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Conversion of Ethylene to Aromatics Using Fixed-Bed Reactor

Bachelor Research Project Rijksuniversiteit Groningen

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Abstract

Light aromatic compounds such as benzene, toluene, xylenes are valuable products which can be produced from upcycling processes of plastic waste. Light olefins, especially ethylene, tends to be the side product from these upcycling processes. Ethylene, which can also be derived from other non-conventional resources like biomass, natural gas etc., can be subjected to aromatization using zeolite catalyst (ZSM5) in order to increase the overall yield of aromatics from these upcycling processes. Moreover, using a suitable promoter along with HZSM-5 catalyst, higher selectivity of para-xylene can be obtained which in turn would prove to be beneficial in terms of the economics of the process since para-xylene is one of the most sought-after aromatic compounds. In this study, phosphorus is studied as the promoter on HZSM-5 as it has the potential to be an effective catalyst considering its behaviour in aromatization of methanol, which has a similar reaction mechanism as that for ethylene. The result from this work showed that the use of small amounts of phosphorus in the catalyst does improve the selectivity and overall yield of para-xylene as compared to unmodified ZSM-5. Different amounts of phosphorus catalyst were tested to find the most optimum ratio to obtain better selectivity of p-xylene. These catalysts were characterized using NH_3 -Temperature programmed desorption, X-ray diffraction, and N_2 -physiosorption techniques.

1. Introduction

Plastic waste is one of the main sources for pollution in the environment due to its slow rate of degradation. Its accumulation has been an issue to the environment because the production rate is higher than its recycling rate. There have been some short-time solutions such as: burning and landfills, however all these methods are damaging the environment in the long run. As the awareness of detrimental effects of plastics products grew, alternatives have been proposed to recycling of plastic waste. Recently, chemical recycling or upcycling plastic waste has been identified as one of the potential solutions to utilize the plastic waste to produce light aromatics such as benzene, toluene and xylenes (BTX). The chemical upcycling of plastic waste is usually done via pyrolysis or catalytic dehydrogenation to produce BTX, which can be used for manufacturing range of polymers and specialty chemicals[1]. This method can be one of the solutions to achieve a circular carbon economy.

These upcycling processes of plastic waste produce long chain alkanes and aromatics along with short chain olefins ($\text{C}_2 - \text{C}_4$) as side products[2]. According to previous studies, light olefins, especially ethylene, can react in the presence of a catalyst to yield BTX range of hydrocarbons. Alternatively, ethylene can also be produced from catalytic fast pyrolysis of biomass, natural gas and hydrocarbon extraction of shale gas[3]. Therefore, these olefins hold a significant potential to be used as starting materials for producing aromatics. Among the BTX range of aromatics, para-xylene (PX) has the highest commercial value and its selective production is much more economically favorable[4]. Thus, the main focus of this research is to identify ways to improve the PX selectivity from ethylene.

ZSM-5, a type of zeolite, is a solid acid catalyst which has been effective in aromatization of ethylene. Owing to its microporous nature and tunable acidity, this catalyst was chosen for this study. The majority of strength of acid sites cannot be too strong as it will lead to cracking and also not too weak because it will produce olefins[5].

Addition of promoters in the catalyst enhances its performance by either improving the selectivity or catalyst lifetime. Different promoters such as gallium (Ga), zinc (Zn), and silver (Ag) have been studied to increase the BTX selectivity from ethylene owing to their dehydrogenation capability[3][5][6]. This study proposes the use of phosphorus as a promoter in the catalyst due to its ability to restrict pore size and

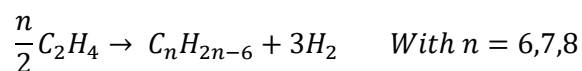
regulate the acidity of zeolite[7]. This effect has been observed in case of methanol aromatization and toluene alkylation where the selectivity of para-alkyl groups was enhanced as compared to ortho- or meta-alkyl groups [8]. Due to its similarities in reaction mechanism with methanol aromatization, it is hypothesized that phosphorus will have the same effect when ethylene is being used as starting material. This research will investigate the effects of impregnating phosphorus to the catalyst which has never been done before for the aromatization of ethylene.

From all the background and research done, the main research question for this thesis is “What is the effect of phosphorus as promoter towards the selectivity of PX from ethylene?”. The sub-question of this research would be to determine optimum amount of Phosphorus in the catalyst.

2. Theory

2.1. Reaction

Ethylene aromatization reaction is endothermic in nature with number of steps such as oligomerization, cracking, hydrogen transfer/dehydrogenation, cyclization, and isomerization. This reaction usually takes place at high temperature (500°C) under atmospheric pressure and in the presence of a zeolite-based catalyst.



