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Variation of temperature and time on stream in the conversion of methanol to hydrocarbons using a catalytic fixed bed reaction

Parameter alteration on an home-made catalytic fixed bed reactor using a ZSM-5 zeolite catalyst

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Abstract

The Methanol to Hydrocarbons reaction was investigated at different reaction temperatures (400°C, 450°C, 500°C) and times on stream (TOS) (2 hours, 4 hours, 6 hours at 450°C) using a home-made setup. The results show a clear influence of the varied variated parameters over product distribution and catalyst coking. The catalyst was analysed using TPD, XRD, N_2 physisorption and TGA, which elucidated changes in structure and activity between the pristine and spent samples. It was made clear that higher temperatures lead to faster and more extensive formation of coke, when compared to low-temperature conditions at the same TOS. Coke generation goes to reduce the active surface, volume and acid sites of the catalyst, but does not appear to extensively modify its framework.

Gas chromatography was employed in the characterisation of gaseous and liquid products, revealing that at higher temperatures, alkenes and BTX aromatics are preferred over their corresponding alkanes and poly-substituted aromatics. The proposed explanation for the observed changes was identified in hydrocarbon cracking, catalyst coking and dealumination, which can change the selectivity of the final products and the coking processes of the catalyst.

1. Introduction

The Methanol to Hydrocarbons (MTH) reaction has been increasingly explored in the last decades due to its potential in producing hydrocarbons without depending on oil but rather on low cost feedstocks such as natural gas, coal or biomass[1]. The reaction is catalysed by zeolites, crystalline aluminosilicates possessing strong Brønsted acidity dispersed within a microporous network. Their frameworks, made up of 4-coordinated atoms forming tetrahedra linked together by their corners, are a defining feature of zeolites and allow for a rich variety of structures[2,3].

Although first deemed interesting mainly for aromatic products, it was soon discovered that the MTH reaction could be fine-tuned to obtain all kinds of hydrocarbons, which allowed for the selective formation of olefins and alkanes[5]. Currently, its potential is being explored in the production of fuel (MTG process)[6] and light aromatic hydrocarbons (benzene, toluene and xylene, usually abbreviated as BTX), which are used as intermediates in the petrochemical industry.

As the technology is quite recent, its mechanism is still under investigation, with several plausible theories available. At the moment, the most widely accepted version is the dual cycle hydrocarbon pool mechanism[5], showed in Figure 1 as described by Martinez-Espin et al.[4].
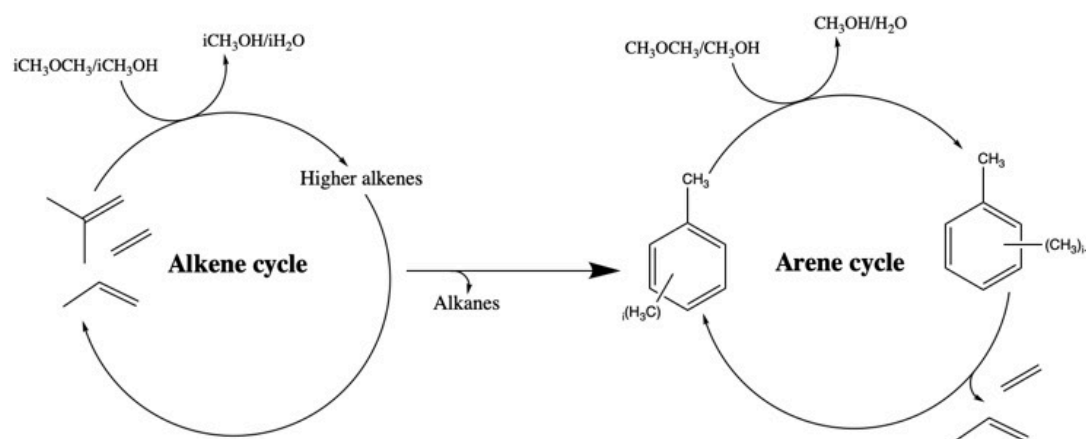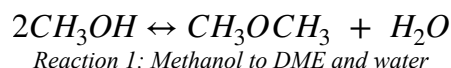

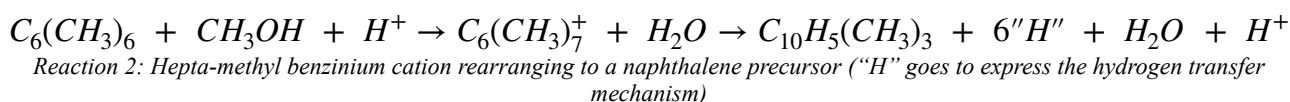Figure 1: Dual cycle hydrocarbon pool mechanism [4]

This theory suggests that methanol dehydrates to dimethyl ether (DME) (Reaction 1), to which follows the formation of olefins, aromatic hydrocarbons and alkanes.

