

AROMATISATION OF FURAN OVER PHOSPHOROUS MODIFIED ZSM-5

Master's research project

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Abstract

The aromatisation of both 2-methylfuran and 2,5-dimethylfuran was studied over phosphorous modified HZSM-5. Presence of phosphorus modifies acidity and surface area of the zeolite. Advanced characterisation techniques such as FT-IR, ²⁷Al, ²⁹Si, ³¹P MAS, 2D ²⁷Al MQMAS solid state NMR were used to elucidate the phosphorus – zeolite interactions. Using FT-IR and ²⁷Al NMR, formation of AlPO species can be observed with increasing weight loading. Furthermore, ³¹P NMR revealed a wide range of free and condensed phosphorous compounds which were partly removed by washing, resulting in a significant improvement of acidity, and surface area. Introduction of phosphorus results in the decrease of side reactions during the aromatisation of both 2-methylfuran and 2,5-dimethylfuran. Thermogravimetric analyses revealed that lower coke was formed for the PHZSM-5 catalyst, and after washing and calcining, selectivity also improves considerably. Co-feeding ethylene further reduces side reactions, resulting in lower deactivation reaction rates, whilst increasing BTX yield.

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1. Introduction

With the ongoing depletion of crude oil, alternative sources need to be explored in order to ensure enough supply for future chemical processes. Benzene, toluene, and xylene, otherwise known as BTX, are valuable platform compounds widely used for further conversion into commercially viable chemicals. Benzene is mostly used for the production of styrene, phenol, nylon, and aniline¹. Furthermore xylene, or especially, p-xylene is mostly used to produce terephthalic acid and dimethyl terephthalate, both are used as precursors for the production of polyethylene terephthalate (PET). Toluene is mostly used for the conversion into benzene and xylenes². Nowadays BTX are produced from the steam cracking of naphtha, but more sustainable routes are becoming available. One way that has been widely investigated is the upgrading of biomass into BTX aromatics using acidic zeolites as catalysts.

Increasing concerns to reduce carbon emission has inspired the community to investigate more sustainable chemical processes while reducing the usage of fossil fuels, however a large pathway still needs to be overcome in order to move totally to environmentally friendly feedstocks. Therefore, the objective is the gradual incorporation of renewable processes to the common fossil routes to eventually, move towards a partial CO₂-neutral methodology by incorporating renewable feedstocks into current fossil processes. The usage of biomass is suggested as a potential feedstock due to its low carbon footprint, but it also brings up some challenges with most of the biomass available being used for different purposes, the so-called first-generation biomass³. The first-generation biomass is the one that is used directly by society, such as crop plantations produced by the agricultural sector, giving rise to major competition. However, a second option is also available in the form of second-generation biomass which consists of lignocellulosic biomass and/or inedible forms of biomass that are usually waste and residual material from first-generation biomass.

Lignocellulosic biomass is considered one of the most promising bio-derived complexes to be converted into commodity chemicals. Lignocellulosic biomass is a bio-polymeric mixture composed of lignin, cellulose, and hemicellulose, present in different percentages depending on the precedence of the biomass source. This type of biomass serves little purpose as first-generation biomass which makes it an ideal and non-competing biomass source for usage in the industrial sector. However, in order to convert the lignocellulosic biomass towards valuable products it first needs to be treated accordingly.

The upgrading of lignocellulosic biomass is done via 3 major routes; pyrolysis, gasification or hydrolysis. Pyrolysis of biomass consist of heating the biomass source, either at a fast or slow heating rate, to high temperatures (from 400°C to >700°C) for a limited amount of time to produce a variety of products. By controlling temperature and contact time, the distribution of products varies considerably. This process mainly yields tars and oils, or non-condensable gases at very high temperatures^{4,5}. Secondly, biomass can also be submitted to harsh temperatures thereby resulting in gasification of the material. This yields ashes and other gases such as CO/CO_2 which can be further used in Fischer-Tropsch⁶ or electrocatalytic processes⁷. The third possible route for lignocellulosic biomass conversion is the hydrolysis of the biopolymer. In an excess of water, either acid or base catalysed, biomass is converted into a variety of sugars or disaccharides^{8,9}.

1.1 Furan derivates as model compounds from biomass

Furans can be obtained from the dehydration of sugars such as xylose or glucose, which can be further converted via acid-catalysed reactions into furfural, or 5-hydroxymethylfurfural. Formation of furfural



Figure 1, Two available routes for biomass conversion into furfural compounds via various sugar intermediates.

is mostly done via the dehydrogenation of xylose^{9,10}, and in a similar way 5-hydroxymethylfurfural could also be produced from fructose^{11,12} (Figure 1). Further conversion of furfural and 5-hydroxymethylfurfural via decarbonylation/decarboxylation would result in the formation of 2-methylfuran and 2,5-dimethylfuran, respectively^{13,14}. The conversion of lignocellulosic biomass via sugars, such as glucose/xylose, makes it a relatively plausible production route since it valorises biomass routes.

One of the most investigated routes in literature is the conversion of furan derivates into aromatics such as benzene, toluene, and xylenes by means of acidic catalysts such as zeolites. It is known that Brønsted and Lewis acid sites present in zeolites catalyse the conversion to BTX aromatics, but this process is known to suffer from rapid deactivation rates due to low carbon selectivity. In order to improve the efficiency and selectivity of the process, further investigations need to be performed to elucidate the formation mechanism of aromatics. In general, the most suggested route to form aromatics is via decarbonylation/decarboxylation followed by a carbon rearrangement or by addition of another carbon source such as olefins, which can either be formed by cracking of the furan ring or added via co-feeding and is otherwise known as the [4+2] Diels-Alder cycloaddition (Figure 2). Even though an improved selectivity is obtained by co-feeding, this reaction still has a low carbon selectivity since it forms a reasonably large amount of coke via condensation reactions. Besides the high rate of side reactions, a high concentration of water is also produced during the reaction which is detrimental for the structural integrity of the zeolite due to, at such harsh conditions, facilitating the removal of framework aluminium by steaming. Therefore, despite all the efforts put into improving the furan to aromatics process, further investigations in catalyst design and reaction conditions need to be carried out.

1.2 Zeolites as Catalyst

The conversion of furan is usually performed in the presence of a zeolite catalyst. Zeolites consist of solid porous aluminosilicates arranged in tetrahedral coordination with very well-defined crystalline frameworks. A wide variety of frameworks are available, however, industrially only a few zeolites are actually used, the so-called big five; MFI, Beta, Mordenite, Faujasite, and Ferrierite. The zeolite





commonly used for the conversion of furan to aromatics is the ZSM-5 zeolite with MFI topology (Figure 3). The framework consists of a combination of 10 membered-ring pore windows creating an accessible pore size of 6.36 $Å^{15}$.

The ability to catalyse reactions arises from, the earlier mentioned, Brønsted and Lewis acid sites. These sites are formed due to a charge unbalance in the structure. To counter this charge unbalance in the zeolite framework a positive cation is necessary. During synthesis this requirement is fulfilled by sodium ions, but could also be easily exchanged for other cations, such as protons or other alkali/alkaline-earth ions. When protons are present, Brønsted acid sites are formed. The zeolite could also catalyse reactions via Lewis acid sites in which there is a negative charge present on the alumina, but a positive charge on the silica (framework defect) which behaves as an electron acceptor. Moreover, extra framework alumina moieties can also act as Lewis acid sites. Additional Lewis acid sites can also be generated via the addition of metal cations, for example gallium, zinc, or molybdenum. The acidity, either Brønsted or Lewis, of the zeolite can be influenced by the silica to alumina ratio of the framework (SiO₂/Al₂O₃). This ratio greatly influences acidity, which prevails due to the charge difference between silicon and aluminium, higher ratios result in less acidic structures. However, with lower ratios, more acidic zeolites are obtained but the structural stability of the framework is intrinsically affected¹⁶.

Another drawback of highly acidic zeolites is the ease of aluminium removal from the framework creating extra framework aluminium species, a common way of zeolite deactivation. Especially in the presence of water at elevated temperatures, zeolites will eventually undergo leaching of aluminium, and consequently removing the zeolite's Brønsted acid sites. The small pore size of the framework makes it ideal for shape-selective reactions but could also lead to deactivation by pore blockage due to the formation of larger coke species which cannot diffuse throughout the framework, such as naphthalene or higher condensed aromatics (>2 rings).

1.3 Phosphorous modified zeolites

A common and easy practice to improve the catalytic performance of zeolites is by means of postsynthesis modifications. The modification can be achieved with a variety of techniques to obtain different results, as an example mesopores can be introduced by leaching experiments, but the chemical environment of the zeolite can also be modified by the addition of promotors. It is well-known that the addition of phosphorous species to the zeolite significantly improves catalytic lifetimes by preventing aluminium leaching from the framework^{17,18}. Several authors reported that phosphatation can result in a promoted catalytic effect depending on the synthesis method applied. Phosphorus loadings greatly



Figure 3, Zeolite MFI framework of ZSM-5 consisting of 2 types of channels, straight (left) and sinusoidal (right) Image from (¹⁵).

influence the physicochemical properties of the zeolite since they induce acidity changes, in terms of strength and amount, and pore narrowing. Moreover, another phenomenon taking place during the impregnation of phosphorus is a controlled dealumination, which is known to be dependent on the phosphorus loading and post-synthetic method employed.