The reaction mechanism to form aromatics from ethylene is initiated with Bronsted acid on the catalyst which combines with ethylene molecules to form ethyl cationic species. These species then further combine with ethylene molecules to form oligomers with carbons number between C₆-C₁₀. After oligomerization, depending on the catalyst's properties, it can proceed in different directions as mentioned in **Figure 1**. These oligomers then undergo cyclization to form cyclo-olefins which can then proceed via hydrogen removal to form aromatic hydrocarbons. Depending on the use of promoter, the removal of hydrogen can take place via hydride transfer route or dehydrogenation route. Hydrogen transfer is prominent when there is excess of Bronsted acid sites as compared to Lewis acid sites and these route can be identified from the formation of 3 moles of alkanes for every mole of aromatic formed. Dehydrogenation is facilitated by active metal phase which acts as Lewis acids and this route is characterized by formation of hydrogen along with the aromatics [3][9].

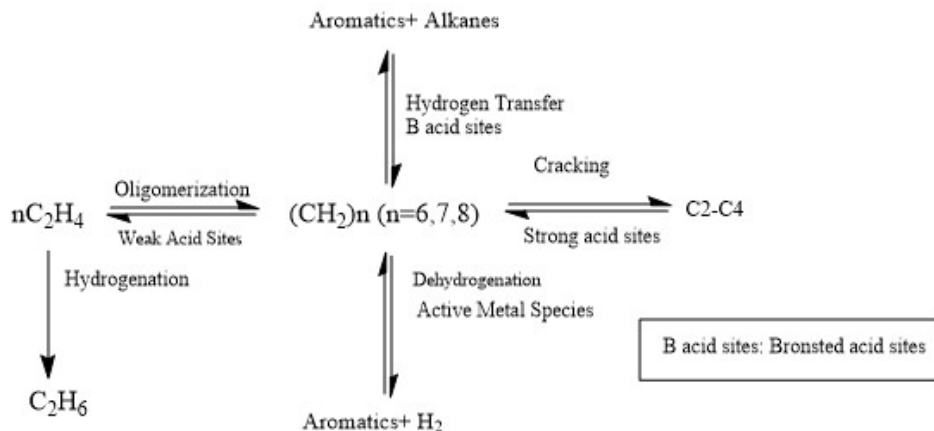


Figure 1 Reaction Routes for Ethylene to Aromatics

Along with the catalyst's properties, there are other factors which affect the selectivity of para-xylene. One of them is the space velocity. The space velocity used in the reactor affects the conversion and aromatic selectivity of the product. When ethylene is converted, the primary aromatics produced are xylenes (p-xylene and o-xylene). Based on other research, the faster space velocity will increase the selectivity of producing para-xylene because then no further side reaction such dealkylation and disproportionation can occur[10].

2.2. Catalyst

Zeolites are crystalline aluminosilicate materials that are microporous in nature. Their characteristics include uniform pore structure, tunable acidity and high surface area. ZSM-5 is one of the most commonly used zeolites in the industry as an adsorbent and as catalyst or catalytic support. Due to its shape selectivity, microporosity and moderate acid strength it is considered to be a suitable catalyst for aromatization of ethylene. Depending on the Si/Al ratio, the properties of ZSM-5 change significantly more so with respect to its acidity. A commercial ZSM-5 comprises of different types of acidity based on its strength and nature (Bronsted and Lewis acid sites). The addition of a promoter influences the acidic nature as well as other physicochemical properties such as micropore area, external surface area, pore size etc. which may improve the catalyst performance[1][3]. In case of ethylene aromatization, a number of promoters have been tested including Ga, Zn, Ag, Ni, Mo etc. These metal promoters too affected the acid sites distribution, their strength, external and micropore surface area etc. and have been found to be effective. This study however focusses on the effect of a non-metal promoter, phosphorus, on ethylene aromatization and its contribution to improve p-xylene selectivity.

2.3 Catalyst synthesis techniques

There are different methods of incorporating promoters to the zeolite catalyst including physical mixing, ion exchange, incipient wetness impregnation, and wet impregnation. Physical mixing is the simplest method for preparing a catalyst where the oxide of the promoter and zeolites are mixed together using mortar pestle [11]. The ion exchange method allows for introducing the promoter in an aqueous form

to the catalyst. Then the ionic species from aqueous solution are attracted electrostatically to the surface of the catalyst [11].