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

Reaction 1: Methanol to DME and water

However, through the length of the catalyst bed the reaction proceeds differently. The catalyst bed can in fact be divided into three zones, if conversion of methanol is assumed to be 100%. The first of the three areas is the initiation zone. It is usually described as the inlet segment and it is the location in which methanol is partially converted to DME, parallel to the slow formation of autocatalytic species such as alkenes and arenes. The accumulation of these species eventually leads the autocatalytic reaction to dominate over product formation, which generates the second area, the so-called autocatalytic zone. The last section corresponds to the bed outlet and is known as the product zone. Here, oxygen-containing molecules (oxygenates) are fully consumed and only hydrocarbon interconversion reactions take place[7].

In the formation of the desired products, (poly-)aromatic coke precursor molecules are given space to form. Their gradual increase in dimensions eventually leads them to reach a size too big to pass through the catalyst's pores, which then causes clogging. As the reaction proceeds, the precursors convert to graphitic-type coke and eventually lead to catalyst deactivation[7].

The exact reaction responsible for coking and catalyst deactivation has been under investigation since the development of the MTH process and several possible explanations have been offered since. Plausible mechanisms involve reactions between methanol and hydrocarbon pool species via methylation and hydrogen transfer[8], which would lead to products that can subsequently rearrange into naphthalene precursors. An example of this explanation is given as Reaction 2.

$$C_6(CH_3)_6 + CH_3OH + H^+ \rightarrow C_6(CH_3)_7^+ + H_2O \rightarrow C_{10}H_5(CH_3)_3 + 6''H'' + H_2O + H^+$$

Reaction 2: Hepta-methyl benzinium cation rearranging to a naphthalene precursor ("H" goes to express the hydrogen transfer mechanism)

It is also believed possible that hydrocarbon pool species can react with one another to yield polycyclic coke precursors, as exemplified by Reaction 3:

$$C_6H_6 + 2C_3H_6 \rightarrow C_{10}H_6(CH_3)_2 + 6''H''$$

*Reaction 3: Formation of polycyclic coke precursor*
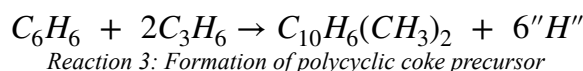
Although the catalyst specifications (topology, acid site distribution, surface modifications) influence greatly deactivation patterns and product distribution, the variation of parameters such as temperature, pressure and time on stream can also lead to substantial changes. In particular temperature and pressure can slow down or increase the deactivation rate of the catalyst and influence the extent of hydrocarbon cracking occurring during the process. Therefore all tuneable parameters need to be taken into account when evaluating catalysts' lifetimes and product selectivity. In fact, as Yarulina et al.[9] explain, the deactivation of the catalyst occurs by sections and the switch to the next reaction zone is made when the previous has reached a temperature maximum and has therefore completely been deactivated. This temperature maximum refers to the in situ rise in temperature due to the exothermic reactions occurring in the catalyst. Increasing the reactor's temperature (via temperature and/or pressure variation) would therefore theoretically expedite this mechanism, leading to a shorter catalyst lifetime.

A supplementary temperature- and pressure-dependent mechanism occurring in the reactor, which then influences the final selectivity of gaseous and liquid products, is hydrocarbon cracking. This

process has been known for more than 100 years and is mainly conducted using feedstocks obtained from petroleum and natural gas to produce olefins such as ethylene and propylene and light aromatics (BTX, butadiene)[10]. Hydrocarbon cracking substantially consists in the breakage of C-C bonds in long hydrocarbons, leading to the formation of ions (catalytic cracking) and radicals (thermal cracking) that normally rearrange in shorter alkenes[11]. As catalytic cracking is performed using zeolites at about 500°C and relatively low pressures[12], this mechanism is expected play a role in the MTH reaction by causing different product distributions as the temperature varies: for example, it can be predicted that the concentration of poly-substituted aromatics (alkyl aromatics, methyl aromatics) will decrease with increasing temperature, especially if compared to the BTX content in the corresponding liquid samples[13]. Similarly, the gas samples will likely show higher selectivity for propylene or ethylene, rather than for their corresponding alkanes propane and ethane [10,12].

