



**university of  
 groningen**

**faculty of science  
 and engineering**

**University of Groningen**

**Phosphorus addition to ZSM-5 zeolite in the methanol to hydrocarbons (MTH)  
 process using a fixed-bed reactor**

**Bachelor's Thesis**

To fulfill the requirements for the degree of  
 Bachelor of Science in Chemical Engineering  
 at University of Groningen under the supervision of  
 Dr. ir. Jingxiu Xie (Engineering and Technology Institute Groningen, University of Groningen)  
 and  
 Prof. dr. Jun Yue (Associate Professor, Faculty of Science and Engineering, University of  
 Groningen)

**Loek Pieké  
 S3221725**

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## Abstract

Phosphorus modified ZSM-5 (Si/Al = 23) catalyst samples were synthesized using the incipient wetness impregnation method and the acid reflux method. Structural and characteristic effects of phosphorus modification were analyzed by x-ray diffraction, nitrogen physisorption and ammonia temperature programmed desorption. The performances of the catalyst samples in the methanol to hydrocarbons process were studied by analyzing gas and liquid products using gas chromatography. Coke formation on the spent catalyst was analyzed using thermogravimetric analysis. The obtained results indicated that phosphorus addition increases catalytic performance by increasing olefin and *para*-xylene selectivity and decreasing the production of aromatic byproducts. It was also found that phosphorus addition significantly increases the catalyst durability by decreasing coke formation. By comparing the two treatment methods, it was found that even though it is more expensive and time consuming, the acid reflux method is more reliable than the incipient impregnation method.

# 1 Introduction

The production of olefins, aromatics and liquid hydrocarbon fuels used to be mainly dependent on the extraction of crude oil [1]. In the end of the 20<sup>th</sup> century, a new method for the production of olefins, aromatics and liquid hydrocarbon fuels was discovered. The new method converts methanol to hydrocarbons in the C<sub>1</sub>-C<sub>12</sub> range with the help of a zeolite catalyst. This production method is called the methanol-to-hydrocarbons (MTH) method. The MTH method can be divided into three specific processes, which yield specific ranges of hydrocarbons. The first process is methanol-to-olefins (MTO), which selectively yields light olefins. The second process is methanol-to-aromatics (MTA), which selectively yields aromatics. The last process is methanol-to-gasoline (MTG), which selectively yields liquid hydrocarbon fuels. The MTH method was first patented by scientists at ExxonMobil in 1977 [2]. For this process, a specific zeolite catalyst called Zeolite Socony Mobil-five (ZSM-5) was patented. The chemical formula of ZSM-5 is Na<sub>n</sub>Al<sub>n</sub>Si<sub>96-n</sub>O<sub>192</sub>·16H<sub>2</sub>O, with 0 < n < 27 [3].

The structure of the catalyst is made out of 5-membered rings that are interconnected. This configuration forms larger 10-membered rings, which form channels inside the catalyst and pores on the outer surface. Molecules can diffuse in and out of the catalyst through these channels. A visualization of this structure can be seen in figure 1. The channels that can be seen here run in one direction through the catalyst, but there are also channels that run perpendicular to these through the catalyst. The network of these channels create a large surface area, which increases the reaction rate. The pores and channels have a diameter that is close to the molecular diameter of the reaction products, *e.g.* benzene. Therefore, the range of products that is produced is limited by the molecular diameter. This means that ZSM-5 is a shape-selective catalyst [4]. An example of this selectivity is the product dimethylbenzene, or xylene. There are three isomers of xylene: *ortho*, *meta* and *para*. Most of the xylene that is produced with the MTH method is *para*-xylene, because it has the smallest molecular diameter. *Para*-xylene is used a lot in the chemical industry as a feedstock for producing synthetic fibers. Therefore, catalytic selectivity for *para*-xylene is desirable [5].

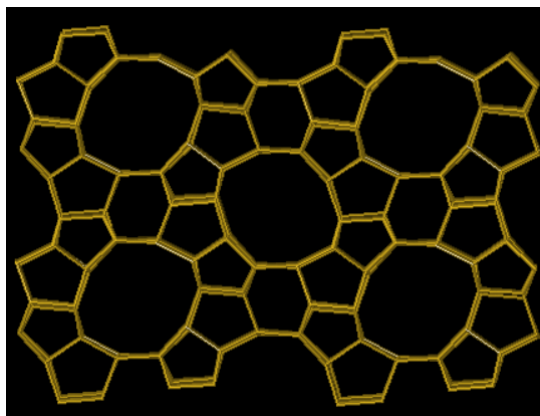


Figure 1: ZSM-5 catalyst structure. Image from [3]

The chemical reaction that converts methanol to paraffins, olefins and aromatics, is quite complicated. The mechanism is still not completely discovered, although most of it can be explained. Dahl and Kolboe proposed a hydrocarbon-pool mechanism, in which methanol is dehydrated over the acid sites in the catalyst and converted to unsaturated hydrocarbons (olefins) such as ethylene, propylene and butene. These olefins can react with methanol again to form even higher olefins. These olefins would then rearrange to form aromatics or saturated hydrocarbons (paraffins). A depiction of the reaction equation as

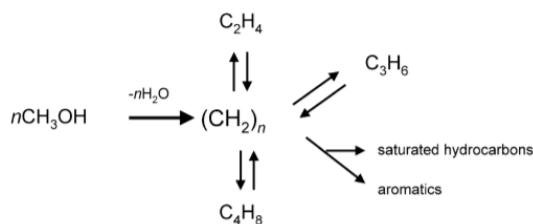


Figure 2: Hydrocarbon-pool mechanism proposed by Dahl and Kolboe. Image from [6]

proposed by Dahl and Kolboe is shown in figure 2. However, later research pointed out that there was more going on than just methylation of olefins. A new theory proposed that there are two mechanistic cycles running simultaneously. The first mechanistic cycle is the methylation of lower olefins (e.g. propene) to higher olefins, which then rearrange to form aromatics or lower olefins/paraffins. The second mechanistic cycle is the methylation of lower methylbenzenes to higher methylbenzenes, which then rearrange to lower methylbenzenes by releasing ethylene and propylene. This theory is known as the autocatalytic dual-cycle concept and is a more refined version of the hydrocarbon-pool mechanism proposed by Dahl and Kolboe [6]. A depiction of the autocatalytic dual-cycle is shown in figure 3.

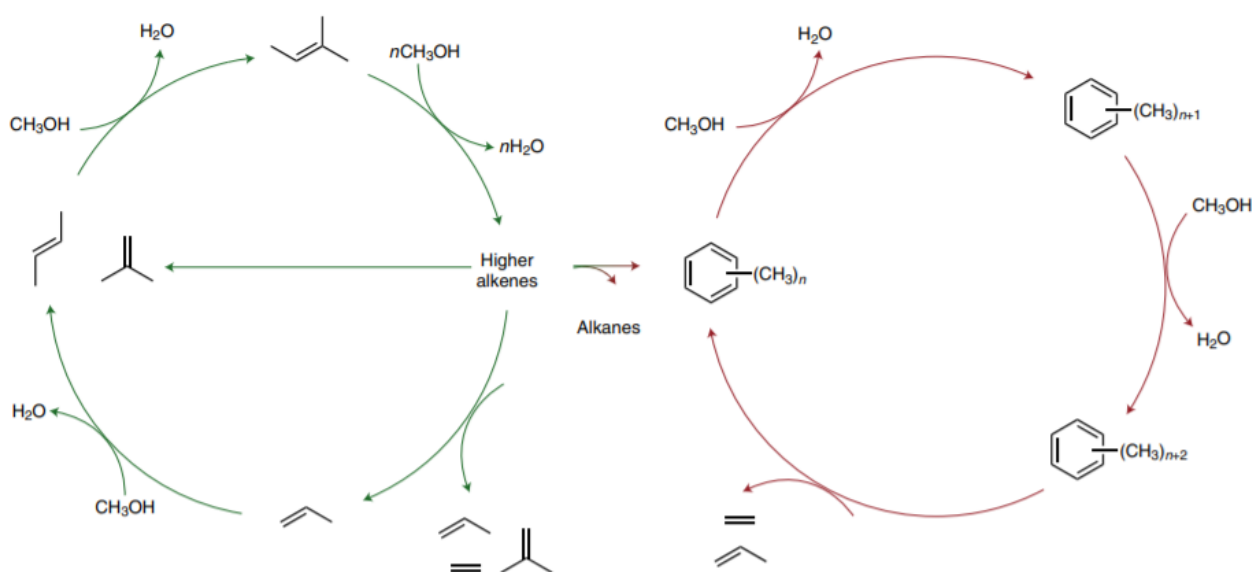


Figure 3: Autocatalytic dual-cycle mechanism. Image from [2]

Selectivity in reaction products can be influenced by the size of the catalyst pores as stated before, but also by modifying the acidity of the catalyst. The density and strength of the Brønsted acid sites on the surface of the catalyst determine whether higher olefins form aromatics via hydrogen transfer reaction with paraffins as byproduct, or via dehydrogenation reaction with hydrogen as byproduct [7]. It has been found that the catalyst can be treated with phosphorus to weaken the Brønsted acid sites and narrowing the pores. This resulted in a higher shape selectivity for *para*-xylene in the toluene alkylation reaction [8].