The method of catalyst preparation was done incipient wetness impregnation for 0.5wt%P-1.5wt%P and wet impregnation for 3wt%P and 5wt%P. These methods were chosen because of its simplicity as it can be done at atmospheric pressure and room temperature [12]. During incipient wetness impregnation, the precursor solution is added just in sufficient quantity to fill the pores of zeolite. Whereas for wet impregnation, a solution of the promoter was used. Overall synthesis procedure consists of three main steps including mixing of zeolite and precursor (usually a salt or an acid) for promoter, drying of sample and calcination. Drying was carried out in the oven for 12 hrs and it is usually done to crystallize the salts on the pores and produce impregnated particles. Calcination then removes other volatile components from the catalyst sample [12].

2.4 Catalyst Characterization Methods

Characterizations of catalysts are needed to determine their nature and properties which can then be tailored to suit the needs of a reaction. In this study, catalysts were subjected to surface area analysis, X-ray diffraction (XRD), and Ammonia-temperature programmed desorption (NH₃-TPD). The N₂-physisorption measurements gives information about the total surface area, pore volume, pore diameter, external surface area and micropore area. The micropore volume is very useful to know the adsorptive capacity of the catalyst and the frequency of regeneration of the catalyst from the absorption and desorption cycles [13]. The areas were calculated using the instrument software.

The formula of BET equation was used to calculate surface area of the samples. The BET formula was with X= weight of nitrogen adsorbed at specific relative pressure, $\frac{P}{P_0}$ specific relative pressure, n = quantity of adsorbate adsorbed, X_m= monolayer capacity (volume of gas adsorbed at STP), and C= BET value [14].

$$\frac{1}{X[(P_0-P)-1]} = \frac{1}{X_m \times C} + \frac{C-1}{X_m \times C} \left(\frac{P}{P_0}\right) \quad (1)$$

A plot with a linear line with positive slope can be formed using the BET equation. Then the slope and y-intersection can be known using linear regression. The slope=i and the y-intercept = s. After knowing both slope and y-intercept, the monolayer capacity (X_m) can be calculated using equation 4.

$$\text{Slope}(i) = \frac{C-1}{X_m \times C} \quad (2)$$

$$Y - \text{intercept}(s) = \frac{1}{X_m \times C} \quad (3)$$

$$X_m = \frac{1}{s+i} \quad (4)$$

After X_m was calculated, the BET Surface area can be calculated using equation 5.

$$S_{BET} = \frac{X_m \cdot L_{av} \cdot A_m}{Mv} \quad (5)$$

The micropore volume was calculated with t-plot method by comparing to the reference adsorption isotherm of a nonporous material surface at corresponding relative pressure[6].The t-plot will have positive intercept due to the micropores. Then the intercept of the plot will be the micropore volume, when it is being converted to the liquid volume [7].

The NH₃-TPD was used to calculate the estimation of the number of acids on the zeolite and the strength of the acids. In this characterization method, ammonia is absorbed and desorbed by the acid sites in the catalyst. Then the temperature will increase steadily and how high the temperature of the desorbed ammonia will tell the strength of the acid sites in the catalyst [8]. From this characterization, a graph between TPD signal and temperature can be made. The temperature range for low temperature acid peaks is below 200°C, intermediate acid between 200°C-300°C, and strong acid peaks at higher than 300°C.The number of acids were estimated using the area underneath the graph. The number of acids is the same as the number of moles of ammonia desorbed[5].

The XRD is used to see the crystal structure of the catalyst itself [9]. This method measures the intensities and scatter angle of X-rays from the material after it had been irradiated with incident X-rays. The final result from XRD will be graphs with peaks at different scattered angles of X-rays. From this, it can be identified the different types of components that are present in the sample. The formula that was used to calculate the results of XRD was based on Bragg's law as in equation 6. d is the spacing between diffracting planes, θ is the incident angle, n is an integer, and λ is the beam wavelength.

$$2d \sin(\theta) = n \times \lambda \quad (6)$$

2.5 Product Analysis

The liquid and gaseous products obtained from the reaction were analyzed using Gas Chromatography with flame ionization detector (FID) and thermal conductivity detector (TCD). In the gas chromatography, the components in gas were separated using a capillary column coated with stationary phase. Then the components were propelled with an inert gas where each component has different retention time depending on its polarity and boiling point [10]. GC-FID or gas chromatography with flame ionization detector can be used to detect different types of analytes in gas streams. These analytes will give different retention times and areas which will identify what compounds are present and the quantity of it in the sample. Calibration was done for the GC data of each component among BTX aromatics. The mass and composition of each component in the liquid and gas phase was calculated using the calibration and the total product collected after every interval. Lastly, mass balance on both phases (gas and liquid) was used to find the overall selectivity of each component in this reaction when using different catalysts.