In the current project, an home-made fixed bed reactor with methanol feed was made available and it was decided to observe how the reaction temperature over 6 hour long runs would affect the product distribution, while using an unmodified H-ZSM-5(23) catalyst. ZSM-5 (Zeolite Socony Mobil-5, framework type MFI) catalysts belong to the pentasil (eight five-membered rings) family of crystalline zeolites and possess the chemical formula[14]

$$Na_n AL_n Si_{96-n} O_{192} \cdot 16H_2O \ (0 < n < 27)$$
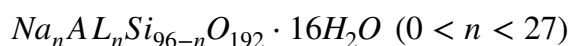
Catalyst acidity, which strongly depends on aluminium content, is vital in catalysing reactions such as hydrocarbon isomerisation and alkylation of hydrocarbons. The ZSM-5 catalyst presents a high silicon to aluminium ratio, which leads to high acidity. This characteristic, added to its highly regular 3D structure, make the ZSM-5 catalyst an ideal choice for the MTH reaction[15].

The temperatures selected for testing were equal to 400°C, 450°C and 500°C. In order to elucidate the deactivation mechanisms of the catalyst, the spent and fresh catalysts were characterised with comparable techniques, so as to determine how temperature and time on stream (TOS) affect coke formation. Tested TOS were 6 hours, 4 hours and 2 hours, and the shorter times were exclusively performed at 450°C.

2. Experimental

2.1 Catalyst and characterisation

An ZSM-5 zeolite with a SiO_2/Al_2O_3 molar ratio of 23 (abbreviated as ZSM-5(23)) was obtained from Zeolyst International (product No. CB-V2314) in the ammonia form. The received ZSM-5(23) was converted to its H-form by calcination at 800°C for 6 hours. The product was then pelletised using a bench-top pellet press at 1 ton cm^{-2} pressure for 30 sec. After, the samples were crushed manually using an Agate mortar and then sieved in 3 fractions of different diameter ranges equal to 212-300, 300-500 and 500-800 μm, from which the second was employed in the reactor setup.

The pristine catalyst and a sample of the catalyst used at 450°C were characterised via temperature programmed desorption of ammonia (NH_3-TPD or TPD) for acid site density using an AutoChem II 2920, from 120°C to 900°C.

In an ASAP 2420 Surface Area and Porosity Analyser, N_2 physisorption was conducted to determine the surface area and pore volume of the pristine and used catalyst at 500°C for 6 hours.

X-ray diffraction patterns (XRD) were acquired through a D8 Advance Powder Diffractometer with Cu Kα radiation. Using XRD, the crystallinity of the catalyst used at 400°C was observed and compared to the pristine version of H-ZSM-5(23).

A TGA 4000 analyser (PerkinElmer) was used to obtain thermogravimetric data on the spent catalysts from all runs. The analysis was performed from 50°C to 700°C under air atmosphere at 50 mL/min.