The most common technique for the impregnation of phosphorus on ZSM-5 is wetness or incipientwetness impregnation due to the ease and effectiveness of the method. With phosphorous modification usually performed by wetness impregnation with a phosphorous precursor¹⁸. In literature mostly two different precursors are used, orthophosphoric acid (H₃PO₄; P) and diammonium hydrogen phosphate ((NH₄)₂HPO₄; DP). The use of phosphoric acid as precursor indirectly favours dealumination due to the very low pH ~0-1, therefore the precursor DP is also used due to its slightly basic character (pH ~7-8). Although DAP does not induce dealumination, it could potentially induce desilication¹⁹.

The distribution of phosphorous species over the zeolite after synthesis is mostly known to be found at the surface, especially at high weight loadings (>5% phosphorus), at which most of the phosphorus is deposited on the external surface of the zeolite^{20,21}. The addition of phosphorus results in the interaction of phosphorus monomeric species with silica (SiO₂) and alumina (Al₂O₃) from the zeolite, with the phosphorus actively searching out the aluminium on the zeolite to bind, as was demonstrated in previous studies²². Nevertheless, the origin of the phosphorus-zeolite interactions still remains unclear (Figure 4). In literature, several interactions were proposed, such as the incorporation of phosphate species and the framework, as shown in Figure 4e, and 4h. However, amongst the different proposals there is still a lot of controversy. Formation of Si-O-P bonds are proposed but its formation seems unlikely due to being energetically unfavourable^{23–25}. However, some studies revealed that Si-O-P bonds can be formed under specific synthesis conditions²⁶. The protonation of phosphorous species via the acid sites present on the zeolite framework was also suggested, thereby binding the phosphate to the surface (Figure 4e). Blasco *et al.*¹⁷ suggested with this model that the binding of a Brønsted acid



Figure 4,Proposed zeolite-phosphate interactions from: (a.) Keading et al. ⁵⁸, (b.) *Zhuang et al.* ⁵⁹, (c.) *Xue et al.* ⁴⁹, (d.) Van der Bij et al. ²⁷, (e.) Blasco et al. ¹⁷ (f.) Lercher et al. ⁶⁰, (g.) Caro et al. ²⁰, (h.) Abubakar et al. ⁶¹.

site would stabilise another near acid site. This model assumes the close proximity of acid sites within the framework, but in the case of high SiO_2/Al_2O_3 ratios zeolites, this model would not be possible.

Other possible interactions are the hydrogen bonding between monomeric phosphates and the zeolite structure (Figure 4h). Phosphorus is also known to dealuminate the zeolite structure by forming aluminium phosphate phases (Figure 4g). The incorporation of phosphate into the zeolite structure with partially dislodged aluminium has also been proposed by van der Bij et al. (Figure 4b) in which a single phosphate is bound to framework aluminium, but additionally the formation of bidentate structures (Figure 4d) was suggested, forming so-called SAPO interfaces within the zeolite structure such as $(SiO)_2Al(O_2P(OR)_2)$ or $(SiO)_2Al(O_2P_2O_2(OR)_3)$, where R is either a phosphate or a polyphosphoric species²⁷. Besides the direct attachment of phosphorus to the framework the formation of condensed polyphosphates can also take place thereby decreasing pore volume, or even blocking the pores. The formation of phosphorus interactions with aluminium favours the aluminium to be kept in the zeolite framework during steaming conditions, consequently preventing the Si-O-Al bond of being removed. Furthermore, with the impregnation of phosphorus several physicochemical changes such as micropore volume and BET surface area decrease. This induced pore narrowing of the zeolite framework is optimal for improving shape-selective reactions, such as the production of p-xylene over m- or o-xylene²⁸⁻³⁰. Moreover, after phosphorus impregnation, strong acid sites are known to decrease while the amount of weak acid sites increase slightly with increased phosphorus loading^{31,32}. Regeneration of the acid sites and pore volume after phosphorus impregnation was found to be possible, indicating that most of the interactions are reversible in nature^{33,34}. This confirms the need for a calcination step after the impregnation method to obtain irreversible phosphorous-zeolite interactions.

Regarding all the research done in the development of gas phase conversion of furan derivates, several improvements still need to be done. Different side reactions can take place during the gas phase conversion resulting in a broad distribution of products with low carbon selectivity³⁵. Production of large amounts of CO/CO_2 and coke species causes a decrease in the carbon atom efficiency. Co-feeding of olefins, either ethylene or propylene, is known to improve selectivity to BTX, consequently reducing coking and formation of CO/CO₂³⁰. In combination with ethylene co-feeding, another novel approach to improve the catalyst is via the introduction of phosphorus into the zeolite. Previous reports revealed that the use of phosphorus as promotor during the conversion of methanol to olefins enhances selectivity towards smaller compounds by blocking formation of coke compounds, but also enhances hydrothermal stability by preventing aluminium leaching because of the high release of water during the MTO process. Due to the high oxygen content present in our system, incorporation of phosphorus is expected to have a similar effect as in the MTO process. Addition of phosphorus to the zeolite is expected to reduce side reactions due to the enhanced acidity strength and the pore narrowing induced upon the binding of phosphorus to the zeolitic acid sites. However, regardless of all the efforts to elucidate the actual phosphorus - zeolite interactions, understanding and effect of phosphorus interactions within the intra-zeolitic framework of the HZSM-5 zeolite remains unsolved yet.

In this research, we aim to synthesize a phosphorous modified HZSM-5 zeolite catalyst to improve catalytic performance of furan aromatisation in gas phase conversion, by performing a post-synthesis modification of a commercial HZSM-5 zeolite. Addition of phosphorus to a zeolite was demonstrated to reduce removal of aluminium via steaming. Moreover, the effect of ethylene co-feeding to enhance the production of aromatics is also investigated. We investigate if the presence of phosphorus can better facilitate Diels-Alder cycloadditions, thereby enhancing BTX selectivity.

2. Experimental Methods

2.1 Catalyst preparation

To obtain the phosphorous modified ZSM-5 materials, a wetness impregnation method was performed using two different precursors solutions with either, orthophosphoric acid (H₃PO₄) or diammonium hydrogen phosphate ((NH₄)₂HPO₄) in 40 ml demi water. The orthophosphoric acid solutions had a pH = \sim 2, while all diammonium phosphate solutions had a pH = \sim 8. Subsequently, 2 g commercially available ZSM-5 zeolite (Zeolyst, CBV3024E SiO₂/Al₂O₃ = 30 and CBV8014 SiO₂/Al₂O₃ = 80) was added to the solution and stirred for approximately 15 minutes. Afterwards, the zeolite was recovered by rotary evaporation under vacuum. The recovered zeolite was dried overnight (~16 hours) at 120°C followed by calcination at 550°C (5°C/min ramp) for 3 hours. The materials obtained are shown in Table 1. All samples were named using the phosphorus weight loading in percentage followed by the precursor used, P for orthophosphoric acid (H₃PO₄) and DP for diammonium phosphate ((NH₄)₂HPO₄).

Several of the phosphorous modified samples were also washed after calcination to check the removability of the phosphorous compounds from the zeolite framework. This step was done by adding 20 ml of demi water to the zeolite, after which it was stirred and then evacuated by vacuum filtration. This washing step was repeated four times followed by a drying step overnight (~16 hours) at 120°C. The obtained washed samples were calcined at 550°C for 3 hours. Samples after washing are abbreviated as W. The additional calcination step is noted as W_C.

Samples	SiO ₂ /Al ₂ O ₃	Phosphate	Weight loading	ICP Determined
	Ratio	precursor	phosphorus (wt%)	(wt%)
[Z]	30	-	-	-
[Z80]	80	-	-	-
1P[Z]	30	H_3PO_4	1	1.04
2P[Z]	30	H_3PO_4	2	1.85
2P[Z80]	80	H_3PO_4	2	-
2DP[Z]	30	(NH ₄) ₂ HPO ₄	2	1.98
2DP[Z80]	80	(NH ₄) ₂ HPO ₄	2	-
3P[Z]	30	H_3PO_4	3	2.98
5P[Z]	30	H_3PO_4	5	-
5P[Z80]	80	H_3PO_4	5	-
5DP[Z]	30	(NH ₄) ₂ HPO ₄	5	-
5DP[Z80]	80	(NH ₄) ₂ HPO ₄	5	-
W-2P[Z]	30	H_3PO_4	-	1.29
W_C-2P[Z]	30	H_3PO_4	-	1.40
W-2DP[Z]	30	(NH ₄) ₂ HPO ₄	-	1.45
W_C-2DP[Z]	30	(NH ₄) ₂ HPO ₄	_	1.50

Table 1, Synthesised we	eight loadings p	phosphorus on	HZSM-5 using 2	2 different	precursors.
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2.2 Characterization techniques

The crystallinity was checked by X-ray powder diffraction on a Bruker D2 phaser diffractometer in Bragg-Brentano mode equipped with a Lynxeye detector. X-rays were generated with a Co X-ray source (K $\alpha_{1,2}$, $\lambda = 1.79026$ Å) operated at 30kV and 10 mA. Samples were collected from 5° - 50° 2 θ degrees at 0.02°/step with 1 s step time. Finally, the samples were referenced to an XRD database to confirm the presence of ZSM-5. Acidity of the zeolite samples was measured by NH₃ temperature-programmed desorption (NH₃-TPD) on a Micrometrics autochem II equipped with a TCD detector. Prior to the NH₃ adsorption, samples were dried at 550°C for 1 hour using a temperature ramp of 10°C/min under a helium atmosphere. After cooling down to 100°C, ammonia was pulsed 10 times to ensure saturation of the samples. Subsequently, desorption experiments were performed by heating up the samples at 10°C/min up to 550°C.