3. Experimental section/Methodology

3.1. Materials of Reaction

ZSM-5 zeolite (Si/Al=11.5) was purchased from Zeolyst International and was calcined at 550°C for 4 hrs before using it for further modification. Phosphoric acid (H₃PO₄, M.W = 97.994 g/mol) as 85% solution was purchased from EMD Millipore Corporation and ethylene gas (C₂H₄, M.W =28.05g/mol) with 99.5% purity was supplied by Linde Corporation.

3.2. Catalyst synthesis

The catalyst was prepared by using the wet impregnation method and 2 grams of HZSM-5 was used in each sample. The concentrated (85%) H_3PO_4 solution was made into a 0.2 M solution with demi water according to the different percentages of metals desired. The zeolite was placed into a round bottom flask and corresponding amount of H_3PO_4 solution was added dropwise into it. After all the solution had been added into the catalyst, the mixture became slurry and it was mixed for 2 hours at room temperature. The slurry-like sample was put in the oven overnight for drying at 110°C . After drying, the sample was calcined in a furnace at 550°C with a ramp rate of 3°C to remove other volatile components. The samples with different phosphorus content (by wt.) were prepared i.e., 0.5%, 1%, 1.5%, 3% & 5% phosphorus.

Table 1 Synthesis protocol for Phosphorus modified ZSM-5 with different composition

Phosphorus (% by wt.)	Mass of H_3PO_4 (g)	Mass of HZSM-5 (g)	Water (mL)	Molarity
0.5	0.0372	2	1.6	0.2
1	75	2	3.26	0.2
1.5	0.113	2	4.9	0.2
3	0.23	2	10	0.2
5	0.392	2	17	0.2

3.3. Characterization of the Catalyst

The textural properties of the catalysts were determined using N_2 adsorption-desorption isotherm measured at -195.8°C on a Micromeritics TriStar II I instrument. Before the analysis, the sample was degassed at 300°C for 8 h. The micropore area and volume were calculated using the t-model. The total surface area was calculated by adding external surface area and micropore area. The average pore size was calculated using the BJH model desorption.

The acidity of the catalyst was measured with NH_3 -TPD (ammonia temperature-programmed desorption) using MicromeriticsAutoChem II 2920 chemisorption instrument equipped with a thermal conductivity detector (TCD). Prior to the analysis, the catalyst was pre-treated with helium and heated up to 550°C with a ramping rate of $10^\circ\text{C}/\text{min}$. Upon cooling to 120°C , the gas flow was switched from helium to ammonia. Ammonia was dosed to the sample for 1 h before the test began. For this characterization, the temperature was raised from 120°C to 900°C with a heating rate of $10^\circ\text{C}/\text{min}$ and the moles of ammonia desorbed were recorded as a function of temperature.

For XRD (X-ray powder diffraction) was recorded with Bruker D8 Advance. The scan type used was Coupled $2\theta/\theta$ and the scan mode is continuous PSD fast with variable rotation is $20^\circ/\text{min}$.

3.4. Ethylene to Liquid Aromatics Reaction

The reactor used was a fixed bed reactor with length of 4cm and diameter of 1cm. The catalyst was inserted at the bottom of the reactor and gas flow was directed from bottom to top. 200 mg of catalyst sample was crushed and sieved in mesh with sizes between 212-500 micrometer and was loaded into the reactor. The feed consisted of a mixture of nitrogen and ethylene (1:1) and fed into the reactor with space velocity of 3600 ml/g/hr. The reactor was operated at 500°C, with ramp rate of 5 °C/min and under atmospheric pressure. The outlet of the reactor was connected to a heater line at 250°C to keep all products in the vapor phase. The reactor outlet was cooled down using a chiller till -15°C to condense the aromatic liquid. The condensed liquid was then collected through a vessel controlled with on/off valve. For the gas product, a trapper was setup to collect any liquid that might have entrained along the gas stream. The product gas was sent to the mass flow meter to calculate the output volumetric flow rate and further direct towards GC analyzer. The condensed liquid products and the gas products are collected separately every one hour until 6 hours for all the catalyst samples. The P&ID of the reactor can be seen in the appendix.

4. Results & Discussions

4.1. N₂-Physisorption

For this characterization method, the BET Surface area, external area, micropore area and volume were observed. The overview results for BET Surface Area can be seen in the table below. Based on the result, it can be seen that the catalysts with 0.5%P, 1% P, and 1.5%P have smaller pore sizes, micropore area, external area, and BET area than unmodified catalyst (H-ZSM-5). The decrease in pore size and volume could be attributed to deposition of phosphorus in the pores. This is as expected that phosphorus will have an effect on blocking the pore opening which would enhance the selectivity of producing para-xylene.