The treatment of the catalyst with phosphorus is usually performed using a phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) solution [9]. There are two methods for performing the phosphorus treatment: the incipient wetness impregnation method and the acid reflux method. Incipient wetness impregnation (IWI) is a fast, but precise method of catalyst preparation [10]. The H<sub>3</sub>PO<sub>4</sub> solution enters the pores due to capillary forces. The amount of solution that can be added is dependent on the pore volume of the catalyst. If too much of the solution is added, the transport process of the solution into the pores is no longer determined by capillary forces, but by diffusion. Since diffusion is a very slow process, it is less favourable than capillary action. Therefore, the solution must be added slowly and in the right amount. The maximum phosphorus loading using this method is determined by the solubility of H<sub>3</sub>PO<sub>4</sub> in water [11]. The acid reflux method (AR) is a slower and more costly method [12]. The transport process of the H<sub>3</sub>PO<sub>4</sub> solution into the pores is determined by diffusion. An excess amount

of solution is added to the catalyst and then refluxed for several hours. This treatment method can be very harsh on the catalyst and can decrease its efficiency by partially breaking down the structure. Because of the disadvantages, this method is not often used in the industry.

Phosphorus treatment might also be helpful to fight the biggest problem in the MTH process: coking. Coking is the buildup of carbonaceous residues on the internal and external surface area of the catalyst [13]. These residues block the Brønsted acid sites, which will in time deactivate the catalyst entirely. The exact chemicals that cause the formation of this coking layer vary widely, but are mostly larger aromatics (*e.g.* naphthalene). It has been discovered that the addition of phosphorus in the catalyst can decrease the deposition of carbon and thus increase the durability of the catalyst [14].

## 1.1 Goal

The goal of this research is to find out what the influence of phosphorus addition to ZSM-5 (Si/Al = 23) is on the methanol to hydrocarbons process using a fixed-bed reactor. The catalyst will be treated with phosphorus using both the incipient wetness impregnation method and the acid reflux method with a phosphorus loading of 1, 2, 4 and 8wt%. After phosphorus treatment, the catalyst will be characterized using x-ray diffraction (XRD), nitrogen physisorption (BET) and ammonia temperature programmed desorption (TPD). The catalyst samples that will be tested in the reactor are 1, 2 and 8wt% from the incipient wetness impregnation method and 2 and 4wt% from the acid reflux method. The reaction products, both liquid and gas, will be characterized using gas chromatography (GC). The spent catalyst will be characterized using thermogravimetric analysis (TGA).

## 2 Experimental

### 2.1 Catalyst preparation

#### 2.1.1 Incipient wetness impregnation

To a 50 mL round bottom flask, around 600 mg of ZSM-5 (Si/Al = 23) was added. A phosphoric acid solution with the desired phosphorus concentration was made in a 10 mL graduated cylinder using 85% phosphoric acid and distilled water. Then, around 0.2 mL of phosphoric acid solution was added drop wise to the round bottom flask. If the droplets stayed on top of the catalyst, the flask was shaken until the droplets were absorbed by the catalyst. After all of the solution was added, the catalyst was poured from the round bottom flask into a test vial and then covered with perforated aluminum foil. The vial was placed in an oven overnight at 120°C to dry the catalyst. The catalyst was calcined in an oven at 550°C for 8 hours. The catalyst was then pressed and sieved to obtain a particle size of 300-500 $\mu$ m. To achieve different phosphorus loading, 4 different phosphoric acid solutions were used. The amount of components used to achieve a certain phosphorus loading is specified in table 1.

Table 1: Contents of phosphoric acid solutions for incipient wetness impregnation samples

Phosphorus loading	Phosphoric acid (mL)	Water (mL)	Zeolite (g)	Solution (mL)
1 wt%	0.133	1.946	0.602	0.2079
2 wt%	0.265	1.793	0.589	0.2058
4 wt%	0.530	1.486	0.579	0.2016
8 wt%	1.060	0.872	0.556	0.1932

#### 2.1.2 Acid reflux

A 100 mL three necked flask was equipped with a reflux condenser and a stopper. A CAT hot-plate/stirrer was placed under the three necked flask. A stirring egg was added to the flask, along with around 600 mg of ZSM-5 (Si/Al = 23). A phosphoric acid solution with the desired phosphorus concentration was made in a 100 mL beaker using 85% phosphoric acid and distilled water. Then, 25 mL of phosphoric acid solution was added to the three necked flask and the flask was closed with a second stopper. The mixture was heated to 165°C and left to reflux for 2 hours. The mixture was then filtered over a Büchner funnel and the catalyst was washed with water. After the catalyst was dry, it was scraped off the filter paper into a test vial and then covered with perforated aluminum foil. The vial was placed in an oven overnight at 120°C to dry the catalyst. The catalyst was calcined in an oven at 550°C for 8 hours. The catalyst was then pressed and sieved to obtain a particle size of 300-500 $\mu$ m. To achieve different phosphorus loading, 4 different phosphoric acid solutions were used. The amount of components used to achieve a certain phosphorus loading is specified in table 2.

Table 2: Contents of phosphoric acid solutions for acid reflux samples

Phosphorus loading	Phosphoric acid (mL)	Water (mL)	Zeolite (g)	Solution (mL)
1 wt%	1.6	23.4	0.599	25
2 wt%	3.2	21.8	0.589	25
4 wt%	6.6	18.4	0.576	25
8 wt%	13.7	11.3	0.559	25

## 2.2 Catalyst characterization

The crystallinity of the catalyst samples was acquired using x-ray diffraction. For every catalyst, a 200 mg sample of the unpressed powder catalyst was analyzed from an angle of  $5^\circ$  to  $55^\circ$ . The data was plotted using R. The surface area and pore volume was determined by nitrogen physisorption for the following catalyst samples: unmodified ZSM-5, 1% IWI, 4% IWI, 8% IWI, 2% AR and 4% AR. The samples were in powder form and in the same quantity as was used for x-ray diffraction. The data was processed in excel. The amount and strength of the acid sites were determined by ammonia temperature desorption for the unmodified ZSM-5 and 2% IWI sample. A 100 mg sample of the unpressed powder catalyst was analyzed from  $120^\circ\text{C}$  to  $900^\circ\text{C}$ . The data was plotted using R.

## 2.3 Catalyst testing

The setup that was used to test the catalyst samples is not an ordinary setup. It can be described by the piping & instrumentation diagram shown in figure 4.

Nitrogen runs through a flow controller to a methanol saturator. The methanol is kept in a water bath at  $40^\circ\text{C}$  to stimulate methanol flow. Nitrogen then feeds the methanol through an  $80^\circ\text{C}$  heated line to the reactor. A bypass line was installed around the methanol saturator to be able to heat up the catalyst bed under nitrogen. Premature methanol flow would cause coke formation before the reaction temperature is reached. The bypass line is also useful to flush the system when necessary. A pressure indicator was installed before the reactor to prevent any danger caused by overpressure. The reactor is a glass U tube, with a fixed filter to keep the catalyst in place, in an oven. The catalyst side of the tube is placed at the gas entrance, to create a fixed-bed reactor. After the reactor, the nitrogen carries the products through a check valve (to insure there is no backflow) to a condenser. The condenser is cooled by a water/glycol mixture, which is cooled to  $-10^\circ\text{C}$  and circulated. Paraffin and olefin products will remain gaseous and flow out through a valve, which is equipped with a syringe adapter to take out samples. The aromatic products and water byproduct will condensate and are kept in a liquid container at the bottom, which is equipped with a valve to take out samples. A hazard and operability study (HAZOP) of this reaction setup can be found in appendix A.