FT-IR transmission spectroscopy experiments were performed to measure effects on hydroxyl region and structural changes of the zeolite modified samples. Transmission FT-IR was performed in an autoclave under vacuum positioned in a Thermo Scientific Nicolet iS5 FT-IR spectrometer. In the autoclave a self-supporting wafer of ~25 mg was placed. Prior to measurements, evacuation under high vacuum (10^{-5} mbar) was reached. Subsequently, the wafer was dried at 550°C (10° C/min) for 2 hours. After cooling, a FT-IR spectrum was taken at room temperature. Furthermore, to quantify Brønsted acid sites (BAS) and Lewis acid sites (LAS), pyridine probed FT-IR experiments were performed. This was performed by dosing the dried self-supporting wafer with pyridine (vapour pressure of ±25 mbar) for 30 minutes. Afterwards, pyridine was evacuated for 30 minutes to ensure only physisorbed pyridine on the surface. For the quantification of BAS and LAS, the wafer was dried at 150°C (ramp 2.5°C/min) and held for 30 minutes at that temperature. A spectrum was taken after 30 minutes heating. After baseline correcting and normalizing the spectra, both Brønsted and Lewis acid sites concentrations were calculated following a method described elsewhere³⁶.

Furthermore, argon physisorption experiments were performed to determine surface area and micropore volume for all samples. The physisorption experiments were performed on a Micromeritics Tristar II plus using argon as pore filling agent. Samples were degasified for 16h at 300°C (ramp 10°C/min) under nitrogen atmosphere before the measurements.

²⁷Al, ²⁹Si, and ³¹P magic angle spinning (MAS) solid-state NMR (ssNMR) experiments were performed at 11.7 T (500MHz) on a Bruker Avance III spectrometer equipped with a 3.2 mm MAS probe. Spectra were recorded at ambient temperature and referencing was done externally to Al(NO₃)₃, TMS, and NaP, respectively. For all the measurements the rotors were filled with the same amount of sample (30 mg). A MAS of 16 kHz was applied for ²⁷Al and ³¹P experiments. An RF field of 50 kHz was used for the ²⁷Al π/12 pulse followed by 4.4 ms acquisition. An inter-scan delay of 1s was applied and 10240 scans were accumulated for [Z], 2P[Z], 2DP[Z], and 5DP[Z] samples, for W-2P[Z] and W_C-2P[Z] samples 4096 scans were used. The spectra were processed with a line-broadening of 100 Hz. A zero-quantum (ZQ) filtered multiple-quantum magic angle spinning (MQMAS) pulse-sequence³⁷ was used to correlate the ²⁷Al isotropic chemical shift (F1) with the quadrupolar line-shape (F2). The excitation and conversion pulses were applied with an RF field of 50 kHz, instead for the soft, selective pulse following the Z-filter delay an RF field of 6.5 kHz was used. 2400 scans were accumulated using an inter-scan delay of 1 s. Acquisition times of 5 ms and 1 ms were used for the direct and indirect dimensions, respectively. MQ-MAS data were Fourier transformed and sheared, and 100 Hz line-broadening was applied in both dimensions. An RF field of 83 kHz, 12 ms acquisition time and 2048 scans were applied for the 1D ³¹P

spectra, with 5 s recycle delay and 88 kHz SPINAL-64³⁸ proton decoupling and 100 Hz line broadening for spectral processing. For the ¹H-³¹P cross-polarization (CP)³⁹ RF fields of 70 kHz and 57 kHz were used, respectively, and a 70% ramp, with CP contact time of 2 ms and 10 ms acquisition time. Using 88 kHz SPINAL-64 proton decoupling, 2048 scans were recorded with 1.5 s recycle delay and a line broadening of 100 Hz was applied for spectral processing.

For ²⁹Si ssNMR experiments, a MAS frequency of 12kHz was applied. 88 kHz SPINAL-64 proton decoupling and RF field of 54 kHz were used for ²⁹Si 1D spectra, recorded with 512 scans, 13 ms acquisition time and 80 s recycle delay, then processed with 50 Hz line broadening. For the ¹H-²⁹Si CP RF fields of 50 kHz and 42 kHz were used, respectively, and a 70% ramp, with CP contact time of 2 ms, 15 ms acquisition time and 3 s recycle delay. Using 88 kHz SPINAL-64 proton decoupling, 7168 scans were recorded, and a line broadening of 100 Hz was applied for spectral processing. All spectra were processed and analysed using the Bruker software Topspin 3.5.

2.3 Catalytic testing

The catalyst prepared were tested during the conversion of furans to aromatics in a custom-made setup depicted in Figure 5a. 2-methylfuran (2-MF) or 2,5-dimethylfuran (2,5-DMF) were fed into the reactor by a bubbler (1) at WHSV 1 h⁻¹ (nitrogen flow of 1,3 and 3,9 ml/min, respectively). Inside the reactor (2; Linkam cell FTIR-600 from Linkam Scientific) a 55 mg zeolite wafer was placed. The reaction was then heated to 500°C whereby the zeolite pellet was first subjected to an activation-calcination step of 1 hour in 20 ml/min oxygen, followed by 1 hour flushing step with 20 ml/min nitrogen to remove all oxygen. The reaction was monitored by UV-Vis diffuse reflectance spectroscopy (DRS) by means of a UV-Vis



Figure 5, Used setup for furan conversion (a.) using, first a bubbler (1.), which flows to a Linkam cell (2.), and secondly, an online mass spectrometer (3.) to analyse products. The second catalytic setup (b.) allows for the combination of furans from a bubbler (4.) and an ethylene gas line in a mixer (5.) before entering the reactor (6.), products were analysed via an on-line GC.

fibreoptic probe (Avantes). The products formed were analysed using an on-line mass spectrometer (3; OmniStar GSD 320 O3, Pfeiffer) equipped with a faraday detector.

To perform the catalytic test while co-feeding ethylene to the reaction mixture a second setup was used which is depicted in Figure 5b. This setup allows for the combination of both reagents in the mixer compartment (5), both reagents are then mixed using a third nitrogen line to obtain the required concentration. The flows used during the catalytic experiments were chosen to obtain a volume ratio of 1:0.5 furan-to-ethylene with a 3.9 vol.% of either, 2-methylfuran or 2,5-dimethylfuran with respect to the total flow rate. Both reagents were diluted by a nitrogen carrier gas to obtain a total flow rate of 20 ml/min. Afterwards, reactants were fed into the reactor (6) where a 55 mg zeolite wafer was placed, previously subjected to the same activation-calcination step as mentioned before. Products formed during the reaction were analysed using an on-line gas chromatogram (8). Samples were injected via three 25µl sample loops and were analysed with three different columns. A column for analysing C1-C3 (Rt-QBond with 3m length and 0.32mm diameter), a column for C4-C8 plus aromatics (MXT-5 15m length and 0.28 mm diameter), and a column for detecting H_2 , N_2 , and CO_2 (Carboxen 1010 with 10m length and 0.32mm diameter). Compounds were analysed via two FID and a TCD detector, respectively. To obtain conversion values for the reaction both reagents were flowed over the reactor bypass (7). Blank tests were done in the absence of ethylene using SiO_2 as catalyst with a total flow of 20 ml/min. Conversion was calculated via equation 1, with na and nb concentration reagent of 2-methyl-/2,5dimethyl-furan and ethylene, respectively. Carbon yield was calculated via equation 2 with ni the concentration of formed compound and C_{i/a/b} number of carbons per product/reagent. Mass balance was determined via equation 3, whereby $m_{a,b}$ is the gram carbon of reagents and m_i gram carbon of formed product⁴⁰.

Conversion
$$X_{a,b} = \frac{n_{a,b \ in} - n_{a,b \ out}}{n_{a,b \ in}} * 100\%$$
 (1)

Carbon yield
$$Y_i = \frac{n_i}{n_{a,b \ in} - n_{a,b \ out}} * \frac{C_i}{C_{a,b}} * 100\%$$
 (2)

Mass balance
$$m_{a,b\ in} - m_{a,b\ out} - \sum_{i}^{x} m_{i} = 0$$
 (3)

3. Characterization of phosphorous modified ZSM-5

3.1 X-ray powder diffraction

The addition of phosphorus to the zeolite framework is known to change the chemical environment, especially by binding to the Brønsted acid sites or extracting aluminium from the framework. In order to check how the impregnation of phosphorus affected the zeolite structure, X-ray powder diffraction experiments were performed (Figure 6). All samples show the characteristic reflections of a ZSM-5 zeolite with MFI topology indicating that the crystalline structure of the zeolite remains intact after wetness impregnation. However, a drop in intensity of various peaks was observed when increasing weight loadings of phosphorus indicating the presence of the phosphorus in the micropores of the framework.