For catalysts with 3wt%P and 5wt%P, it can be observed that the pore diameters increase. This suggests that the addition of phosphorus destructed the pores by breaking the bonds in zeolite structure. The drastic decrease in external area in **Figure 2** also suggests that most of P are attached on the external surface and not in the zeolite pores.

Table 2 Textural properties of the tested catalysts

Catalyst	D(nm)	Surface Area (m ² /g)			V (cm ³ /g)
		Total	External	Micro	
HZSM-5 (23)	6.38	360.81	117.57	243.24	0.105
0.5% P-ZSM-5(23)	4.76	327.66	91.94	235.72	0.114
1%P-ZSM-5(23)	4.89	311.37	78.41	232.96	0.113
1.5%P-ZSM-5(23)	4.80	313.40	85.58	227.81	0.110
3%P-ZSM-5(23)	9.18	214.67	19.48	195.18	0.095

5%P-ZSM-5(23)	11.23	195.66	11.36	184.30	0.089
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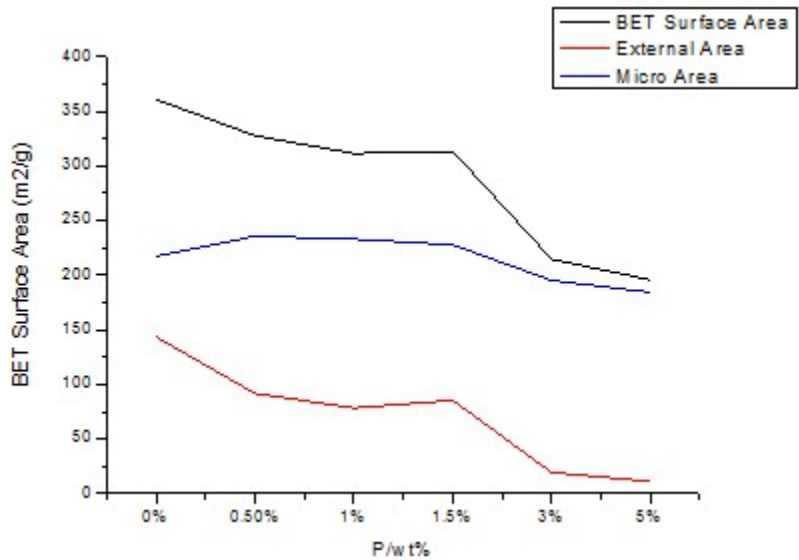


Figure 2 BET Surface Area, External Area, and Micro Area for All Catalysts Samples

4.2 Ammonia- Temperature Programmed Desorption

The graph below shows the distribution and relative concentration of acid sites on different catalysts. It can be seen that the unmodified catalyst has a higher concentration of acid sites, both weak and strong, with peaks observed at 190°C, 380°C, and around 750°C which represent weak, medium, and strong acid sites. However, with addition of phosphorus, the number of acid sites appeared to have decreased with increase in loading of phosphorus on the catalyst. For catalysts with 3% and 5% phosphorus, the peaks around 400 °C are nearly absent while a significant drop in the intensities of the peak at 200 & 750 °C was also observed. This indicates that phosphorus addition drastically reduced the number of acid sites with moderate strength acid sites being nearly absent.