2.2 Testing

The setup was built in situ and is presented in the Piping and Instrumentation Diagram given as Figure 2. An HAZOP table was developed and is presented in Appendix B. The reactor setup corresponds to the first two steps of a normal MTH (or MTG) plant, as it only carries out the conversion from methanol to DME and then from DME to hydrocarbons, without separating the obtained products further than between gaseous and liquid[16,17]. In this project, a fixed catalyst bed was chosen, although research shows that fluidised beds are a precious resource in improving product selectivity and catalyst lifetime[9,18]. However, this solution is still under research and the nature of this project did not demand such an over-complication, therefore the fixed bed arrangement was preferred.
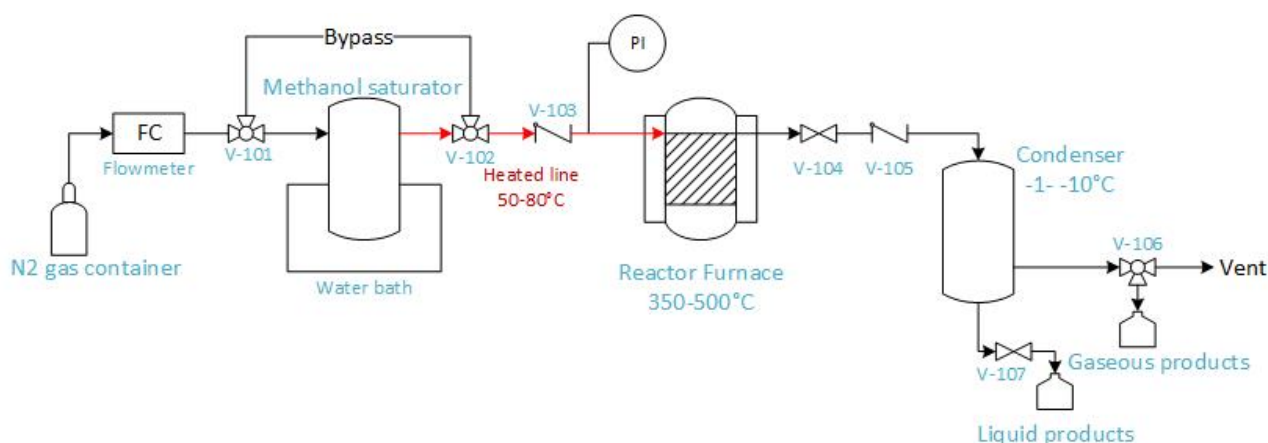

Figure 2: P&ID of the experimental setup

The system was kept under nitrogen at all times via a flow of about 10ml/min during non-operational times. To perform the experiments, the flow was increased up to 41 mL/min, with possible oscillations during the run time. The nitrogen flow was monitored via a flowmeter, while

the pressure in the system was checked through a pressure indicator. The methanol was heated up using a water bath kept at 40°C, while the amount of catalyst employed per measurement was equal to 200 mg. The catalyst was loaded each time after a thorough cleaning of the reactor and before increasing the reactor's temperature. The temperature of the cooling tower was kept at -10°C and the furnace's temperature was kept constant throughout the duration of each run, but changed according to the experiment's parameters. Each run was started as soon as the reactor would reach the wanted temperature by switching the nitrogen flow from bypass to normal (that is, opening V-101 and V-102 simultaneously), leading to a methanol flow of approximately 14.51 mL/min and a weight hour space velocity (WHSV) equal to 5.37 h^{-1}. At the end of each experiment, V-101 and V-102 were closed again, switching the system back to bypass. Nitrogen was left flowing through the system for approximately five minutes, at the end of which the reactor was set to 20°C and the nitrogen flow was reduced to approximately 10 mL/min. All electronics were shut off and the setup was allowed to cool down until the following run.

The furnace temperature was varied three times: first at 450°C, then 500°C and lastly at 400°C. These three runs were given a time on stream (TOS) of 6 hours. The experiment was then repeated two times at 450°C, once for 4 hours and once for 2 hours. The experiment was then repeated once more at 450°C for 6 hours in order to obtain more precise results with GC analysis, due to excessive water (the main side product of the MTH reaction) condensation at the exit of the reactor. The most probable cause for this phenomenon can be identified as the over-cooling of the final section of the reactor, which is in turn caused by low environment temperatures. The problem was solved by using a heat gun at approximately 300°C for 10 minutes. This situation was observed only once, therefore no further investigation was conducted over it.

Every two hours during each run, one gaseous and one liquid sample were collected and examined via gas chromatography (GC). The liquid sample was acquired first by over-pressurising the system by closing the gas vent valve. This allowed for the reaction mixture in the cooling column to condense and be released as a clear liquid with two visible phases. To prepare the sample for GC analysis, 0.3 mL of trichloromethane were added to the vial and the phases were allowed to separate. The bottom (organic) layer was removed and transferred to a GC vial, which was then sealed and sent to analysis. The aqueous layer was discarded.

Gaseous samples were obtained analogously: a valve-equipped syringe was placed in the purposely made outlet and the gas vent valve was turned towards it. This allowed for the gas to enter the syringe. It was observed that the syringe needed a manual impulse in order to start filling up. This problematic did not affect the final results, therefore no modifications were added to the system.