Aluminium phosphate (AIPO) or silicon orthophosphate (SiPO) species were not observed indicating that no crystalline AIPO or SiPO species were formed after impregnation or the percentage formed is below detection limits²⁶.

3.2 Argon physisorption

To measure the impact of phosphorus impregnation on the pore volume and surface area argon physisorption experiments were performed (Figure 7). The increase in phosphorous content results in the decrease of surface area, which is mostly contributed to a decrease in micropore surface area (Figure 7a, b). The decrease in surface area was found to be linearly correlated with the linear increase of weight loading. This indicates that no severe pore blocking is occurring upon the introduction of the phosphorus into the zeolite, even for the sample with the highest weight loading.

All samples showed a similar external surface area value (~55 m²/g) indicating that even at the highest phosphorus loading there were no large phosphorus deposits on the external surface revealing that all phosphorus is predominantly deposited into the pores. This observation suggests that the phosphorus actively searches out the aluminium in the zeolite framework, as was suggested by van der Bij *et al.*²¹

A small difference in the BET surface area can be observed depending on the phosphorous precursors used (Figure 7a, b). Similar physisorption results were found for the 2 wt.% samples which show almost identical micropore and external surface area. For higher weight loading samples, such as the 5DP samples, a slightly higher BET surface area and micropore volume is shown.



Effect of phosphorus on crystallinity

Figure 6, X-ray diffraction patterns from 5-30° for P and DP modified samples.

When performing a washing step after impregnation it is generally assumed that most species can be removed⁴¹. Moreover, thermal treatments are known to stabilize and fix phosphorous species to the zeolite framework, but upon washing the zeolite, a significant restoration of surface area is observed (Figure 7c) for all samples. Performing a subsequent calcination step almost completely restores surface area of the orthophosphoric acid modified zeolite (W_C-2P[Z]). Interestingly, this same effect cannot be observed when calcining the diammonium phosphate modified sample (W_C-2DP[Z]). Washing the DP impregnated sample improves surface area in a similar extent as the phosphoric acid impregnated sample however, subsequent calcination of the washed sample results in a decrease in surface area close to the initial pre-washed value.

Even though a large restoration of surface area is observed after washing, it does not increase beyond the surface area determined for the parent zeolite suggesting that application of a washing and subsequent calcination step does not induce major desilication or dealumination. Washing of higher weight loadings (e.g. 5 wt.%) results in a minor restoration of surface area and therefore, longer washing steps may yield higher restoration of surface areas.

3.3 FT-IR

FT-IR was used to get a better understanding of the interaction between phosphorus species and the zeolite. In Figure 8, the FT-IR spectra taken on dried self-supporting wafers are shown. All the spectra obtained were baseline corrected and normalized.



Figure 7, physisorption data from the orthophosphoric acid prepared samples (a) and the diammonium phosphate prepared samples (b). Micropore, and external surface areas obtained from physisorption data of various washed and calcined samples (c).

The IR spectrum of a zeolite consists mostly of 3 structural peaks which correspond to Si-O bond vibrations, originating from zeolite vibration modes, but when comparing the hydroxyl region (4000-3000 cm⁻¹) clear differences can be seen (Figure 8). For the unmodified ZSM-5, peaks at 3610 cm⁻¹ and 3660 cm⁻¹ are assigned to bridging hydroxyls (Si-(OH)-AI) and to extra framework aluminium (EFAI, Al-OH), respectively. The peak present at 3745 cm⁻¹ is assigned to silanol groups on the external surface of the zeolite crystals and the peak at 3783 cm⁻¹ corresponds to partially dealuminated aluminium hydroxyl species.

With the introduction of different phosphorous compounds, the overall intensities for all peaks drop accordingly. For 2P/2DP samples, the 3610 cm⁻¹ peak starts to decrease indicating a decrease in free bridging hydroxyl, resulting in lower acidity. The use of higher weight loading (5 wt.%) reveals a strong reduction of free hydroxyl groups due to the lower intensity of this peak. The peak corresponding to free EFAI species decreases in intensity upon the introduction of phosphorus, indicating the formation of AlPO phases, which results in the binding of the terminal Al-OH groups to the phosphorous compounds. Furthermore, a peak at 3670 cm⁻¹, present in all the phosphorous modified samples, indicates the presence of P-OH.

Comparison between the FT-IR spectra of phosphorous modified samples with different precursors can be observed. In general, the peak of external silanols at 3745 cm⁻¹ is noticeably smaller using the DP-modified zeolites in comparison with the P-modified samples, indicating some deposition of the phosphorus on the outside of the particle.





[Z80] samples show that both silanols and bridging hydroxyls decrease upon the introduction of phosphorus, without differences found between the use of either precursor. The use of a high silica/alumina ratio does show a major decrease in external silanols in comparison to the [Z] samples upon the introduction of phosphorus, indicating high deposition of phosphorus on the external surface of the zeolite (Figure 8c, d). This observation is in accordance with the physisorption results, which revealed that more phosphorous species can be deposited on the external surface with higher silica/alumina ratios (see Figure S1). Thus, a higher aluminium content results in a larger interaction of the phosphorus within the zeolite pores where predominantly the aluminium is located, while impregnation of phosphorus in zeolites with lower aluminium contents results in higher deposition on the external surface area. FT-IR experiments were also performed on the washed/calcined samples but did not lead to any significant changes in comparison with the impregnated sample (see Figure S2).

3.4 Acidity of modified zeolite

3.4.1 NH₃-TPD

To test the strength and total amount of acid sites of the modified ZSM-5 zeolite NH₃-TPD was performed (Figure 9). The ZSM-5 zeolite shows two desorption peaks corresponding to weak and strong acid sites, as was expected. Upon the impregnation of the zeolite with phosphorus the overall concentration of acid sites decreases (Figure 9a, b). Both weak and strong acid sites seem to decrease equally until a weight loading of 2 wt.%. The use of higher P weight loadings further decreases acidity, while the excess of phosphorus (5 wt.%) almost completely removes strong acid sites.







Figure 10, Determination of acid site concentration from (a) the FT-IR spectrum were integrated to calculate Brønsted and Lewis acid sites concentration for (b) various impregnated samples and (c) washed/calcined samples.

Between the use of both precursors, a clear difference can also be observed. Using orthophosphoric acid as precursor, a higher concentration of weak acid sites is found in comparison with the diammonium phosphate precursor, while strong acidic sites are close in concentration. A further increase of weight loading, (5P[Z] and 5DP[Z]), results in the complete disappearance of strong acid sites and a broader weak acid site peak. This broader peak may suggest that new acid sites with a medium strength have been formed. Total acid site concentrations can be found in Table S1.

Washing the excess of phosphorus from the zeolite results in an improvement of acid site concentration, for the DP modified samples, and acid strength, for both modified zeolites, as can be seen in Figure 9c. This increase in acid strength is not paired with a significant increase in acid site concentration using P-modified samples, remaining similar to the unwashed samples (see Table S1). This strength enhancement in acidity reveals a lower interaction of the phosphorus with the zeolite framework. Calcination of the washed sample does not result in a further shift in strength (Figure 9d). This shift was less pronounced for lower and higher weight loadings.

3.4.2 Pyridine probed FT-IR

In order to determine type and concentration of acid sites in the zeolite, pyridine probed FT-IR spectroscopy experiments were performed (Figure 10). An advantage of using pyridine FT-IR as basic probe is that Brønsted and Lewis acid sites can be distinguished due to different vibrational peaks at 1544 and 1455 cm⁻¹, respectively (Figure 10a). Combined vibrations of both Brønsted and Lewis acid

sites are visible at 1490 cm⁻¹. The peak area was then integrated, and concentrations were calculated via equation 4, whereby A stands for the integrated value of the absorbance, ρ the weight of the pellet in mg per cm², and ε being the extinction coefficient which was earlier determined from literature as 1.67 and 2.22 cm/µmol for Brønsted and Lewis acid sites, respectively^{36,42}.

$$c(BAS/LAS) = \frac{A * 10^3}{\varepsilon(BAS/LAS) * \rho}$$
⁽⁴⁾

As previously shown by NH₃-TPD, upon the introduction of phosphorus, a decrease in acidity is observed (Figure 10b). The use of even higher weight loadings, such as 5P/5DP[Z], results in a larger decrease indicating the low concentration of Lewis acid sites left and hence, the possible conversion of all EFAI into extra framework AIPO species. A similar trend was observed with the ZSM-5 zeolites with [Z80]. Between the use of both precursors no large difference can be found in terms of acid site concentration, which is slightly in discrepancy with the TPD experiments, indicating that total acidity is lower for the diammonium phosphate modified samples. With the washed samples, a shift in acid strength can be found from NH₃-TPD, but similar acid site concentrations were observed. An increase in both Brønsted and Lewis acid sites was found using pyridine probed FT-IR after washing and calcining (Figure 10c). This difference between NH₃-TPD and pyridine FT-IR with respect to acid site concentration is likely caused due to the difference in size of the probe molecules.