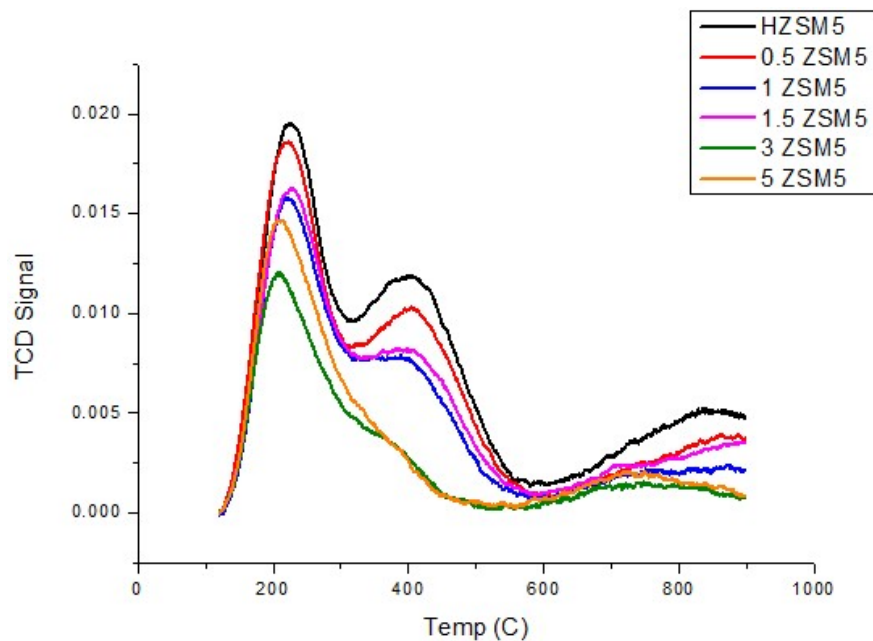


Figure 3 NH₃-TPD results for different catalysts

4.3 XRD

The XRD was taken for three different samples. The catalysts tested are unmodified catalyst, catalyst with 0.5%P, and 3wt%P. From **Figure 4**, it can be observed that the samples have similar peaks corresponding to the peaks of the unmodified catalyst. The peaks which correspond to P₂O₅ were supposed to be between 17°-18° [11] but no peaks were observed even after increasing the phosphorus content. This indicates that P is highly dispersed over the catalyst's surface. The degree of crystallinity is bound to get reduced but could not be exactly determined in this case. However, from the XRD patterns it can be seen that the crystallinity of 3%P ZSM-5 was still retained to a greater extent. The possible loss in crystallinity can occur mainly due to defects caused by dealumination resulting from prolonged exposure to acid solution of the precursor, in this case H₃PO₄.

Based on the reaction results for 3% and 5% P catalysts, it was assumed that during the addition of H₃PO₄ to zeolite, a possible damage to the structure of ZSM-5 would have resulted in the poor performance of those catalysts however from the XRD patterns of 3%P, it is clear that the poor performance may be attributed to excess loss in acid sites in the modified catalyst.

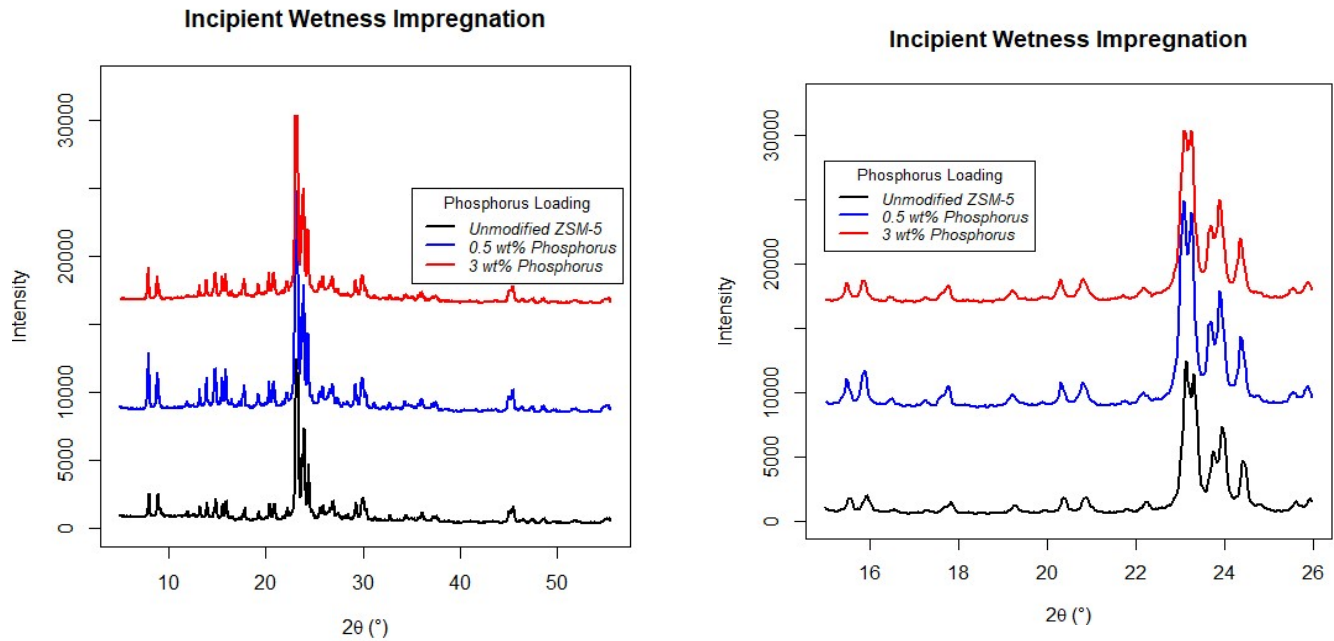
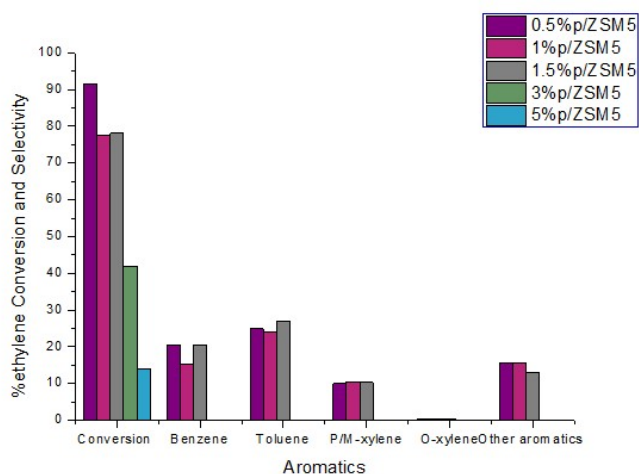