All spent catalysts were collected on the day following the corresponding run, in order to ensure the complete cool-down of the system, by removing the reactor from the system and by pouring the used catalyst in a vial. The samples were then analysed via thermogravimetric analysis (TGA) under air atmosphere. For this analysis, samples of approximately 10 mg were prepared. Additionally, 100 mg of the used catalyst from the first 6 hours run at 450°C were characterised through TPD, while 190 mg of the used catalyst from the 6 hours 500°C run was examined via N_2 physisorption and 190 mg of the catalyst used for 6 hours at 400°C was characterised via XRD.

Compared to literature, the setup uses already seen values for WHSV and TOS, but employs a severely larger amount of catalyst. This was deemed important due to the low availability of the setup to the students involved in the project, for whom having large amounts of catalyst per run was necessary in order to allow the preparation of multiple samples from each experiment.

3. Results and Discussion

3.1 Catalyst characterisation for fresh and deactivated H-ZSM-5(23) catalyst

3.1.1 Acid sites

The acid site distribution in the fresh catalyst and in the spent catalyst from a 6 hour-long run at 450°C was determined via TPD in order to determine how the use of the catalyst would influence the results. The observed peaks at about 230 and 410°C represent the ammonia adsorbed on the weak acid sites and strong acid sites, respectively, and are characteristic of the H-ZSM-5 zeolite[19,20]. As observed in other publications[9], the peak corresponding to strong acid sites decreases severely after use, while the weak acid sites decrease in number and become weaker, yielding a lower peak. As explained by Yarulina et al.[9], these results can point to extensive catalyst dealumination by steaming during the course of reaction, which then leads to a significant loss of acidity and active sites. Steaming has previously been investigated[21] as a treatment to improve catalyst lifetimes, as the dislodging of Al species during dealumination seems to improve the stability, selectivity and activity of the catalyst.
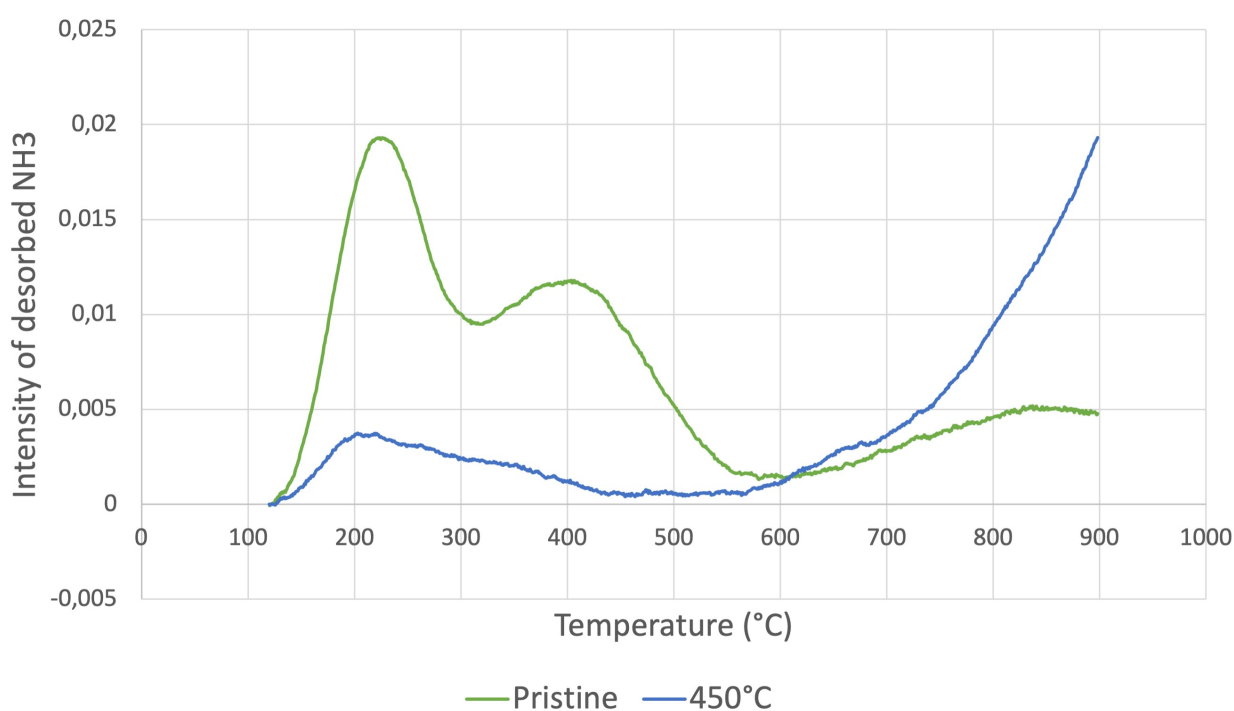