According to ammonia TPD, overall acid site concentration does not increase, nevertheless pyridine FT-IR does show a slight increase in the concentration of acid sites. This suggests that even though the total concentration of acid sites does not increase after washing and calcination (W-2P[Z]/W_C-2P[Z]; NH₃-TPD), it clearly indicates that some of the acid sites that were hindered by the phosphorus excess are now easily reachable by the pyridine. This ease of accessibility to the acid sites is crucial and indicates that more acid sites are available for the conversion of 2-methylfuran and 2,5-dimethylfuran. The even further increase of acid site concentration of the washed and calcined sample (W_C-2P[Z]) suggests the same reasoning as is described above. However, in this case, the amount of acid sites is seemingly larger than the unmodified zeolite which could also be explained by the increase of weaker acid sites. Regarding the samples prepared with the diammonium phosphate precursor a different observation can be made, washing results in a slight increase in acidity, but calcination appears to have no effect, which is in accordance with argon physisorption where similar trends upon washing are observed.

3.5 Insights into formed species by solid state NMR analysis

To get more insight into the type of phosphorous species formed on the zeolite structure multiple solidstate NMR experiments were performed (²⁷Al, ²⁹Si, ³¹P, ¹H-³¹P MAS, and 2D ²⁷Al MQMAS NMR).

3.5.1²⁷Al ssNMR

Presence of tetrahedral framework aluminium species (TFAI) and octahedral aluminium species (OhAI), corresponding to EFAI species, at 55 and 0 ppm are shown in the ²⁷AI NMR spectrum for the parent zeolite, respectively (Figure 11a)²⁶. Literature suggests that octahedral aluminium could also be present in the form of framework aluminium coordinated with water⁴³, but FT-IR experiments confirm the extra framework origin of the OhAI.

Addition of phosphorus to the zeolite results in the formation of two new peaks at 40 and -10 ppm assigned to TFAI and OhAI species in a distorted environment. In this case, phosphorus interaction results in the formation of distorted TFAI (TFAI_{dis}) and AIPO, respectively. Interactions are either by direct binding or electrostatic interactions, but a final conclusion cannot be assigned just from ²⁷AI NMR results. The peak at -10 ppm still shows a major overlap with the non-distorted EFAI species, indicating that not all the extra framework aluminium species are converted to AIPO species.

With higher phosphorus weight loadings (5DP[Z]), a complete shift in octahedral aluminium species is observed (-13 ppm), indicating the binding of mostly all the extra framework aluminium with phosphorus, which is in accordance with the FT-IR experiments shown in Figure 10b. Hereby, we suggest that a large decrease in Lewis acid sites is observed due to formation of AIPO species. A further decrease in TFAI species along with a slight increase in TFAI_{dis} species is found in comparison with the 2P/2DP[Z] sample. The presence of pentahedral coordinated aluminium species is observed for the 5DP[Z] sample (15 ppm) which can be assigned to a partial dealumination of the zeolite framework. This suggests that pentahedral sites may correspond to phosphorus species being bound to the zeolite framework, as peaks corresponding to free partial dealuminated hydroxyl groups were not observed within the FT-IR experiments (Figure 8).

Concerning the ²⁷Al NMR experiments for the washed and calcined samples (Figure 11b) no large differences were observed.



Figure 11, ²⁷Al of phosphorous impregnated samples (a.) and washed/calcined samples (b.).



Figure 12, ²⁹Si NMR spectra of phosphorous impregnated samples (a), and the washed/calcined samples (b)

3.5.2²⁹Si ssNMR

²⁹Si ssNMR spectrum of the unmodified zeolite show two peaks at ca. -105 and -112 ppm (Figure 12a), which are assigned to framework aluminium (Si(OSi)₃(OAl)₁) and silica centres (Si(OSi)₄), respectively²⁶. The addition of phosphorus results in the decrease of framework aluminium species with increasing weight loading, as was demonstrated by ²⁷Al ssNMR and FT-IR. Remarkably, the amount of silica species also decreases with higher phosphorus weight loadings and shifts to lower chemical shifts which can be attributed to a distortion in the chemical environment due to the presence of phosphorus. Even after calcination, no peak is observed for silicon phosphates at -214 ppm, however, direct binding of the phosphorus to the silica cannot be discarded. Overall, washing appears to have no influence on the ²⁹Si NMR spectra (Figure 12b).

3.5.3³¹P ssNMR

With the addition of phosphorus to the zeolite framework different species can be formed however, certainty of which species are being formed is still controversial making identification of species challenging. Next to this, the formation of the phosphorous species within the zeolite pores is highly dependent on the synthesis method used, especially the heat treatment after impregnation. Long calcination times could result in the formation of extra framework species, and even the formation of silicon phosphate species^{26,44}.

 31 P ssNMR spectra shown in Figure 13a, reveal that the peak at -7 ppm was found to be the highest in intensity, which is assigned to either aluminium bound orthophosphate⁴⁵ or end groups in pyrophosphate (P₂O₇) species⁴⁴, with the latter being the most common assignment in literature^{27,44}. Furthermore, the peak at -14.5 ppm is assigned to middle chain groups as can be found in triphosphate/triphosphoric acid species^{26,44}.

Assignment of small phosphorous species is in agreement with literature, but the assignment of species at lower chemical shifts is rather challenging. Phosphoric species at lower chemical shifts, specifically between -30 and -50 ppm, are known to be AIPO and/or condensed polyphosphates^{26,44–46}. With especially the peak at -42 – -46 ppm readily assigned to branched phosphates, such as phosphorus pentoxide species⁴⁴. Several articles also suggested the formation of silicon phosphate phases such as silicon hydrogen orthophosphate (Si(HPO₄)•H₂O) or silicon hydrogen tripolyphosphate (SiHP₃O₁₀). Silicon phosphate species appear at -35 ppm in ³¹P NMR, however presence of those species cannot be



Figure 13, ${}^{31}P$ (a.) and ${}^{1}H-{}^{31}P$ CP (b.) NMR spectra of the phosphorous modified samples.

concluded from our experiments^{26,44}. This suggests that under the experimental conditions used in this work, formation of silicon phosphate phases is highly unlikely. Further assignments of peaks between -20 and -35 ppm remains challenging. According to literature, this region corresponds to phosphorous species bound with aluminium in the second coordination sphere, but this assignment does not distinguish between tetrahedral or octahedral aluminium species⁴⁵. Furthermore, peaks within this region can also be attributed to phosphorus middle chain groups from condensed polyphosphates. Next to these mono- or bidentate structures, other interactions might take place around -29 ppm, such as tetrahedral phosphate⁴⁷ or phosphate ligands binding to aluminium^{27,48} together with extra framework AlPO at -32 ppm⁴⁹. In short, the high degree of overlap occurring within -20 to -35 ppm region makes the assignment of the possible interactions between phosphorous and aluminium rather challenging.

With higher weight loadings the appearance of new peaks arise in the ³¹P NMR spectrum, especially the formation of the peak at 0 ppm, assigned to monomeric phosphate²⁶. Furthermore, higher intensities corresponding to end chain and middle chain groups of pyrophosphates (-7 ppm) and triphosphates (-14 ppm) are also observed. In the -20 and -40 ppm region a significant increase in intensity compared with lower phosphorus loadings is observed which is caused due to a combined increase of both aluminium-phosphate interactions and condensed polyphosphate species.

To gain further insights on the influence of phosphorous species with the zeolite framework ${}^{1}H^{-31}P$ cross polarized (CP) NMR experiments were performed (Figure 13b). With this technique, interaction between the phosphorus and the proton from, for example, Brønsted acid sites can be detected. 2P[Z] displays two clear peaks at -7 and -14 ppm which are assigned to interactions of phosphate groups from polyphosphate species attached to Brønsted acid sites. This interaction between Brønsted acid sites and small phosphates appears only to be present using the orthophosphoric acid precursor. These results clearly indicate that there is a difference between both precursors; the samples prepared with orthophosphoric acid seem to have more interactions with the acid sites in comparison with the diammonium phosphate precursor at low phosphorus loadings. This absence of interaction between phosphorus and hydrogen cannot readily be explained as the ³¹P NMR spectrum show high similarities between the use of both precursors. However, usage of high weight loading phosphorus (5DP[Z]) does show interaction in the ¹H⁻³¹P NMR spectrum between phosphorus and hydrogen (Figure 13b), which suggests that the same interactions are also possible with the diammonium phosphate precursor but at higher weight loadings. This interaction between stress that the same interactions are also possible with the diammonium phosphorus confirms the



Figure 14, ³¹P NMR (left), and ¹H–³¹P CP NMR (right) spectra of various washed samples.

interaction of the phosphorus without direct binding to framework aluminium, which is according to the model suggested from literature by Blasco et al.¹⁷ in which the phosphorus is "protonated" by the acid site.