Figure 4 X-ray diffraction patterns for HZSM-5(23), 0.5% PZSM-5 & 3% PZSM-5

4.4 Overall Selectivity

Table 3 Product spectrum & overall selectivity for all the P-modified catalysts after 2 hrs

Compound	(% Overall selectivity)					
	HZSM-5(2 hr)	0.5%P (2hr)	1%P (2hr)	1.5%P (2hr)	3%P (2hr)	5%P (2hr)
CH ₄	13.44	7.10	5.65	6.22	1.25	1.41
C ₂ H ₆	7.35	4.06	4.75	3.69	5.71	7.48
C ₃ H ₆	15.22	9.43	16.28	10.98	86.12	89.06
C ₃ H ₈ & C ₄ ⁺	7.72 (12.21)	8.49 (0)	7.81 (0)	8.42 (0)	6.93 (0)	2.05 (0)
Benzene	12.84	20.33	15.22	20.39	0.00	0.00
Toluene	16.53	24.87	23.85	26.98	0.00	0.00
p/m-xylene	6.43	9.98	10.49	10.23	0.00	0.00
o-xylene	0.12	0.19	0.34	0.16	0.00	0.00
Other aromatics	8.14	15.53	15.62	12.92	0.00	0.00
Overall Yield for p/m-xylene	5.64	9.14	8.13	7.99	0.00	0.00

**Figure 5 Ethylene Conversion & Selectivity of Aromatics for All Catalyst Samples at 2nd Hour of Reaction**

From **Table 3** and **Figure 5**, the overall selectivity and conversion for all products from all catalyst samples after 2h of the reaction can be found. From **Table 3** and **Figure 5**, it can be seen that the highest selectivity for para-xylene is when the catalyst has 1%P as the promoter but the highest overall yield was given from the catalyst with 0.5%P. It can also be observed that catalysts with 3 wt.%P and 5wt.%P do not produce any liquid aromatic products. The conversion was also observed to decrease as more amount of phosphorus was added to the catalyst.

The conversion of ethylene in the presence of H-ZSM5, 0.5% P-ZSM-5, 1%P/ZSM5, and 1.5%P/ZSM5 catalyst can be seen from **Figure 6**. Unmodified catalyst had the highest ethylene conversion compared to modified catalyst. This was expected as number of acid sites decrease and higher amount of

phosphorus means more dealumination. The trend for conversion was found to be decreasing with time. The decrease in conversion was expected because of the coke formation on the catalyst which might have blocked the pores on the catalyst and hindered the access to active sites for reaction. The coke formation also induced more formation of higher aromatics. This means that the formation of aromatics (> C8) would increase with time. Thus, the selectivity towards para-xylene should increase as shown in **Figure 8**. Then the overall selectivity of aromatics with 0.5%P catalyst can be seen in **Figure 7**. In this graph, it was mainly focused on BTX. From the graph, it can be seen that Benzene and Toluene had high selectivity compared to other aromatics for almost all of the 6h after the reaction. For para-xylene, it can be observed that the overall selectivity decreased from 1h until 5h but it increased at 6h after the reaction started.

