales with the relative proton affinity of the amines. IPA has a secondary carbon center, while TBA has a tertiary carbon center, making TBA more basic with a higher proton affinity and therefore higher observed BAS densities on P-BEA Si/P=3. Unlike TBA, however, a 12 hour of purging with He flow at 240 °C does not remove the IPA, as seen with TBA in 4.11 A.
with 1 hour purge and 12 hour purge at 240 °C in Figure 4.11 B. BAS density after
Additional TBA saturation at 150 °C after the activation and purge time given on the x-
axis, shown as the additive BAS density of the grey and blue stacked bars is given in Figure
4.11 B. The grey bars represent the TBA associated with sites after activation and given
purge time, which decreases with increasing purge time, as TBA is removed during
purging. The stacked blue bars show the sites after additional 150 °C TBA saturation after
the activation and given purge time, which represents the fraction of unoccupied open
sites after activation and purging. As the purge time at 240 °C increases on P-BEA Si/P=3,
the unoccupied open sites, shown in blue, approach the original non-activated BAS
density, suggesting that removal of TBA from the activated sites may allow the sites
opened from the hydrolysis during activation to condense. When IPA is used in activation,
purging at 240 °C does not remove the IPA, and does not close the sites, shown in Figure
4.11 A. Because of the tertiary carbon center in TBA, the isobutene formation from TBA
has a lower energy than the propylene formation in IPA on the secondary carbon center,
and therefore a lower Hoffman elimination temperature, consistent with observations of
amines on aluminosilicates in literature\textsuperscript{122} and therefore the TBA is able to be purged off
at 240 °C while the IPA is not, and purging of sites activated with water/TBA results in
closing of the activated BAS sites while the purging of sites activated with water/IPA does
not. This may support the hypothesis that the association with the amines is preventing
the opened P BAS sites from closing at higher temperatures, and why water cannot increase BAS density above 140 °C, illustrated in Scheme 4.1

**Figure 4.12 BAS density of P-BEA Si/P=3 with variable heating temperature.** P-BEA Si/P=3, which has not been subject to 600 °C calcination initially, and subject to the given *in-situ* heating temperature for 1 hour. Only BAS density measurement with heating lower than 200 °C shows increased BAS density.
Scheme 4.1 Hydrolysis of P-structures with water and water/TBA. Hydrolysis of condensed P structures at 240 °C cofed with TBA and water, which is relatively stable compared to the hydrolysis with water at 140 °C, which closes the opened sites at 240 °C. The sites opened with water/TBA do not close until after the reactive desorption of TBA.

While the activation of P-BEA Si/P=3 with water or water/TBA produces high BAS density, it is important to note that the initial P-BEA Si/P=3 BAS density is dependent on the initial heating temperature of the material, although high BAS density is only observed with initial heating temperature of 100 °C shown in Figure 4.12. The BAS density with 100 °C is similar to the activated BAS density of P-BEA Si/P=3 with 600 °C calcination, but quickly drops off by 200 °C. It is possible the P-OH sites show significant condensation between 100 °C and 200 °C, supported by the additional peak seen in the TGA of humidity-treated P-BEA Si/P=3 in Figure 3.20. As seen previously, the activation of P-BEA Si/P=3 with water/TBA increases the BAS density at temperatures greater than 100 °C, but water
alone is unable to activate the P-BEA Si/P=3 to increase BAS density above 140 °C, which is consistent with these results where BAS density of P-BEA Si/P=3 not previously calcined shows high BAS density at 100 °C.