After washing small phosphates seem to be removed, such as pyrophosphates or triphosphoric compounds, which are known to be soluble in water. This elution of small phosphate species can indeed be observed since lower intensity is displayed by -7 and -14 ppm peaks (Figure 14a), indicating the removal of pyrophosphate and triphosphate, respectively. This observation can be further confirmed by ${}^{1}\text{H}{-}^{31}\text{P}$ CP NMR depicted in Figure 14b, which show a significant decrease in ${}^{1}\text{H}{-}^{31}\text{P}$ CP signal at -7 and -14 ppm indicating the absence of interaction between free phosphate species and Brønsted acid sites. This decrease in interaction between the Brønsted acid sites and phosphorus is in accordance with NH₃-TPD and Pyridine FT-IR experiments, which show an increase in acidity after washing.

Besides the removal of smaller phosphates, removal of condensed polyphosphates is also observed showing a large decrease in intensity (-42 ppm; ³¹P ssNMR). This suggests that condensed phosphates are being hydrolysed during washing. In literature, it is known that highly condensed phosphates such as phosphorus pentoxide or phosphorus trioxide, which have highly branched cage like structures, can be hydrolysed leading to monomeric orthophosphoric acid⁵⁰, which is water soluble therefore easily removable from the zeolite framework.

Performing a calcination step after washing results in a restoration of phosphorus pentoxide species with a similar intensity as the one obtained for the unwashed samples. Strikingly, during calcination, the pyrophosphate and triphosphate species (-7; -14 ppm) are converted into new highly condensed phosphorus such as the phosphorus pentoxide species. This formation of phosphorus pentoxide is thermodynamically favourable under the harsh dehydrating conditions applied during calcination.

The re-formation of phosphorus pentoxide in the P-modified samples is expected to take place by the consumption of small phosphorous species present which are not interacting with the zeolite framework, thereby freeing up the surface area of the P-modified zeolite. The fact that this is increase in surface area is not observed for the DP-modified sample after washing and calcination could indicate that the formation of another phosphorous species is more favourable.

3.5.4 2D ²⁷AI MQMAS ssNMR

The use of 2D ²⁷Al Multiple-Quantum Magic Angle Spinning (MQMAS) ssNMR allows to further identify interactions between phosphorus and the zeolite framework (Figure 15). The parent zeolite ([Z], Figure 15a) displays two symmetric peaks, which are ascribed to tetra- and octahedral aluminium sites in the system. With the addition of phosphorus to the system, (2P[Z]/2DP[Z]; Figure 15b), a third peak is observed which corresponds to TFAl_{dis} species (40 ppm, 60 ppm). This shift indicates a higher quadrupolar environment, which arises from the presence of phosphorus next to the TFAl species in the zeolite. The same applies for the peak assigned to octahedral species, which shifts due to the formation of AlPO species.

At higher weight loadings (5DP[Z], Figure 15c), the octahedral peak is completely shifted towards lower values, suggesting that most of the EFAI present has been converted to extra framework AIPO phases, as was earlier observed by FT-IR and ²⁷AI NMR experiments. A higher phosphorus weight loading (5 wt.%) results in a larger distortion of the TFAI species, as two new interactions can be observed in this region one at (20 ppm, 60 ppm) and one at (40 ppm, 40 ppm). The former interaction is most likely the extended distortion as was already found for the lower weight percent phosphorus (2P/2DP[Z]), while the appearance of the latter more symmetric peak is most likely the appearance of a new interaction between aluminium and phosphorus, which cannot be observed using conventional MAS NMR techniques. The higher symmetry of the peak would suggest that it could potentially be direct bonding of the phosphorus, but direct evidence for this interaction cannot be found. Pentahedral coordinated aluminium sites (10 ppm, 10 ppm) are formed at higher phosphorus loadings and corresponds to partially dealuminated species from the framework.



Figure 15, 2D²⁷AI MQ MAS NMR spectra of [Z] (a.), 2P[Z]/2DP[Z](b.), 5DP[Z] (c.), and combination of said samples (d.).

²⁷Al NMR spectra of the washed samples does not show much difference, but slight differences could be observed in the 2D ²⁷Al MQMAS NMR spectra after calcination (Figure 16). With the application of a washing and subsequent calcination step higher distortion of the asymmetric TFAl_{dis} peak (±35 ppm, 60 ppm) is observed, which suggests that the aluminium is influenced by a higher quadrupole environment due to increased phosphorus presence. This higher quadrupole environment results in a stronger interaction between phosphorus and the zeolite framework.



Figure 16, 2D ²⁷Al MQ MAS NMR spectra of washed and washed/calcined sampled.

4. Conversion of furan over phosphorous modified ZSM-5

4.1 Conversion of 2-methylfuran

Catalytic activity of the phosphorous modified catalysts was tested in the conversion of 2-MF and 2,5-DMF using the setup described in Figure 5a. The highest conversion of 2-methylfuran was obtained when using the benchmark ZSM-5 catalyst, with the phosphorous modified zeolites giving lower conversion values.

The formation of CO₂ during the reaction indicates the formation of hydrocarbons from 2-methylfuran via isomerisation and decarbonylation/decarboxylation reactions forming a variety of lower olefins, benzene, toluene, and a variety of alkylated benzenes, depending on the length of the olefin. This is expected to be the main route of aromatic production during the reaction³⁰. Selectivity to benzene is higher than selectivity to toluene suggesting that the aromatic formation does not purely go via Diels-Alder cycloadditions, as this would result solely in the formation of toluene. Exact reaction pathways of benzene formation are not readily known but a hypothesis is that it could be formed via olefins similarly to the Methanol-to-Olefins process. Other proposals found in literature suggest that benzene can be formed from the cracking of benzofuran, which is suggested to be formed via Diels-Alder cycloaddition of 2 furan molecules³⁰. Time-resolved UV-Vis DRS spectra were monitored to gain insights on the formation mechanism of aromatics during the reaction and to spot difference between the non-modified and modified phosphorus catalysts. However, when comparing different catalysts, no significant differences were observed in terms of peak evolutions (supporting information, Figure S6), concluding that both type of catalysts undergo similar reaction mechanisms. A detailed study in the UV-Vis assignment is specified in Table S3.

Addition of phosphorus results in a lower activity with increasing weight loading of phosphorus (Figure 17), which can be assigned to the lower acidity of the modified zeolite. Formation of BTX is found to be lower in comparison with the parent zeolite. An identical selectivity towards BTX can also be observed with the diammonium phosphate precursor. When using DP-modified zeolite as catalysts, a higher conversion is obtained followed by a higher formation of CO_2 (Figure S3) while having similar selectivity to aromatics as the P-modified samples.



Figure 17, Conversion of 2-methylfuran, and production of BTX over various phosphorous modified zeolites.

4.2 Conversion of 2,5-dimethylfuran

Conversion of 2,5-DMF lead to a similar product distribution as its analogous where benzene is the dominant BTX product (Figure 18). Formation of xylene which could be found with 2-MF, is significantly lower when using 2,5-DMF. If the mechanism would proceed via Diels-Alder cycloaddition, the formation of xylene would be the most favourable, absence of significant xylene production therefore suggests different formation mechanisms. Furthermore, production of benzene and toluene shows similar ratios as was found during the conversion of 2-MF. Besides the formation of aromatics, a significant amount of CO₂ is being formed (Figure S3) suggesting that aromatics formation from 2,5-DMF via decarbonylation/decarboxylation is preferred.

Addition of phosphorus to the zeolite framework results in a lower formation of BTX aromatics upon increasing weight loading when compared to the parent zeolite. In contrast to the catalytic results obtained for the aromatisation of 2-MF, comparable conversions values are observed in comparison with the parent zeolite. The highest conversion was obtained when using the 2DP[Z] sample, which is in accordance with the increased formation of CO_2 . Thus, in this case, the addition of phosphorus results in the reduction of side reactions like coke formation. In short, due to a higher formation of CO_2 the samples prepared with the DP precursor show higher conversion during the aromatisation of 2,5-DMF, than the samples prepared with the P precursor.

4.3 Effect of washing on furan conversion

Catalytic tests for the washed and washed/calcined samples during 2-MF aromatisation resulted in a much lower conversion and an improved BTX yield in comparison to the unwashed samples (Figure 19a), with toluene selectivity considerably being enhanced in comparison with the unmodified parent zeolite. This increase in selectivity can mostly be assigned to an enhancement of acidity and better accessibility of the acid sites as is determined by pyridine probed FT-IR and argon physisorption. The enhancement of selectivity could also be attributed to the on-average weaker acid sites of the modified zeolites, thereby resulting in more suitable acid sites for the formation of BTX and less coke formation. Therefore, washed and washed/calcined samples yield improved catalytic performance within the conversion of 2-MF when using the catalyst prepared with the orthophosphoric acid precursor.

This improvement can also be found with the conversion of 2,5-DMF (Figure 19b) in which a considerable enhancement in benzene and toluene selectivity can be observed between the washed/calcined samples and the unwashed samples.





As revealed by argon physisorption and pyridine probed FT-IR, acidity and surface area of the diammonium phosphate modified samples did not improve after washing and calcination as with the orthophosphoric acid prepared samples. This improvement in acidity was also observed in the catalytic performance, in which P-modified samples yield better performance for both 2-MF and 2,5-DMF than the DP-modified samples, due to higher BTX selectivity.