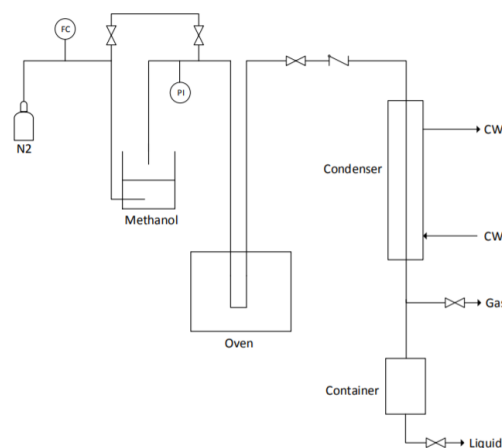


Figure 4: Piping &amp; instrumentation diagram



The setup was used the same way for all catalyst samples. The system is first set to bypass mode, so no methanol can be fed through the reactor before the system is ready. Nitrogen flow was kept constant at 40 ml/min. The cooler for the water/glycol mixture was turned on and set to  $-10^{\circ}\text{C}$ . The line heating was turned on and set to  $80^{\circ}\text{C}$ . The methanol level in the saturator was checked and the water bath was set to  $40^{\circ}\text{C}$ . To the reactor tube, 200 mg of catalyst with a particle size of 300-500 $\mu\text{m}$  was added. The reactor tube was placed in the oven and added to the system. A leak check was performed by closing the outlet valve and then quickly stopping the nitrogen flow. A small pressure of around 70 mbar was build up in the system and over a minute, it was checked that the pressure did not drop. The liquid container was flushed with nitrogen to remove all leftover liquid. Then, the oven was turned on and slowly heated up to  $450^{\circ}\text{C}$ . Once the temperature had stabilized, the system is switched from bypass mode to the methanol saturator. The pressure in the system was kept below 100 mbar if necessary, but never became higher then 20-35 mbar. The reaction was run for a duration of 6 hours, whilst a gas and liquid sample were taken every 2 hours. After the reaction, all equipment was turned off, the system was switched to bypass mode and the nitrogen flow was lowered to 10 ml/min.

## 2.4 Product analysis

After each reaction, there are 3 liquid product samples, 3 gaseous product samples and the spent catalyst. The liquid and gaseous samples was analyzed using gas chromatography, whilst the spent catalyst was analyzed using thermogravimetric analysis.

### 2.4.1 Gas chromatography

The gaseous samples were taken in a 50 mL syringe, equipped with a valve. The gaseous samples were analyzed the same day that they were taken from the system, since the gaseous products will decompose. Before analyzing the samples of one run, a reference measurement was taken from a gas tank with known concentrations of components. Around 25 mL of the gaseous sample was fed to a gas chromatograph using a syringe adapter. The chromatography was run for 13.5 minutes following a preset program. The peaks were integrated properly and the data was processed in excel.

The liquid samples were taken in a 4 mL sampling vial. Using a 1 mL syringe, 0.3 mL of dichloromethane was added to the sampling vial and the lid was screwed on tightly. The sampling vial was shaken until the liquid was mixed well. The sampling vial was left for 1 minute to let the liquid layers separate. The bottom organic layer was taken from the sampling vial using a syringe and transferred to a GC vial, which is equipped with an insert. The GC vial was then labeled and placed in a gas chromatograph, which used a preset program to analyze the samples. The peaks were integrated properly and the data was processed in excel.

### 2.4.2 Thermogravimetric analysis

After each reaction, the spent catalyst was transferred from the reaction tube to a 4 mL sampling vial. From the sampling vial, around 15 mg of catalyst was weighed off and poured into another 4 mL sampling vial. The 15 mg sample was then used for thermogravimetric analysis between  $25^{\circ}\text{C}$  and  $700^{\circ}\text{C}$  ( $10^{\circ}\text{C}/\text{min}$ ), under air atmosphere (50 mL/min). The data was plotted using R.

### 3 Results and discussion

#### 3.1 Catalyst characterization

##### 3.1.1 X-ray diffraction

X-ray diffraction patterns show if the crystallinity of the catalyst samples has been altered by the phosphorus treatment. By comparing the pattern of every sample with the pattern of the unmodified ZSM-5, the influence of phosphorus treatment becomes very clear. The x-ray diffraction patterns of the treated and untreated catalyst samples are shown in figure 5.

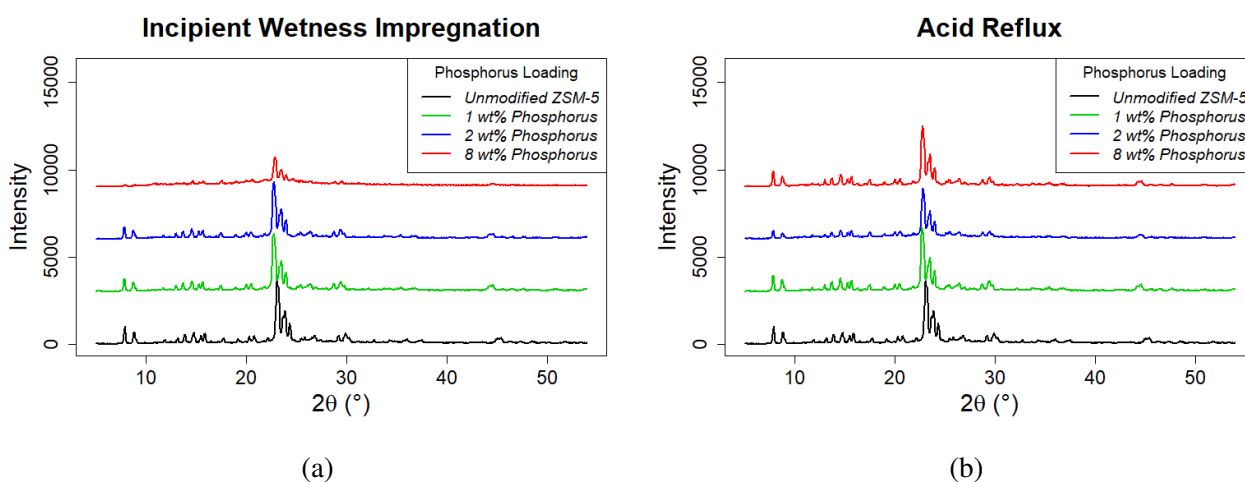


Figure 5: XRD results of unmodified ZSM-5 catalyst compared to phosphorus modified catalyst via the incipient wetness impregnation method (a) and the acid reflux method (b)

It can be seen from figure 5a that the intensity and position of the peaks for the 1% IWI and 2% IWI samples are almost the same as for the unmodified ZSM-5 sample. This means that the structure of these catalyst samples was barely affected by the phosphorus treatment. However, the 8% IWI sample shows a large decrease in peak intensity compared to the rest. This indicates that the structure of this catalyst is severely damaged by the phosphorus treatment. It can be seen from figure 5b that the intensity and position of the peaks for every sample is the same. This means that the structure of these catalyst samples was also not affected by the phosphorus treatment. This is not what was expected, since the acid reflux method is a very harsh method of catalyst treatment. It was expected that the incipient wetness impregnation samples showed no decreased crystallinity, whereas the acid reflux samples would show a larger crystallinity decrease as the phosphorus loading increases. A possible explanation for the decreased crystallinity in the 8% IWI sample is that the phosphoric acid solution was too concentrated, which would break the catalyst structure down. However, since the 8% AR sample was synthesized with a phosphoric acid solution with the same concentration, it is unknown what caused this damaged structure. The fact that the crystallinity of the acid reflux samples was not affected by the phosphorus treatment, means that even though it is a more costly and time consuming method, it is more reliable than incipient wetness impregnation. From this data, it can be expected that the 8% IWI sample will not be an efficient catalyst, since the MFI structure that is very characteristic for ZSM-5 catalysts is badly damaged. Nitrogen physisorption will indicate whether the surface area and pore volume have been affected as well.