The increases in BAS density observed with the activation using water/TBA and water treatment of P-zeosil materials and silicon phosphate materials are important for future industrial applications of the catalysts for relevant renewable reactions. Future studies of the activation may help identify the active site structures and mechanisms for reaction which lead to a high selectivity. It is likely less oligomerized P structures provide the active sites, as fully condensed structures lack the P-OH BAS site, though it remains uncertain which hydrolyzed, or partially condensed P structures are active for a particular reaction. It is also possible that different P structures are active in different reaction systems, and therefore tailoring the P site distribution, such as with water/TBA and water activation, would be necessary to help these P-containing catalysts achieve their highest possible activity in a particular reaction.
4.4 Conclusion

It was found that P-BEA and other P-materials can be activated with cofeeding 180 torr of water and 10 torr of TBA, which can lead to a substantial increase in the BAS density. The activation using water/TBA led to a collapse of silicon phosphate crystal structure as well as a large decrease in the $Q_3$ and $Q_4$ structures of P species in the catalysts. It is likely that the hydrolysis of silicon phosphate and condensed polyphosphate structures resulted in a large increase in the available acid sites. The heating temperature of the P-materials prior to the water/TBA activation is important for how susceptible the P-material is to the activation. P-BEA Si/P=27 and 10 also showed an increase with the water/TBA activation, though the effect was less than the one on P-BEA Si/P=3, which is likely due to P-BEA Si/P=3 having more condensed phosphates and silicon phosphate phase. It was found that the P-BEA samples activated with water/TBA exhibited adsorbed TBA. The adsorbed TBA can be purged away from the surface, but the sites opened from the activation began to close during the desorption. Therefore, the activated BAS sites may remain open due to their association with TBA, which prevents condensation back to closed sites.
4.5 Appendix to Chapter 4

The appendix for Chapter 4 contains the inlet calculation to achieve approximately 180 torr water and 10 torr TBA used for the activation, and the trials to determine the adequate number of injections necessary to fully activate the materials. \( p \)-Xylene reaction results with the TBA/water activated P-BEA Si/P=3 are shown. Multiple sequential water/TBA activation and 400 °C heating were performed on P-BEA Si/P=3 to determine any lasting effect of activation which may remain after 400 °C heating. To understand the activation with only water versus water/TBA cofeed, the P-BEA Si/P=3 samples after activated at 140 °C with water was flushed with \( n \)-heptane, in an attempt to remove water, as it is possible residual water remains on the surface after water injections at 140 °C, which then during the TBA saturation activates the material. Sections of the chromatogram output of the RGC are also shown to identify potential reaction selectivity differences between initial materials and activated materials, which may indicate different types of acid sites.

Inlet partial pressure of water and TBA were approximated using Dalton’s Law, comparing the volumetric flow rates of the helium carrier gas with the volumetric flow rates of the injected water and TBA. Injection speed of liquid components used was 3 \( \mu \text{L/min} \) with 5 \( \mu \text{L} \) total, with inlet pressure set at 1.8 psig or 832 torr with 18 mL/min of flowing helium. A 4:1 mass ratio of water/TBA liquid sample was used. Calculations were
carried out to achieve 180 torr of water and 10 torr of TBA to mimic the partial pressures used for the activation under flow conditions:

\[ 3 \text{ uL/min} = 0.003 \text{ mL/min} \]

\[ 5 \text{ uL total injection} = 0.005 \text{ mL total} \]

\[ \text{Injection speed} = \frac{0.005 \text{ mL}}{0.003 \text{ mL/min}} = 1.66 \text{ min} \]

Density of solution with 4:1 mass ratio water:TBA = 0.93 g/mL.

\[ \text{Total mass injected: } 0.005 \text{ mL} \times 0.93 \text{ g/mL} = 0.00465 \text{ g} \]

\[ \text{Mass water injected: } 0.00465 \times 0.8 = 0.00372 \text{ g} \]

\[ R = 62320 \frac{\text{mL} \text{ torr}}{\text{mol K}} \]

\[ \text{mol water injected: } 0.00372 \text{ g} \times \frac{1 \text{ mol}}{18 \text{ g}} = 0.000206 \text{ mol water} \]

\[ T = 513 \text{ K (240 C)} \]

\[ \text{molar flow rate water: } \frac{0.000206 \text{ mol}}{1.66 \text{ min}} = 0.000124 \text{ mol/min} \]

\[ \text{Volumetric flow rate water using } \dot{V} = \frac{\text{NRT}}{p} = 4.76 \frac{\text{mL}}{\text{min}} \text{ water vapor} \]