Figure 3: TPD results from the pristine catalyst and from catalyst used for 6 hours at 450°C

3.1.2 Crystallinity

An XRD of the unused catalyst was performed and the experiment was repeated for a sample of the used catalyst after a 6 hours-long run at 400°C. The results of the two were compared to a generated X-ray Powder Diffraction (XPD) plot (Figure C.1, Appendix C) and it was established that both showed the characteristic peaks of a MFI framework[19], which the ZSM-5 catalyst possesses. In order to establish differences in crystallinity between the pristine and used catalyst, the plots obtained from each sample were overlapped (Figure 4).

The results indicate that coking does not destroy the structure of the ZSM-5 framework gravely and no new diffraction peak could be observed after the employment of the catalyst in a 6 hours-long run at 400°C. A decrease in the MFI-specific peaks at 7.80, 8.78, 23.80 and 24.14 °2θ can be noticed for the used catalyst, which could point to a decrease in relative crystallinity for this sample.

It is likely that catalysts used at higher temperatures or longer TOS would show an additional increase in the differences between the two spectra, as further coking would affect the framework more severely. Although it was not possible to calculate the relative crystallinity of the second sample, He et al.[1] and Niu et al.[19] previously observed that the relative crystallinity of a catalyst decreases with increasing coking and modifications.
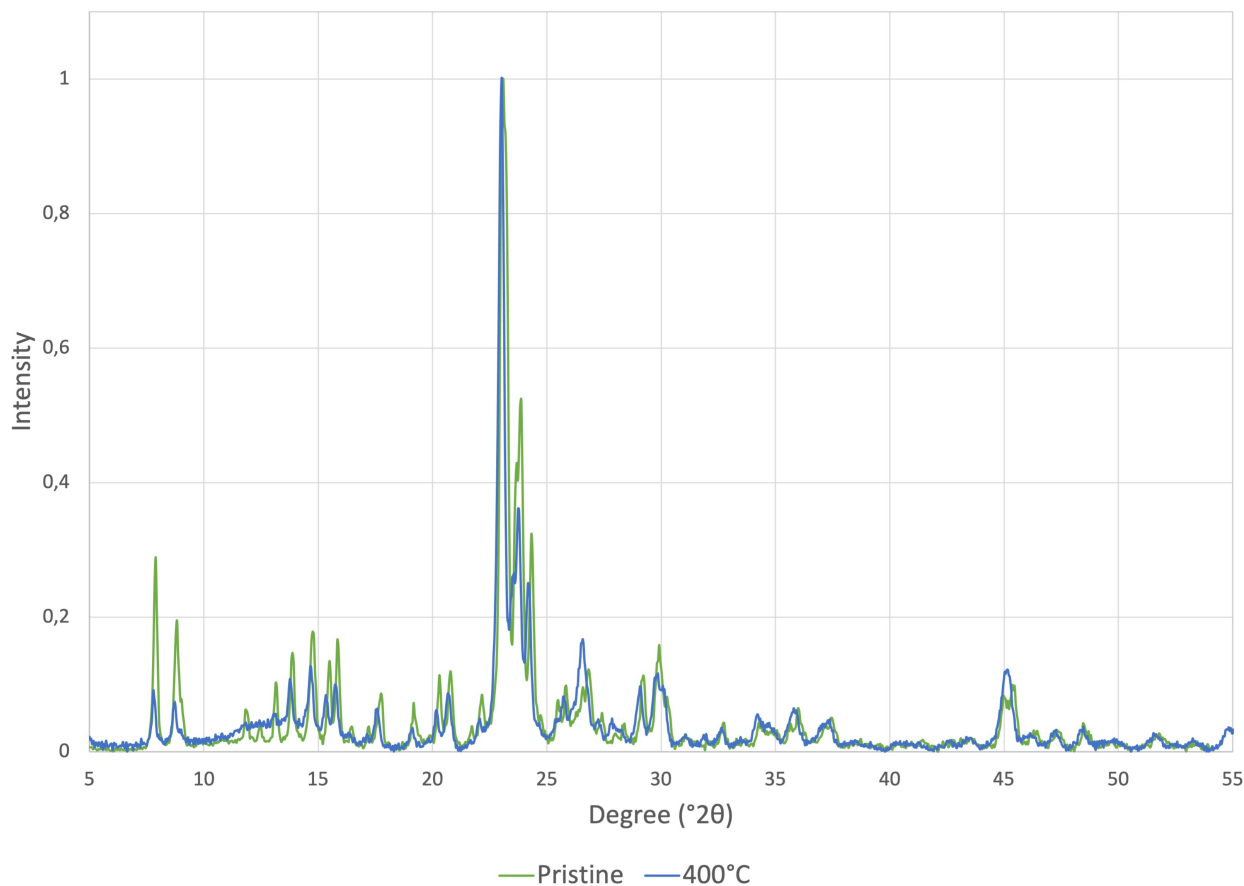