### 3.1.2 Nitrogen physisorption

From the nitrogen physisorption results, the surface area and pore volume can be determined. The surface area can be determined using two different theories: the Brunauer–Emmett–Teller (BET) theory and the Langmuir theory. The BET theory states that the adsorption of nitrogen on the catalyst surface can create several layers of nitrogen molecules in some places. The Langmuir theory states that the adsorbed nitrogen molecules only form one single layer. This means that with a certain amount of adsorbed nitrogen, the Langmuir surface area is much larger than the BET surface area. In reality, the BET theory is more accurate because the adsorbed nitrogen never forms a perfect monolayer. Therefore, the BET surface area was taken as the accurate surface area. The effect of phosphorus treatment on the surface area and the pore volume of the catalyst samples is shown in figure 6a and 6b respectively.

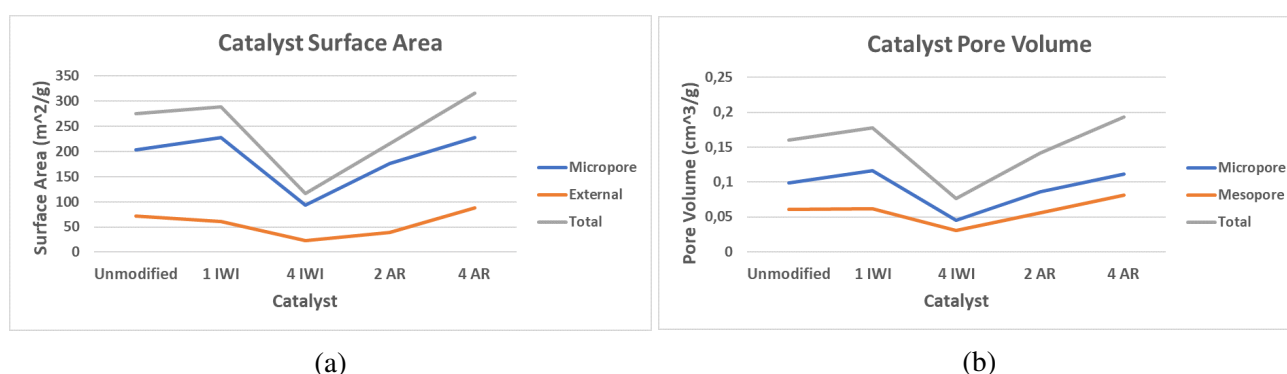


Figure 6: BET catalyst surface area (a) and catalyst pore volume (b)

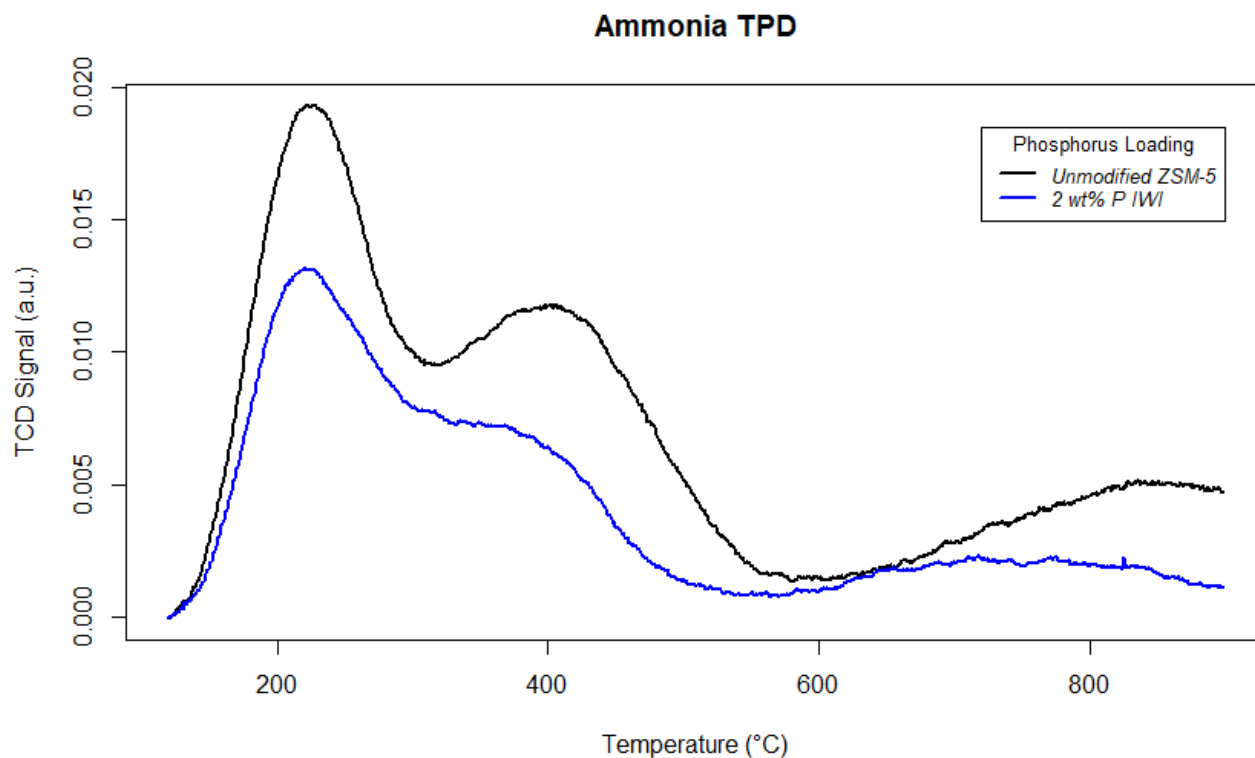
It can be seen that the 1% IWI and 4% AR samples show an increase in surface area and pore volume, whereas the 4% IWI and 2% AR samples show a decrease in surface area and pore volume. However, it should be mentioned that the resolution of the measurement is  $\pm 20\%$ , which means that the actual difference is likely smaller than it shows in the graph. The increase of the surface area and pore volume are most likely caused by the phosphoric acid, which breaks the structure of the catalyst down by a small amount. This creates more space in the catalyst pores and a larger surface area. This could cause the shape selectivity to decrease, but it would mean a longer lifetime of the catalyst. This is because more coke would need to build up to deactivate the catalyst. A smaller surface area and pore volume could be caused by pore blockage, where the phosphoric acid did not enter the catalyst pores properly. It is also possible that the phosphoric acid did enter the catalyst pores, but that it did not break down the structure. The phosphorus would then narrow the pores and this decreases the surface area and the volume. If the pores are very small, the production of aromatics would decrease drastically, because the molecules are too large to diffuse out of the catalyst. From the graphs shown above, it can be expected that the 1% IWI and 4% AR samples show an increased production of aromatics and a longer life time. It can also be expected that the 4% IWI and 2% AR show a decreased production of aromatics and a shorter lifetime. Since the 4% IWI was never tested, the expectation can not be confirmed for this sample. From the XRD results, it became clear that the structure of the 8% IWI sample was badly damaged. This also became very clear from the results of nitrogen physisorption, since there was no pore volume indicated. This strengthens the expectation that the 8% IWI sample will not be an efficient catalyst. The nitrogen physisorption data is shown in table 3, where surface area is given as m<sup>2</sup>/g and pore volume is given as cm<sup>3</sup>/g.