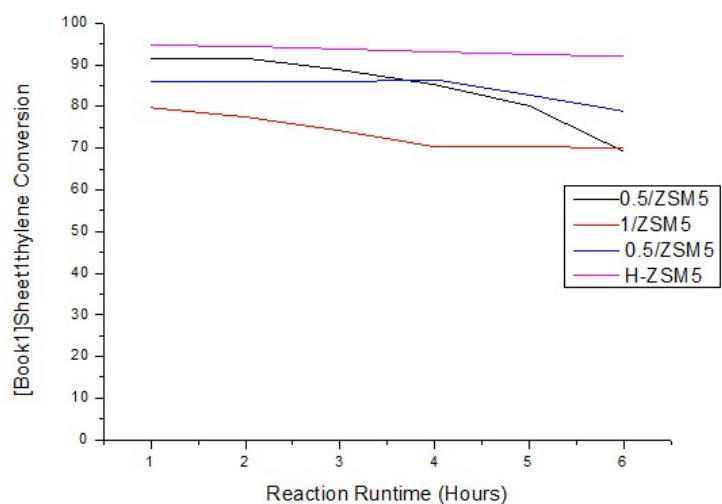


Figure 6 Activity of all catalyst for 6 hrs

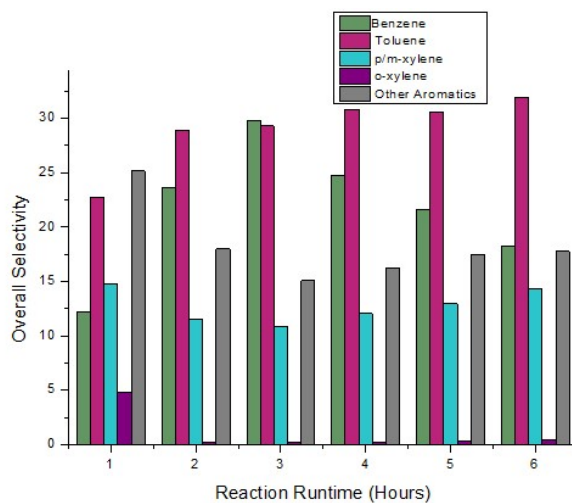


Figure 7 Variation in aromatic selectivity FOR 0.5%P-ZSM-5 until 6 hrs

The selectivity of para-xylene compared to other aromatics for catalyst with 0.5%P for 6h can be seen in **Figure 8** *Variation in aromatic selectivity FOR 0.5%P-ZSM-5 until 6 hrs*. The highest selectivity towards para-xylene was 14.78% and this was observed 1h after the reaction had started. Then the selectivity was observed to decrease until 3h after reaction before it started to increase until 6h after the reaction. The overall selectivity of all catalysts was done at the second hour after the reaction had started because the reaction is allowed to get stabilized until the end of first hour. Out of all the catalysts, the catalyst with highest overall yield (9.14%) for para-xylene was obtained with the catalyst with 0.5 wt.% P. This was predicted because small amount of phosphorus ($\leq 1wt\%$) in catalyst is known to restrict the pores of the catalyst which would enhance the selectivity of para-xylene. This is also supported from the BET results as the micropore area and pore diameters were found to have decreased.

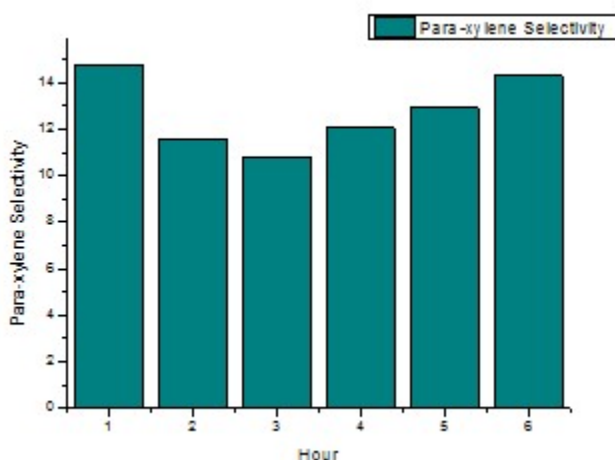


Figure 8 p-Xylene selectivity as a function of time for 0.5% PZSM-5

5. Conclusion & Future Perspective

The small percentage (0.5 % by wt.) addition of phosphorus could enhance the selectivity of producing liquid aromatics due to its ability to narrow the pore sizes. From the results, it could be seen that addition of phosphorus could decrease the external surface area, micropore volume, strength, and number of acid sites significantly. It can also be concluded that the zeolite structure did not collapse even after addition of 3% and 5% by wt. of P as assumed from its XRD results. This means that addition of P did not destruct the zeolite structure completely but there are some indications that showed that the structure is not fully intact. This can be concluded from the increase in diameter pores, much less acid sites, and lack of aromatic products. High amount of phosphorus lowered the amount of liquid product and was detrimental to the reaction performance.

The future research may involve further characterization methods, especially to determine the concentration of Bronsted and Lewis acid sites. This may help give more insights on why the 3 % & 5 % by wt. of P did not produce liquid products. Another possibility to improve catalyst activity and selectivity of p-xylene is to add silica coating on the catalyst which can facilitate passivating excess surface acid sites and reducing the coking tendency. It is also possible to prepare the catalyst with other methods and observe if there is any difference in the quality of the catalyst, especially with 3% & 5% by wt. of P.

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Appendix