Figure 4: XRD results of pristine H-ZSM-5(23) and used catalyst at 400°C for 6 hours

3.1.3 Surface area

The surface area of the pure catalyst was assessed using N_2 physisorption. The surface area of the sampled catalysts was determined using the Brunauer-Emmett-Teller (BET) method, which is the most common method applied to derive a specific surface area (SSA)[22]. As observed by He et al. [1], the deactivated catalyst shows a decrease in three relevant parameters measured by N_2 physisorption, which were identified as BET surface area (S_{BET}), total pore volume (V_{pore}) and micropore volume ($V_{micropore}$).

It was chosen to examine the N_2 physisorption pattern of the catalyst used for a 6 hour-long run at 500°C in order to establish whether a 6 hour run could lead to complete deactivation. The obtained values are presented in Table 1, together with the results for the N_2 physisorption of the pristine catalyst.

Table 1: N2 physisorption results for fresh catalyst and used catalyst after a 6h run at 500°C

Catalyst	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})	$V_{micropore}$ (cm^3 g^{-1})
Fresh H-ZSM-5(23)	274.86	0.16	0.099
Used at 500°C for 6h	12.09	0.016	0.0025

As it can be observed in Table 1, the surface area and pore volume decrease noticeably after a 6-hour long run. As discussed by He et al.[1] and previously analysed by Sing et al.[23], the catalyst appears to have been completely deactivated: it can in fact be found that He et al. presented a deactivated H-ZSM-5(23) catalyst as having values of S_{BET}, V_{pore} and $V_{micropore}$ equal to 10 m^2g^{-1}, 0.02 cm^3g^{-1} and 0.005 cm^3g^{-1}, respectively. Further comparisons with catalyst samples obtained from different TOS and temperatures could elucidate the exact moment in which the catalyst can be declared deactivated and provide further insight on the influence of temperature over coking. Unfortunately, the amount of catalyst required for N_2 physisorption is quite large, and the catalyst testings would have to be repeated several times or in larger scale in order to obtain enough samples for all the characterisations executed for this publication.

N_2 physisorption can also yield data in regard to the porosity of the observed samples. The relative pressure was plotted against the nitrogen volume adsorbed (Figure 5), which allowed to notice a significant change between the curves: compared to the pristine catalyst, the sample tested at 500°C for 6 hours shows different peaks, implying a drastic change in the catalyst's pore structure[24]. The obtained curves were also compared to existing literature[24,25,26] and were determined consistent with the publications taken into account.
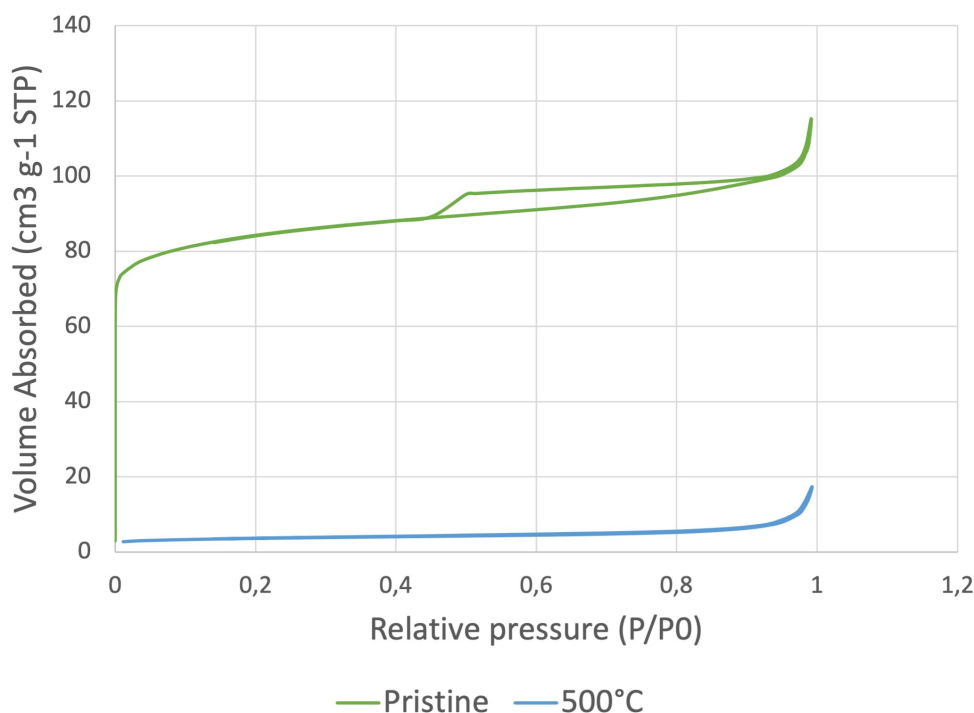