Table 3: Nitrogen physisorption data

Catalyst	$S_{ext}$	$S_{micro}$	$S_{total}$	$V_{micro}$	$V_{meso}$	$V_{total}$
Unmodified ZSM-5	71.4	203.5	274.9	0.0991	0.0606	0.1597
1 wt% IWI	61.1	227.4	288.5	0.1162	0.0617	0.1779
4 wt% IWI	23.1	93.3	116.4	0.0456	0.0303	0.0759
8 wt% IWI	4.6	-	3.9	-0.0004	-	-
2 wt% AR	39.1	176.4	215.5	0.0865	0.0559	0.1424
4 wt% AR	88.3	228.2	316.5	0.1115	0.0813	0.1928

### 3.1.3 Ammonia temperature programmed desorption

Ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) shows the amount and the strength of the acid sites in the catalyst. Every catalyst has Lewis acid sites and Brønsted acid sites. NH<sub>3</sub>-TPD cannot distinguish the distribution between these two acid sites, but it can distinguish weak and strong acid sites. The catalyst first adsorbs ammonia, after which the temperature is increased. At higher temperatures, the ammonia desorbs from the catalyst, which results in a TCD signal. Weak acid sites release ammonia at relatively low temperatures (200°C), whereas stronger acid sites hold on to the ammonia. The stronger acid sites release ammonia at around 400°C. The area under the graph represents the amount of acid sites. The results of the NH<sub>3</sub>-TPD measurement are shown in figure 7.

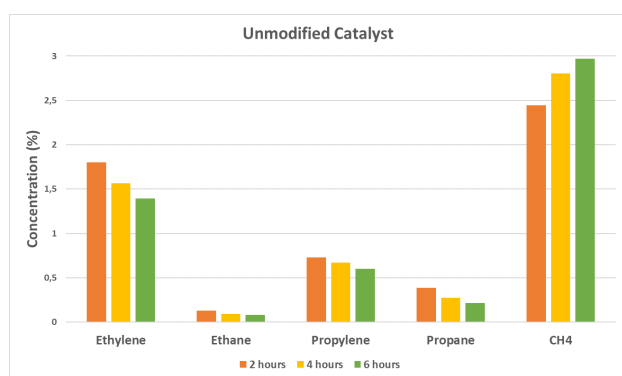
Figure 7: NH<sub>3</sub>-TPD of the 2% IWI sample compared to unmodified ZSM-5 catalyst

From this graph, it can be seen that the phosphorus treatment has two effects on the catalyst. The first effect is that the total area underneath the graph has decreased, which means that the amount of acid sites has decreased [15]. This is most likely due to the structural effect of phosphorus treatment. If the structure is slightly broken down by the phosphorus treatment, the amount of acid sites will also decrease. The second effect of phosphorus treatment is the change in peak temperature. It can be seen that the first peak for both samples is reached at around 220°C, which indicates that the weak acid sites have not been weakened more. However, the second peak is reached at around 410°C for the unmodified ZSM-5 sample and at around 370°C for the 2% IWI sample. This means that the strong acid sites were weakened by the phosphorus treatment [16][17]. The overall decrease of the amount of acid sites could result in a less active catalyst, whereas the weakening of the stronger acid sites could improve the catalysts performance. From this data, it would be expected that the unmodified ZSM-5 catalyst is more efficient than the 2% IWI catalyst.

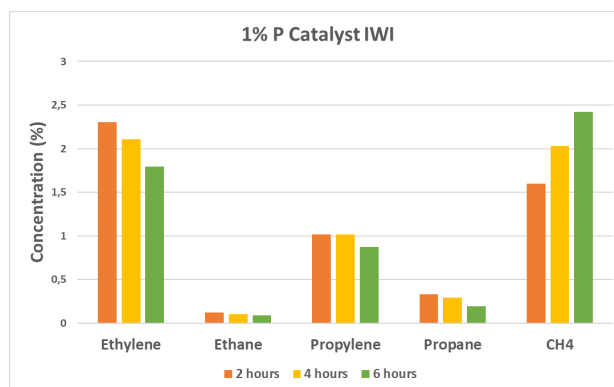
## 3.2 Product analysis

### 3.2.1 Gas products

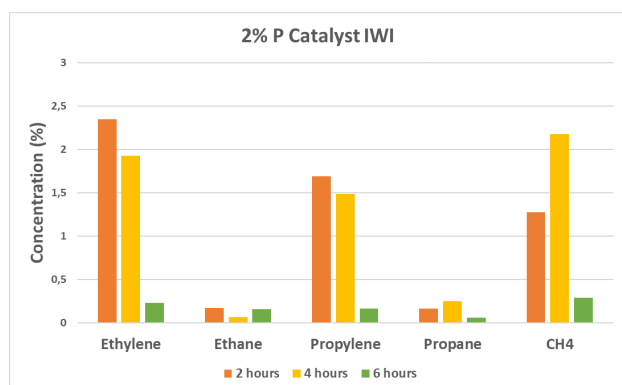
During the catalytic testing, a gas sample was taken after 2, 4 and 6 hours. The results of the gas chromatography (GC) indicated that there were 5 gaseous products: ethylene, ethane, propylene, propane and methane. From these products, ethylene and propylene are the most favourable. The GC results are shown in figure 8a to 8f as a concentration of products in the gas samples.



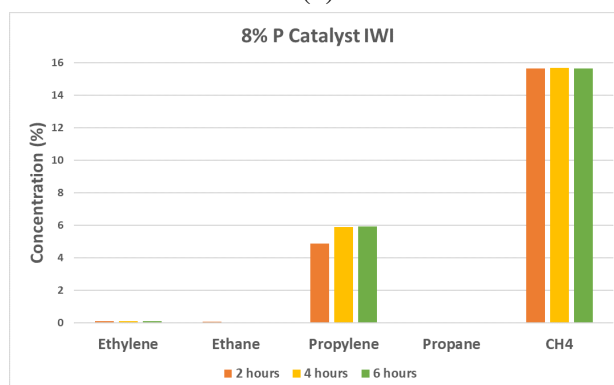
(a)



(b)



(c)



(d)

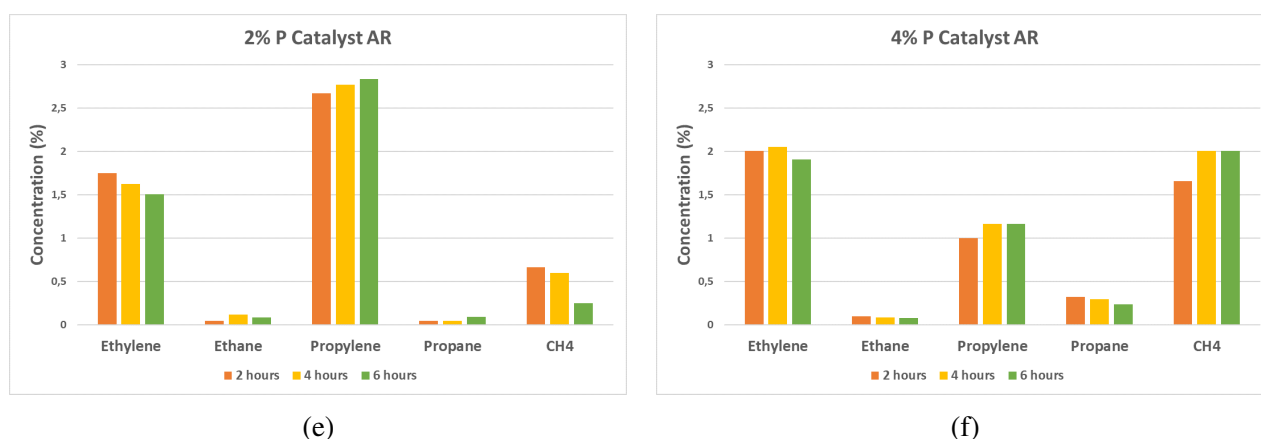


Figure 8: Concentrations of gas products in samples taken after 2, 4 and 6 hours for unmodified ZSM-5 catalyst (a), 1% IWI catalyst (b), 2% IWI catalyst (c), 8% IWI catalyst (d), 2% AR catalyst (e) and 4% AR catalyst (f)

From these graphs, a few conclusions can be made. First of all, it is noticeable that the 8% IWI sample produces much more methane and propylene than any other sample. Propylene is a desired product, but methane is not. No ethylene, ethane and propane were produced during the reaction. It can be said that the catalyst modification for this sample is a success, since the amount of propylene that is formed is higher than the rest. However, from all other data there was no indication that this sample is a successful catalyst. It is also noticeable that the 6 hour sample of the 2% IWI sample shows almost no products. This is due to a fault in the measurement, where the sample had to be tested again the next day. By this time, most of the products had decomposed.