\[ \text{Mass TBA injected: } 0.00465 \times 0.8 = 0.00372 \text{ g} \]

\[ \text{mol water injected: } 0.00372 \text{ g} \times \frac{1 \text{ mol}}{73.14 \text{ g}} = 1.27 \times 10^{-5} \text{ mol TBA} \]

\[ \text{molar flow rate TBA: } \frac{1.27 \times 10^{-5} \text{ mol}}{1.66 \text{ min}} = 7.63 \times 10^{-6} \text{ mol/min} \]

\[ \text{Volumetric flow rate TBA using } \dot{V} = \frac{\text{NRT}}{p} = 0.293 \frac{\text{mL}}{\text{min}} \text{ TBA vapor} \]

\[ \text{Dalton's Law: } \frac{p_i}{p_{\text{total}}} = \frac{\dot{V}_i}{\dot{V}_{\text{total}}} \]

\[ 172 \text{ torr} = p_{\text{water}} = 4.76 \frac{\text{mL}}{\text{min}} \text{ water vapor} \times \frac{832 \text{ torr}}{4.76 \frac{\text{mL}}{\text{min}} \text{H}_2\text{O} + 0.293 \frac{\text{mL}}{\text{min}} \text{TBA} + 18 \frac{\text{mL}}{\text{min}} \text{He}} \]

\[ 10 \text{ torr} = p_{\text{TBA}} = 0.293 \frac{\text{mL}}{\text{min}} \text{TBA vapor} \times \frac{832 \text{ torr}}{4.76 \frac{\text{mL}}{\text{min}} \text{H}_2\text{O} + 0.293 \frac{\text{mL}}{\text{min}} \text{TBA} + 18 \frac{\text{mL}}{\text{min}} \text{He}} \]
Figure 4.13 Activation of P-BEA Si/P=3 using water followed by a \( n \)-heptane flush. P-BEA Si/P=3 activated with 45 injections with water then subject to 15 injections of \( n \)-heptane to remove any residual water. After the \( n \)-heptane flush following water activation, the BAS density was only 50% greater than the initial value of the parent P-BEA Si/P=3. It is possible that the \( n \)-heptane is flushing out residual water, which with saturation of TBA mimics the water/TBA activation. It is also possible that the extended time at 140 °C closes hydrolyzed sites, which are closed quickly at elevated temperatures as seen above in Figure 4.10.

Figure 4.14 Images from the chromatogram using \( t \)-butylamine before and after activation. Typical measurement of P-BEA and other P-materials (A) and from the activated P-BEA and other P-materials with water/TBA and water (B). The activation shows additional peaks, though typically less than 3% of the total peak area. The expected product from the Hoffman elimination of \( t \)-butylamine is isobutene, but the other 3 peaks could be other isomers of butylene: 1-butylene, cis-2-butylene, and trans-2-butylene. Other isomer products may be evidence of different kind of acid sites after activation.
P-BEA Si/P=3 was used in the \( p \)-xylene reaction after activation with water/TBA at 240 °C and 1 hour purging with He. However, the activated catalyst was less active and selective than the parent catalyst as shown in Figure 4.15. P-BEA Si/P=3 with additional 400 °C treatment after the activation was also tested, as it was found that residual TBA may still be present after the 240 °C activation which may have interfered with the \( p \)-xylene reaction shown in Figure 4.11 B. The catalyst after 400 °C treatment still shows a lower activity and selectivity. The lower activity and selectivity might be because the activation with TBA/water resulted in a different type of active site which is less active in the \( p \)-xylene reaction.