In short, surface area does not seem to be a key factor in the improvement of catalytic performance as acidity, since the diammonium phosphate prepared samples show a similar increase of surface area after washing. With the introduction of phosphorus from the orthophosphoric acid precursor more suitable acid sites are formed, which results in improved catalytic performance. Therefore, the improved surface area is not the only reason for the improved catalytic performance, and we suggest that it is a synergetic effect between the increase of acidity and surface area what yields an improved catalytic performance.

4.4 Analysis of coke formation

As was already mentioned, a significant amount of coke is formed during the reaction due to the large number of side reactions. The formation of aromatics could also further evolve to the formation of side products such as benzofuran, which in general could also be regarded as a deactivation product. Larger species such as anthracene, pyrene, or even higher condensed coke species could be formed on the external surface area of the zeolite particles eventually leading to catalyst deactivation.



To analyse the formation of coke during the reaction, thermogravimetric analysis (TGA) was performed on the spent zeolite catalysts after an one hour reaction (Figure 20). In all samples significant loss of mass can be found around 550°C, which corresponds to the burn-off of carbon-rich polycyclic aromatic species (hard coke). Furthermore, multiple peaks can be observed within the region between 150° C – 400° C caused by the burn-off of long, or branched hydrocarbons, which are more hydrogen-rich carbon deposits (soft coke or oligomers), potentially formed within the pores of the zeolite framework^{42,51}.

Spent catalysts obtained after the conversion of 2-MF result in both the formation of soft and hard coke (Figure 20a). Addition of the phosphorus to the zeolite results in a decrease in hard coke, while presence of soft coke remains similar. The presence of the phosphorus does seem to influence the formation of different type of soft coke species due to the formation of two different peaks at the low temperature regime. One of the peaks shifts to a higher temperature while the other shifts to a lower temperature, indicating bigger and smaller soft coke species present, respectively. In the case of the diammonium phosphate modified samples, coke production is higher in comparison with the parent zeolite which could be explained by the higher conversion of 2-MF and the higher formation of CO_2 by these samples.

In the case of 2,5-dimethylfuran conversion, a difference can be observed in the type of coke species formed (Figure 20b). With the phosphorous modified samples, a similar formation of hard coke is observed, but additionally a new type of coke is also observed. This can be explained by the desorption peak in the low temperature regime (around 120°C), which is caused due to the formation of oligomers from 2,5-DMF in the presence of the phosphorus.



Washing and calcination of the orthophosphoric acid prepared samples result in a higher selectivity towards BTX and lower conversion. The impregnated 2P[Z] sample already showed a mild decrease in coke formation in comparison with the parent zeolite, but the washed and the washed/calcined samples show an even further reduction of coke formation (Figure 20c). The washing step significantly reduces the amount of hard coke being formed but increases the amount of soft coke, while the subsequent calcination step after washing further reduces the amount of both soft and hard coke formed during catalytic conversion of 2-MF.

During the aromatisation of 2,5-DMF, formation of coke is similar to the parent zeolite (Figure 20d). Moreover, a reduction of soft coke or oligomers (at 120°C) can be observed for the washed and washed/calcined samples. The calculated coke percentages for all the samples can be seen in Table S2. In short, addition of phosphorus to the zeolite reduces the amount of coke produced when directly converting either 2-methylfuran or 2,5-dimethylfuran to aromatics resulting in improved catalyst life-time.

5. Enhancement of Diels-Alder cycloaddition via ethylene co-feed

5.1 Conversion of 2,5-dimethylfuran

Addition of ethylene to the gas mixture should further reduce coke formation by reducing side reactions³⁰. Catalytic tests of the phosphorous modified zeolite in the co-aromatisation of 2-MF and 2,5-DMF with ethylene were performed using a setup earlier described in Figure 5b. A blank test was performed without the use of ethylene, the differences between both can be seen in Figure S4. Combination of ethylene with 2,5-DMF was already found to greatly improve selectivity towards BTX while reducing the deactivation rate of the reaction.

In Figure 21, overall BTX selectivity and 2,5-DMF and ethylene conversion values are shown. With the addition of ethylene, a BTX selectivity around 55% was found for [Z], but it is noteworthy to mention that flowing only ethylene already results in a relatively high formation of BTX (Figure S4). With the combination of both 2,5-DMF and ethylene, a significant decrease in benzene is observed, while higher selectivity's for both toluene and o/m/p-xylene isomers are obtained (Figure 21). This behaviour is expected as addition of ethylene during the reaction should promote Diels-Alder cycloadditions, resulting in higher xylenes production. Furthermore, an increase in toluene selectivity is also obtained over benzene and o/m/p-xylene suggesting that aromatics are also formed via other reaction mechanisms than via Diels-Alder cycloaddition. This higher formation of toluene can be explained as a higher alkylation degree caused by the presence of propylene in the reaction mixture (Figure S5).

The use of phosphorous modified zeolites as catalyst results in a lower BTX selectivity. Besides reduction of BTX, phosphorous modified samples show a lower conversion of ethylene when being co-fed during the aromatisation of 2,5-dimethylfuran. Performance of the washed phosphorus modified zeolites results in the improvement of BTX formation in comparison with the non-washed zeolites, with especially a larger selectivity to toluene observed. Difference in conversion can be found when co-



Figure 21, Catalytic data of 2,5-dimethylfuran conversion by addition of ethylene. With the carbon selectivity of BTX (left and middle) and the conversion of both 2,5-dimethylfuran and ethylene (right).

feeding ethylene, with the washed samples showing slightly increased conversion of ethylene compared to the unwashed impregnated zeolites. This conversion of ethylene seems to be the driving factor in increasing selectivity of BTX during the reaction, indicating that the higher conversion levels of ethylene result in a higher production of BTX with similar 2,5-DMF conversion.

5.2 Conversion of 2-methylfuran

The addition of ethylene to 2-methylfuran (Figure 22) showed similar trends as the ones observed for the 2,5-DMF aromatisation. Conversion of 2-MF yields similar selectivity to both benzene and toluene, while selectivity to o/m/p-xylenes are relatively low. Upon ethylene co-feeding, toluene and o/m/p-xylene formation increases with a significant decrease in the formation of benzene. As was already concluded from 2,5-DMF, a decrease in benzene is in accordance to the enhancement of Diels-Alder type cycloaddition reactions due to the influence of the ethylene. In this case, the use of phosphorous modified zeolite (specifically 2wt.% phosphorus zeolite) in combination with the addition of ethylene results in a higher yield of toluene. This high carbon selectivity towards toluene is also found when using the diammonium phosphate prepared samples as catalyst. Washing/calcination of the phosphorous modified sample appears to have no positive effect on the reaction, which is in contrast with direct feeding of 2-methylfuran which shows increased performance upon washing excess phosphorus.

5.3 Analysis of the total carbon balance

The use of phosphorous modified zeolites was already found to have a positive effect on reducing coke formation with direct conversion of either 2-methylfuran or 2,5-dimethylfuran. With the addition of ethylene, selectivity towards BTX improved showing a larger decrease in coke formation during the reaction. After determining the amount of coke, a total carbon balance can be made (Figure 23). It should be noted that the only major products quantified were BTX and lower olefinic compounds such as ethylene and propylene. Furthermore, the leftover percentage of the carbon balance is assumed to



Figure 22, Catalytic data of 2,5-dimethylfuran conversion by addition of ethylene. With both the carbon yield of BTX and conversion of both 2,5-dimethylfuran and ethylene shown.

be CO/CO_2 and other non-condensable gases such as CH_4 , propane or ethane (detected by the GC but not quantified) together with other unidentified products.

Overall, conversion of 2-MF is similar for most of the samples (80-90%), while major differences can be found in terms of ethylene conversion with the parent zeolite giving the highest ethylene conversion (Figure 23a). In comparison, all phosphorous modified samples show significantly lower conversion of ethylene. 2P[Z]/2DP[Z] catalysts show similar BTX yield in combination with a lower conversion of ethylene, while formation of coke is found to be lower with the phosphorous modified samples. As was already mentioned, phosphorous modified zeolite does not seem to have a positive influence on the BTX production while it reduces coke formation (especially hard coke) in comparison with the parent zeolite. This results in a non-identified product fraction which is relatively large in comparison, which could mean that more CO/CO_2 is produced, but this cannot be confirmed due to a large number of possible compounds being responsible for the non-identified fraction. An identical observation could also be made for the washed/calcined samples, which also shows lower selectivity to BTX aromatics during the conversion of 2-MF (Figure 23a) and a relatively large non-identified fraction.

The usage of 2,5-DMF (Figure 23b) shows significantly higher formations of BTX over the usage of 2-MF. Conversion levels of 2,5-DMF were similar with respect to each sample, and only differences can be found in terms of ethylene conversion. In comparison with 2-MF, ethylene conversion is mostly identical. Furthermore, formation of coke is also found to be lower, with increasing BTX formation of washed/calcined samples in comparison with the non-washed samples. The higher formation of BTX while using 2,5-DMF, and the lesser coke formation during the reaction suggests that conversion of 2,5-DMF using washed samples is more favourable when using ethylene as co-feed.