In most samples, it can be seen that the concentration of gas products increases over time. This is due to coking, which decreases the pore size and pore volume. Due to a smaller pore size, larger molecules (such as aromatics) cannot diffuse from the catalyst and are trapped inside the pores. They will reform to smaller molecules (such as propylene), which will be able to diffuse from the catalyst. This is seen as an increase of gas product concentrations over time.

It can be seen that the addition of phosphorus increases the production of ethylene and propylene and reduces the production of methane, which is very favourable. By comparing the 1% IWI, 2% IWI, 2% AR and 4% AR samples, it can be seen that 2% phosphorus samples show the best results. Because 4% phosphorus shows a decrease in propylene production and an increase in methane production, it can be stated that phosphorus treatment is less effective at higher concentrations. By comparing the 2% IWI sample with the 2% AR sample, it can be seen that the acid reflux method has the best results. This could be caused by a slightly different phosphorus loading. Another explanation might be that the acid reflux samples are hydrothermally treated during the phosphorus treatment. This may give the acid reflux samples the advantage of having more acid sites affected, resulting in a higher selectivity for olefins. The gas product selectivity of every catalyst sample can be plotted in a graph as average concentrations over different catalyst samples, as shown in figure 9.

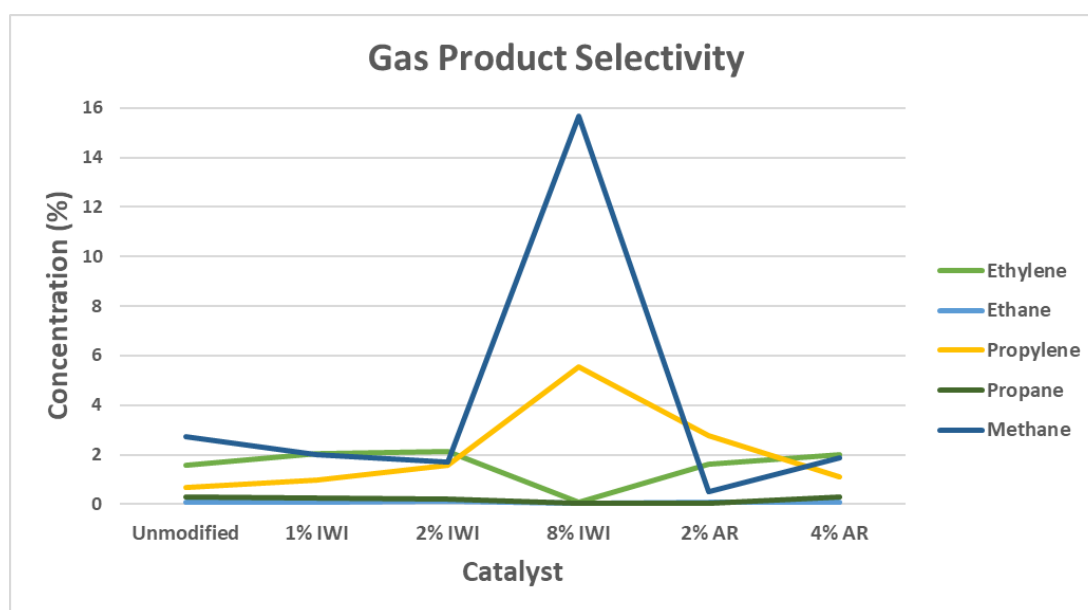
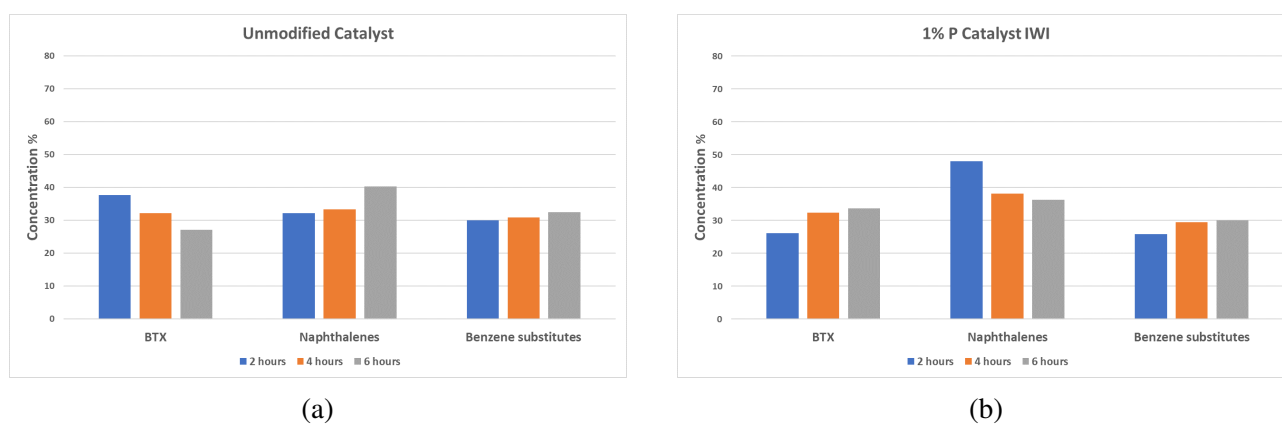


Figure 9: Gas product selectivity as average concentration over different catalyst samples

From figure 9, it is shown that the 8% IWI sample produces significantly more propylene than any other catalyst. However, it was shown from other data that this sample is not a good catalyst, since the structure of the catalyst was completely destroyed. Therefore, the next best gas product results are from the 2% AR sample, with the highest propylene production and the lowest methane production. Analysis of the liquid product samples will show if the 2% AR catalyst is indeed better than the other catalyst samples.

### 3.2.2 Liquid products

Next to a gas sample, a liquid product sample was also taken after 2, 4 and 6 hours. The GC analysis indicated that a lot of different liquid products were formed, all of which were aromatics. From these products, three different categories were made: BTX (benzene, toluene and xylene), naphthalenes and benzene substitutes. The BTX group is the most favourable, since these products are widely used in the chemical industry. Naphthalenes are not favourable, since they can be considered as precursors of coke. Benzene substitutes are not very favourable, since they need reforming to become benzene, toluene or xylene. The GC results are shown in figure 10a to 10f as a concentration of products in the liquid samples. Detailed results including all liquid products are shown in appendix B.