Figure 4.15 \( p \)-Xylene reaction results with activated P-BEA Si/P=3 compared to P-BEA Si/P=27 and 3. Initial reaction rate (A) and selectivity (B). Initial reaction rate shows the activated P-BEA Si/P=3 has a slower initial rate compared to the parent P-BEA Si/P=3 sample. The residual TBA may have interfered with the reaction. \( p \)-Xylene selectivity vs DMF conversion shows the activated P-BEA Si/P=3 is not as selective as the parent P-BEA Si/P=3.
Figure 4.16 Multiple water/TBA activation and 400 °C heating cycles on the same bed of P-BEA Si/P=3. After the first two 45-injections then 400 °C heating, the BAS density of the P-BEA Si/P=3 increases by 20% after the water/TBA activation and 400 °C heating, leading to an increase of approximately 50% above the initial BAS density, but subsequent activations and 400 °C heating cycles do not further increase the BAS density above 50% of the initial value. The activated BAS density also increases after each subsequent water/TBA activation, increasing by 20% of the initial activated BAS density value.
Scheme 4.2 Diagram of synthesis of silicon phosphate with comparison to the synthesis with BP-2000. The addition of BP-2000 results in a 10x increase in silicon phosphate surface area.
CHAPTER 5

CONCLUSIONS

In Chapter 2, it was observed that liquid phosphoric acid and silica supports can associate in the reaction medium, leading to increased selectivity and reaction rate above that of just the liquid phosphoric acid in the $p$-xylene reaction. This is reflected in the stability of the phosphoric acid on both silica support added \textit{in-situ} and P-zeosils prepared with impregnation and calcination prior to the reaction. The higher the amount of silica support relative to the liquid phosphoric acid, the higher selectivity and reaction rate are observed. The type of silica support likely influences both the phosphoric acid distribution between the liquid reaction medium and the adsorption onto the silica support, and the activity of the adsorbed phosphoric acid on the silica support. P-zeosils such as P-BEA lead to exceptional selectivity in $p$-xylene production from DMF and ethylene. It is the association and dispersion of phosphoric acid within the silica zeolite support which greatly improves both $p$-xylene selectivity and initial DMF conversion rate. Other supports also provide beneficial activity to phosphoric acid such as metal oxide supports (except ZrO$_2$) and carbon supports, which show higher selectivity than liquid phosphoric acid. However, silica supports show superior reaction rate. Despite Al-BEA showing increased activity in 1,4-dioxane, \textit{n}-heptane solvent showed highest activity with P-BEA. In attempts to create a bifunctional catalyst containing both Lewis and Brønsted acid sites, Cu catalysts CuCl$_2$ and Cu-impregnated and ion-exchanged BEA showed high activity and
selectivity in 1,4-dioxane, but not n-heptane. Because of the low activity of seen with P-BEA in dioxane, the impregnation of phosphoric acid on Cu-catalysts did not improve the reaction rate.

Chapter 3 provides a closer investigation into how the synthesis parameters including Si/P ratio and calcination temperature of the P-BEA affected the P species distribution and zeolite structural stability. Lower Si/P ratio led to more oligomerized P structures. There is good agreement between the initial reaction rate of P-BEA with varying Si/P ratio and the measured BAS density using t-butylamine as a probe molecule. The stability of zeolite supports during phosphoric acid impregnation and calcination is also important to the activity of the P-zeosils in the reactions. High-temperature calcination with low Si/P ratio leads to damages to the BEA structure and formation of highly condensed silicon phosphate structures like Si$_3$O(PO$_4$)$_6$, reducing available surface area and condensing the P-OH functional groups into P-O-P or P-O-Si bonds. Surface chemistry of the silica supports, such as defect Si-OH density of different types of silica, may also affect both the p-xylene reaction rate and observed BAS density, as well as the stability of the silica structure during phosphoric acid impregnation.

In Chapter 4, oligomeric and condensed P structures are susceptible to hydrolysis under certain conditions, which can greatly improve the observed BAS density, and further supports the hypothesis that the active sites are more likely P species with a lower degree of oligomerization. Cofeeding with 180 torr of water with 10 torr of TBA led to
greatly increased BAS density at 240 °C, while water alone was only able to increase the BAS density at a temperature of 140 °C. It is possible the water/TBA cofeed is able to increase the BAS density at 100 °C greater temperature than water alone because the association of TBA with the hydrolyzed P-OH sites, which do not condense until the TBA has reactively desorbed. This is seen by purging the sample at 240 °C, which slowly reactively desorbs the TBA, closing the sites as TBA reactively desorbs. Cofeeding IPA/water can also activate the material, and the activated open sites stay open during purging at 240 °C, because IPA has a higher reactive desorption temperature.
CHAPTER 6
FUTURE DIRECTIONS