6. Conclusion

The post-synthesis modification of ZSM-5 with phosphorus was achieved via wetness impregnation using different phosphorous precursors to obtain weight percentages in the range of 1-5%. These phosphorus weight loadings were obtained using two different phosphorous precursors, orthophosphoric acid (H₃PO₄), and diammonium hydrogen phosphate ((NH₄)₂HPO₄). Addition of phosphorus to the zeolite results in several physicochemical changes. Acidity, especially strong acid sites, decreases with increasing weight loading of phosphorus as was confirmed by both NH₃-TPD and pyridine probed FT-IR. Besides acidity, a decrease in surface area and micropore volume is also observed with increasing weight loading the deposition of most of the phosphorus in the zeolite pores. In comparison between both phosphate precursors no large physical differences were observed on the modified zeolites.

Identification of the phosphorus species was performed via FT-IR and ²⁷Al, ²⁹Si, ³¹P NMR experiments. From ²⁷Al, and 2D ²⁷Al MQMAS NMR, peaks shift to lower chemical shift values, indicative of the close interaction of phosphorus to both TFAI and EFAI species, the latter leading to the formation of AlPO species. Appearance of pentahedral aluminium species was also observed when using high weight loadings. Addition of phosphorus results in slight dealumination of the zeolite as is observed from ²⁹Si NMR experiments. ³¹P NMR spectra revealed the presence of a high number of free monomeric and condensed phosphates. Further identification of aluminium phosphate species remains challenging. Aluminium phosphate interactions could be observed, but no distinction could be made between phosphorus interaction with tetrahedral aluminium and octahedral aluminium.

After washing, the excess of free phosphorus was removed and phosphorous pentoxide (P_4O_{10}) were hydrolysed. A subsequent calcination step results in the restoration of P_4O_{10} species, by consuming smaller phosphates. Removal of the excess of phosphorus improves surface area and acidity. This positive effect was only observed with the samples modified with the orthophosphoric acid precursor.

In general, addition of phosphorus does not lead to an increase of BTX formation. BTX formation is significantly higher with the addition of ethylene alongside either furan derivate, with toluene being the dominant product formed. Washed and calcined samples yield a higher conversion of either furan derivates, with a considerably higher selectivity to toluene in comparison with the unmodified zeolite. Phosphorus incorporation has a positive influence on the reduction of side reactions such as coke formation. A significantly lower formation of hard coke was observed specially for the washed samples. Addition of ethylene to the feed in combination with phosphorous modified zeolites results in a further reduction of coke formation.

7. Outlook

Usage of phosphorus modified zeolites is a relatively easy way to improve chemical properties of the zeolite, and results in a better stabilized acid site, but within literature there is a wide range of contradictory results which makes it hard to optimize the catalyst for a specific reaction. The interaction between phosphorus and both aluminium and silicon is largely unknown and is highly dependent on the synthesis method used. Therefore, we propose that more research needs to be performed to better understand the phosphorus-aluminium/silicon interactions.

In literature (incipient) wetness impregnation is the preferred method of phosphorous incorporation because of its ease in application. However, even though similar synthesis procedures are used, the resulting phosphorus-zeolite interactions may differ quite a lot. As an example, evidence for direct binding of phosphorus to tetrahedral framework aluminium is implied by the non-reversible nature of the interaction, but no direct evidence of this interaction has been found upon writing. More research is thus needed to understand what happens during the synthesis procedure, different precursors, on first glance, result in the same properties, but on nanoscale interactions are proven to be slightly different in nature as it was observed by ¹H-³¹P NMR. Experiments with, for example, X-ray absorption spectroscopy (XAS) or scanning transmission X-ray microscopy (STXM), could be used to further elucidate aluminium phosphorus binder interactions.

Usage of different zeolites may also prove to change product distributions, with especially larger pores sizes being interesting to look at, such as zeolite Beta or Y. As usage of zeolite ZSM-5 results mostly in the formation of toluene, while xylene, in theory, is the most favourable product. In reaction conditions it could be hard to place an ethylene molecule next to a 2,5-dimethylfuran molecule, therefore usage of a larger pore size could improve the facilitation of the Diels-Alder cycloaddition within the zeolite pores.

The enhancement of the gas phase Diels-Alder cycloaddition also has large room for improvement. A high improvement over direct conversion can already be achieved by addition of half an equivalent of ethylene with significantly longer lifetimes and higher carbon yields of BTX being found. Experimentation with different ratios and reaction temperatures should lead to more optimal reaction conditions, which was not investigated in depth in this work due to time constraints. Usage of different co-feeding reagents is also an interesting subject to investigate. Addition of propylene could also lead to different reaction distributions, possibly enhancing the formation of xylene from 2-methylfuran.

Phosphorous modified zeolites are also known for their dehydration reactions from ethanol-toethylene⁵², which also opens pathways to combine both reagents for *in situ* formation of ethylene in the conversion of furan-to-aromatics.

8. Acknowledgements

I want to acknowledge the following people for helping me this past year with my master's thesis. Beatriz Luna Murillo for being my daily supervisor, and Pieter Bruijnincx and Florian Meirer for examining my thesis. Furthermore, I want to thank Alesandra Lucini Paioni for performing all the solid state NMR experiments, and Dennie Wezendonk for the large amount of TGA samples he measured during my master's project.

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10. Supporting Information



Figure S1, External surface area of zeolites with SiO₂/Al₂O₃ ratios of 30 and 80.

In Figure S1 the difference in external surface area can be found for the usage of 2 different silica/alumina ratios, namely 30 and 80. Decrease in external surface area can be observed using a high weight loading on [Z80], while this does not happen on [Z30].

Table S1, Table containing acid site concentrations determined via two different techniques, NH₃-TPD, and pyridine FT-IR.

Acid site concentrations		Pyridine FT-IR [μmol/g]		
Sample	NH₃-TPD [mmol/g]	Brønsted	Lewis	
[Z]	1.014	104.9 ±10.81	37.83 ±5.224	
1P[Z]	0.714	118.4 ±5.26	45.01 ± 2.206	
2P[Z]	0.543	80.81 ±1.93	31.37 ±3.609	
2DP[Z]	0.446	74.01 ±4.344	21.64 ±0.396	
5P[Z]	0.272	38.12 ±1.843	9.977 ±0.0474	
5DP[Z]	0.247	35.7 ±1.649	8.136 ±0.0161	
W-2P[Z]	0.560	89.44 ±2.105	34.55 ±0.939	
W_C-2P[Z]	0.570	116.78 ±8.105	42.73 ±1.455	
W-2DP[Z]	0.526	81.04 ±3.230	25.81 ±1.161	
W_C-2DP[Z]	0.608	82.99 ±0.4605	31.25 ±1.858	



Production of CO_2 during conversion of either 2-methylfuran or 2,5-dimethylfuran can be seen in Figure S3. With both reagents a larger amount of CO_2 accompanied with a higher conversion can be observed for the DP modified samples. This higher conversion leads to the slightly higher formation of coke for the DP-modified samples.



Figure S3, CO2 vs Conversion of various modified zeolites.

Blank measurements of various GC experiments can be seen in Figure S4. By using only MF/DMF in the reaction a higher yield of benzene can be observed in comparison with co-feeding MF/DMF plus ethylene. Usage of only ethylene in the reaction already results in the relatively high formation of BTX aromatics. Combination of both flows results in a net higher BTX yield in comparison by addition of separate flows.



Figure S4, combination of blank measurements using only one of either reagent for both 2-methylfuran, 2,5-dimethylfuran, and ethylene.

2-MF	Percentage Coke (%)	MF + ethylene	Percentage Coke (%)
[Z]	8.97	[Z]	12.1
2P[Z]	8.30	2P[Z]	4.34
W-2P[Z]	8.23	W-2P[Z]	6.14
W_C-2P[Z]	8.04	W_C-2P[Z]	6.03
2DP[Z]	8.72	2DP[Z]	2.38
W-2DP[Z]	-	W-2DP[Z]	3.17
W_C-2DP[Z]	-	W_C-2DP[Z]	2.75

Table S2, Absolute coke percentages of various reactions with or without ethylene co-feed in percentages.

2,5-DMF	Percentage Coke (%)	DMF + Ethylene	Percentage Coke (%)
[Z]	8.42	[Z]	3.44
2P[Z]	9.10	2P[Z]	2.56
W-2P[Z]	6.81	W-2P[Z]	2.33
W_C-2P[Z]	8.39	W_C-2P[Z]	3.26
2DP[Z]	9.99	2DP[Z]	2.91
W-2DP[Z]	-	W-2DP[Z]	2.49
W_C-2DP[Z]	-	W_C-2DP[Z]	3.31



Figure S5, Chromatogram showing presence of methane, ethane, propylene, and propane in the reaction mixture.



Table S3, Assignment peaks from UV-Vis data (Figure S6).

Figure S6, UV-Vis spectra of various reactions with both 2-methlfuran, and 2,5-dimethylfuran. Both reactions show identical UV-Vis patterns and modifying the zeolite with phosphorus does not change this pattern. Hence can be concluded that no large differences in mechanism can be observed from UV-Vis.