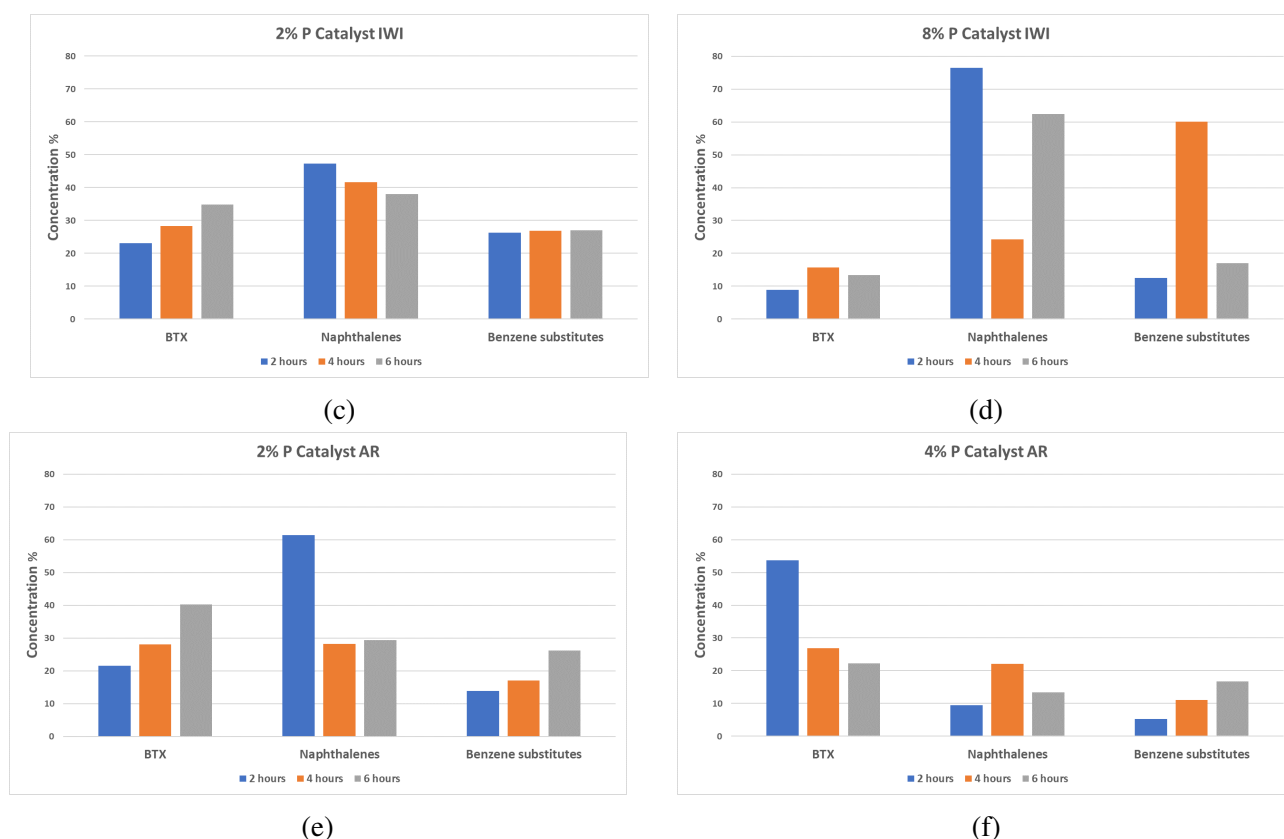


Figure 10: Concentrations of liquid products in samples taken after 2, 4 and 6 hours for unmodified ZSM-5 catalyst (a), 1% IWI catalyst (b), 2% IWI catalyst (c), 8% IWI catalyst (d), 2% AR catalyst (e) and 4% AR catalyst (f)

Again, the obvious outlier in the results is the 8% IWI catalyst sample. It shows that there is a large decrease in BTX production and a large increase in naphthalene production. The large differences in different time samples might be caused by unwanted condensation in cold spots in the reaction setup, which are flushed through later. However, since this has not happened in any other sample whatsoever, it is highly unlikely. Therefore, the large differences in different time samples indicate that this catalyst is not functioning effectively, which confirms previous statements.

It can be seen that the concentration of the desired product group (BTX) decreases over time with the unmodified catalyst. The concentration of naphthalenes increases over time, which is an indication of coking. Phosphorus treated catalyst samples show the opposite, where BTX concentrations increase and naphthalene concentrations decrease over time. This is due to the fact that the pore size of phosphorus treated catalyst samples is larger in the beginning of the reaction. The pores are large enough for naphthalenes to diffuse from the catalyst. However, over time coking will decrease the pore size, making it more difficult for naphthalenes to diffuse, whilst BTX products are still able to diffuse from the catalyst.

By comparing the BTX and naphthalene concentrations for all catalyst samples, it can be seen that the BTX concentration decreases a little bit with the incipient wetness impregnation samples. The naphthalene concentration increases with these samples, which is not favourable. For the acid reflux samples however, the concentrations of BTX do slightly increase compared to the unmodified catalyst. Next to that, the naphthalene concentration decreases with increasing phosphorus content using



the acid reflux method. It should be mentioned that the GC results of the 4% AR catalyst were not very reliable, since there was a slight error with the machine, causing the retention times to be inaccurate. The results were processed as accurately as possible, but the difference with other samples is so large that it is still considered inaccurate. The liquid product selectivity of every catalyst sample can be plotted in a graph as average concentrations over different catalyst samples, as shown in figure 11. Next to that, the selectivity of *para*-xylene was shown to improve by phosphorus addition in literature [5]. The selectivity of xylene isomers can be plotted in the same way, as shown in figure 12.

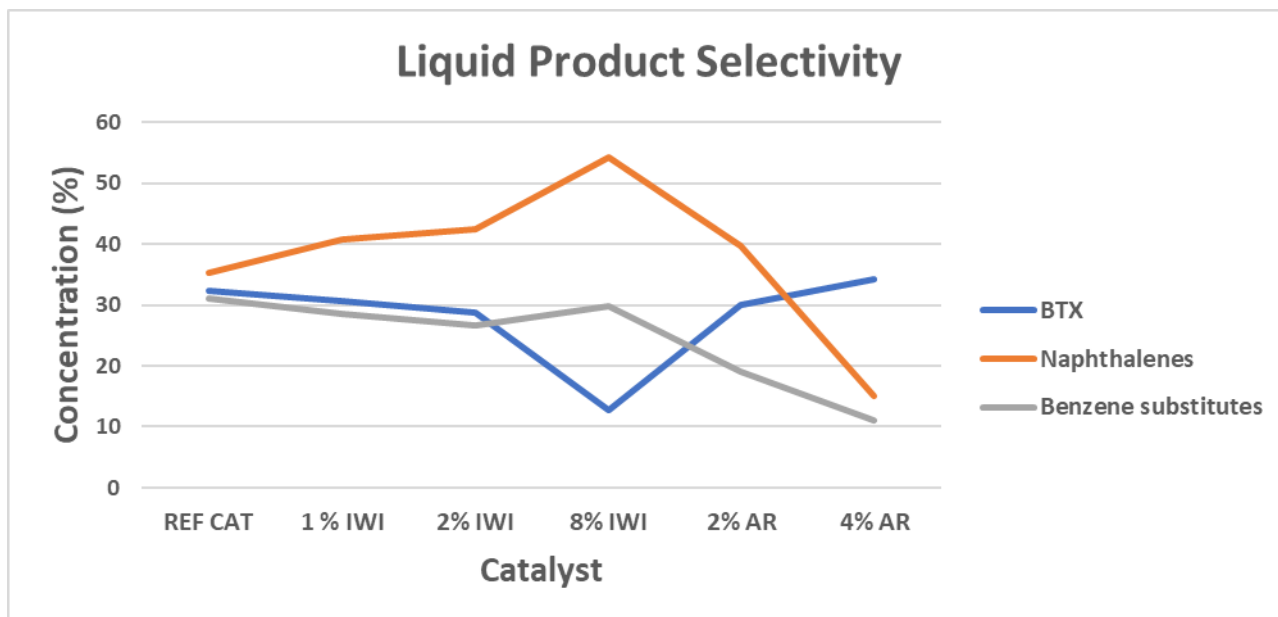


Figure 11: Liquid product selectivity as average concentration over different catalysts