In Chapter 2, the phosphoric acid-impregnated zeolites have been shown to be highly selective in $p$-xylene production, and it has been found that P species with lower oligomerization are likely the active sites, but activity of each type of P species remains unknown in the $p$-xylene reaction. Despite the large increase in BAS density observed with water/TBA activation, it was not found to increase the rate in $p$-xylene reaction. However, if the type of P species on P-BEA before and after activation can be confidently identified, it may narrow down the type of P sites which are most active in $p$-xylene reaction. However, the $p$-xylene’s reaction temperature of 250 °C may restrict certain kind of P sites, as elevated temperatures may condense $Q_0$ or $Q_1$ sites, changing the P-site distribution. An alternative liquid phase reaction, cyclohexanol dehydration to cyclohexene,$^{123,124}$ may prove more useful in determining if activated P-materials could provide benefits in liquid-phase reactions, as the reaction temperature is significantly lower and could be operated at a low enough temperature to prevent significant P-species oligomerization, but P-species could be intentionally oligomerized with higher temperature calcination prior to reaction to test the difference. The cyclohexanol reaction temperature is also low enough to test the effect of activation of the P-materials with water, as the elevated temperatures in the $p$-xylene reaction may condense the active sites generated with water activation. Furthermore, the addition of Lewis acids into the
P-materials remains an attractive proposal to increase the reaction rate, despite the low activity of Cu-materials in \( n \)-heptane or P-materials in 1,4-dioxane.

In Chapter 3, changing synthesis conditions such as Si/P ratio and calcination temperature led to identification of different P species on P-BEA, with correlations made to the activity of the P-BEA, as decreasing Si/P ratio led to less activity per P. While this led to the understanding that less coordinated P were more active, the activity of each type of P acid site remains elusive. *In-situ* spectroscopic techniques may be necessary, with temperature and atmospheric controls, to accurately identify the types of P sites present. *In-situ* NMR has been used in literature to observe the structural changes in acid sites during the association of probe molecules, as well as structural changes in the probe molecules.$^{125}$ *In-situ* reaction within FTIR also provides an interesting tool to study reaction intermediates on the acid sites, unveiling possible steps within the catalytic mechanism and hints about the nature of the active sites.$^{126}$ *In-situ* XANES may also be worth investigating when atmosphere and humidity controls are possible to view changes in the P structure during *in-situ* heating or reaction. When combined with activity of probe molecule reactions and confident identification of P sites under reaction conditions, the active site can be isolated and more closely understood.

Chapter 4 shows promising techniques to improve the BAS density using water and TBA at elevated temperatures, the availability of opened active sites was limited by the association with the TBA probe molecule, and attempts to remove the TBA led to the
closure of the activated sites. Alternative amines could be used in place of TBA which could be removed at lower temperatures without closing the sites. As secondary amines such as IPA had a higher reactive desorption temperature, a tertiary alkylamine with bulkier and more electron-donating side groups, such as longer carbon chains off the tertiary carbon may decrease the reactive desorption temperature. However, bulkier alkylamines may not fit within the confined zeolite pores, and therefore mesoporous supports could be considered, allowing access to bulkier tertiary alkylamines while also increasing available surface area for P dispersion. Alternatively, it is proposed that gaseous ammonia may be able to activate the P-materials in conjunction with water, which would likely have a low desorption temperature. If ammonia is able to hydrolyze the P materials and increase BAS density, using ammonium phosphate as a P source in synthesis may prevent P oligomerization. Calcination temperature should also be optimized, as 600 °C is likely too high as structural damage occurs to the BEA support. Calcination time and temperature would need to be optimized when using ammonium phosphate in synthesis such that temperature is elevated enough to remove the ammonia, but not condense the remaining P species. This could lead to P-materials with isolated P species leading to higher BAS density than observed on the P-BEA materials.
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