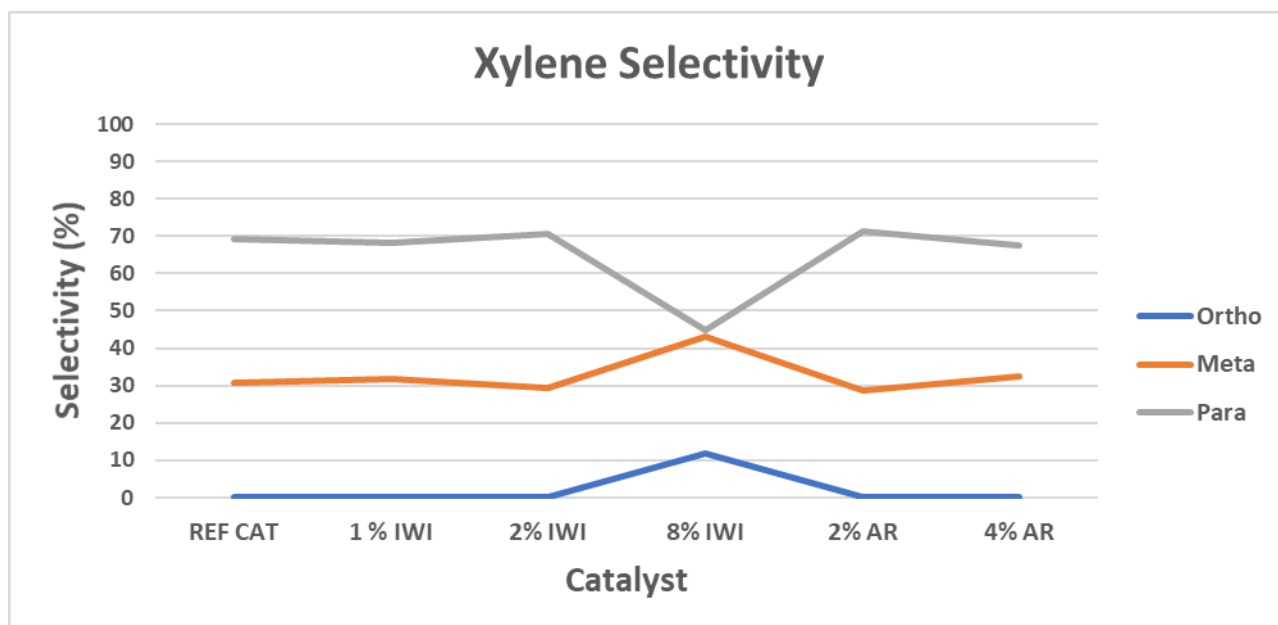


Figure 12: Xylene isomer selectivity over different catalysts

From figure 11 and figure 12, it can be seen that the 2% phosphorus samples result in minimal loss of BTX concentrations and minimal increase of naphthalene concentrations. However, this is using average concentrations. When looking at the 6 hour results, it can be seen that phosphorus addition increases BTX selectivity and decreases naphthalene selectivity. Both samples show a slightly increased *para*-xylene selectivity. From these two catalyst samples, the 2% AR sample produces the least amount of benzene substitutes. This is favourable, since less byproducts means less waste and less necessary reforming to BTX products. Therefore, the 2% AR sample shows the best results in liquid product analysis.

### 3.2.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) shows the weight loss of spent catalyst samples over increasing temperatures. At high temperatures (around 600°C), the coke layer on the catalyst surface burns off. The decrease of weight shows the amount of coke that has formed on the catalyst surface during the reaction. The weight loss of spent phosphorus modified catalyst samples compared to unmodified ZSM-5 catalyst is shown in figure 13a and figure 13b.

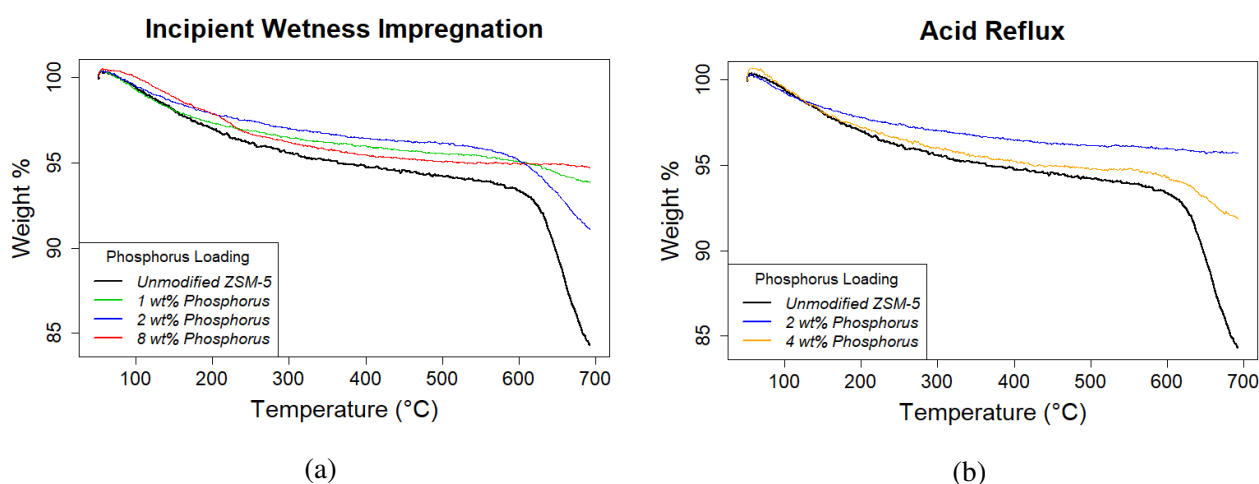


Figure 13: TGA results of unmodified ZSM-5 catalyst compared to phosphorus modified catalyst samples via the incipient wetness impregnation method (a) and the acid reflux method (b)

From figure 13, it can be seen that phosphorus treatment on ZSM-5 catalyst significantly decreases coke formation. Figure 13a shows that the 8% IWI sample forms the least amount of coke, which is to be expected since the other data confirms that the catalyst is not functioning properly. For the incipient wetness impregnation method, it can be stated that the formation of coke increases with an increasing phosphorus content. Figure 13b confirms that this also applies to the acid reflux method. However, the amount of coke formed on the surface of the acid reflux samples is significantly less than on the incipient wetness impregnation samples. This is most likely due to the better integration of phosphorus in the acid reflux samples, which was explained in section 3.2.1. From TGA analysis, the 2% AR sample shows the least coke formation during the reaction and is therefore the most favourable catalyst. This was also visible by looking at the catalyst samples after the reaction. Where most catalyst samples turned completely black during the reaction, the 8% IWI and 2% AR sample only turned grey, which indicates less coke formation on the catalyst surface.

## 4 Conclusion

this research investigated the influence of phosphorus addition to ZSM-5 (Si/Al = 23) on the methanol to hydrocarbons process using a fixed-bed reactor. Catalyst samples were treated with phosphorus using the incipient wetness impregnation method and the acid reflux method. The catalyst samples were analyzed before the reaction using x-ray diffraction, nitrogen physisorption and ammonia temperature programmed desorption. The gaseous and liquid products were analyzed using gas chromatography and the spent catalyst was analyzed using thermogravimetric analysis. After processing the results, the following conclusions were reached.

Phosphorus treatment slightly damages the catalyst structure, but does not affect the characteristic MFI framework. Incipient wetness impregnation is a more cost efficient method and is in theory able to incorporate all phosphorus in the catalyst. However, results show that it does not guarantee a successful integration of phosphorus in the catalyst. The acid reflux method is less damaging to the catalyst structure than originally expected, but is more expensive and time consuming. The pore size and pore volume can increase and decrease, depending on the treatment method and the phosphorus content. The addition of phosphorus decreases the total amount of acid sites and weakens the stronger acid sites in the catalyst. The addition of phosphorus increased olefin selectivity in the gas products, while decreasing the methane production. For the liquid products, phosphorus addition using the acid reflux method slightly increased the selectivity for benzene, toluene and xylene. The production of benzene substitute side products was significantly decreased by the addition of phosphorus. The selectivity of *para*-xylene was slightly increased by phosphorus addition. The formation of coke on the catalyst surface is significantly decreased by the addition of phosphorus. Catalyst samples with lower phosphorus contents show the least coke formation.

Phosphorus addition to ZSM-5 (Si/Al = 23) increases catalytic performance in the methanol to hydrocarbons process if the phosphorus content is between 1-4wt%. The optimal catalyst modification was found to be 2wt% phosphorus via the acid reflux method.

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## Appendices

### A Hazard and operability study

Deviation	Cause	Consequence	Safeguards	Action
Pressure too high	Blockage	Pressure buildup may cause breaking glasware. It could also flush the system with methanol, which is not desirable.	Pressure indicator is watched by the student.	Stop the flow of N2 and look for the blockage.
Pressure too low	Leakage	Product may escape through the leakage, the results of the experiment are then unreliable.	Pressure indicator is watched by the student.	Check all connections for leakages untill the pressure is at good levels.
Temperature too high	Oven malfunction	Glass could melt and reaction efficiency decreases.	Oven is watched by the student.	Stop the flow of N2 and replace the oven.
Temperature too low	Oven malfunction	Reaction efficiency decreases	Oven is watched by the student.	Stop the flow of N2 and replace the oven.
No condensation	Cooler malfunction	No liquid product, less characterization possibilities	Liquid sample is checked every hour by the student.	Check if the condensor is installed properly and replace the cooler.
No flow	Empty N2 tank	No flow of N2 means no flow of methanol, so no reaction.	Pressure indicator is watched by the student.	Close the valves and replace the N2 tank.

Figure 14: Hazard and operability study

## B Detailed liquid product results



Figure 15: Detailed depiction of liquid products in samples taken after 2, 4 and 6 hours for unmodified ZSM-5 catalyst (a), 1% IWI catalyst (b), 2% IWI catalyst (c), 8% IWI catalyst (d), 2% AR catalyst (e) and 4% AR catalyst (f)