Figure 5: Relative pressure vs Volume adsorbed curves obtained from N_2 physisorption for the pristine and used (500°C, 6 hours) catalyst

3.1.4 Coke burning

TGA is one of the most common methods for catalyst regeneration, accompanied by methanol leaching and calcination. The samples are heated at a constant rate and the weight difference or weight difference percentage are calculated at each temperature or moment in time. The technique works by vaporising or decomposing organic molecules deposited on the catalyst, including water and other volatile substances.

TGA results of the used catalyst samples show that the minimum temperature required to remove the coke by air oxidation is 615°C, approximately. As it appears from the comparison of the obtained curves, the catalyst used at 500°C for 6 hours started with the largest amount of coke: the total weight loss percentage for this sample is consistently higher than for the sample used at 450°C or 400°C (Figure 6A). As the formation of coke depends on exothermic reactions, higher reactor temperatures favour its quicker origination and lead to more abundant coking at the same moment in time. It appears that this increase occurs at a constant rate, implying a linear correlation between coke formation and reactor temperature.

At different moments in time for runs carried out at 450°C (Figure 6B), an increase in total weight loss percentage with TOS can be observed, as previously noticed by Aguayo et al.[27] for a SAPO-34 catalyst. The linear increase of total weight loss percentage with TOS suggests that coke formation proceeds at the same rate throughout the whole duration of the reaction, once again showing a linear trend between coke formation and time on stream. TOS studies can help shine a light over coke formation rate and catalyst deactivation patterns, especially in the case of modifications to the catalyst and feed. These studies can and have[7] helped in identifying which loadings and feeds allow for the longest catalyst lifetimes and best performances.
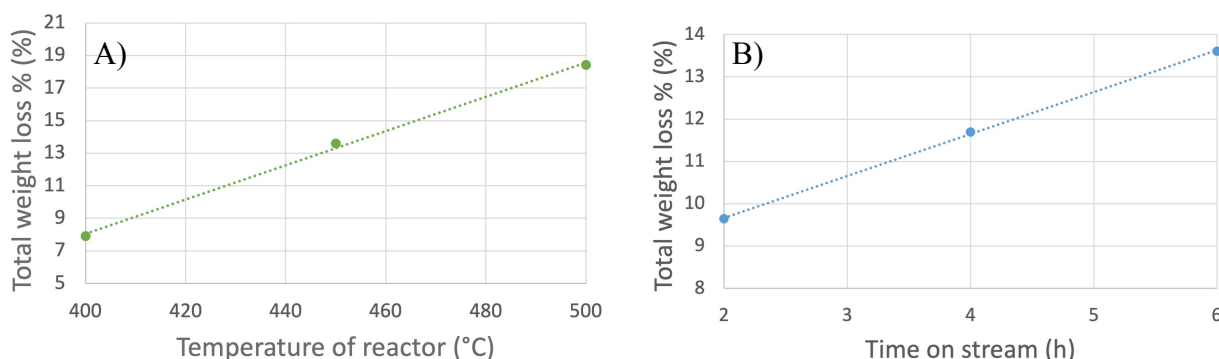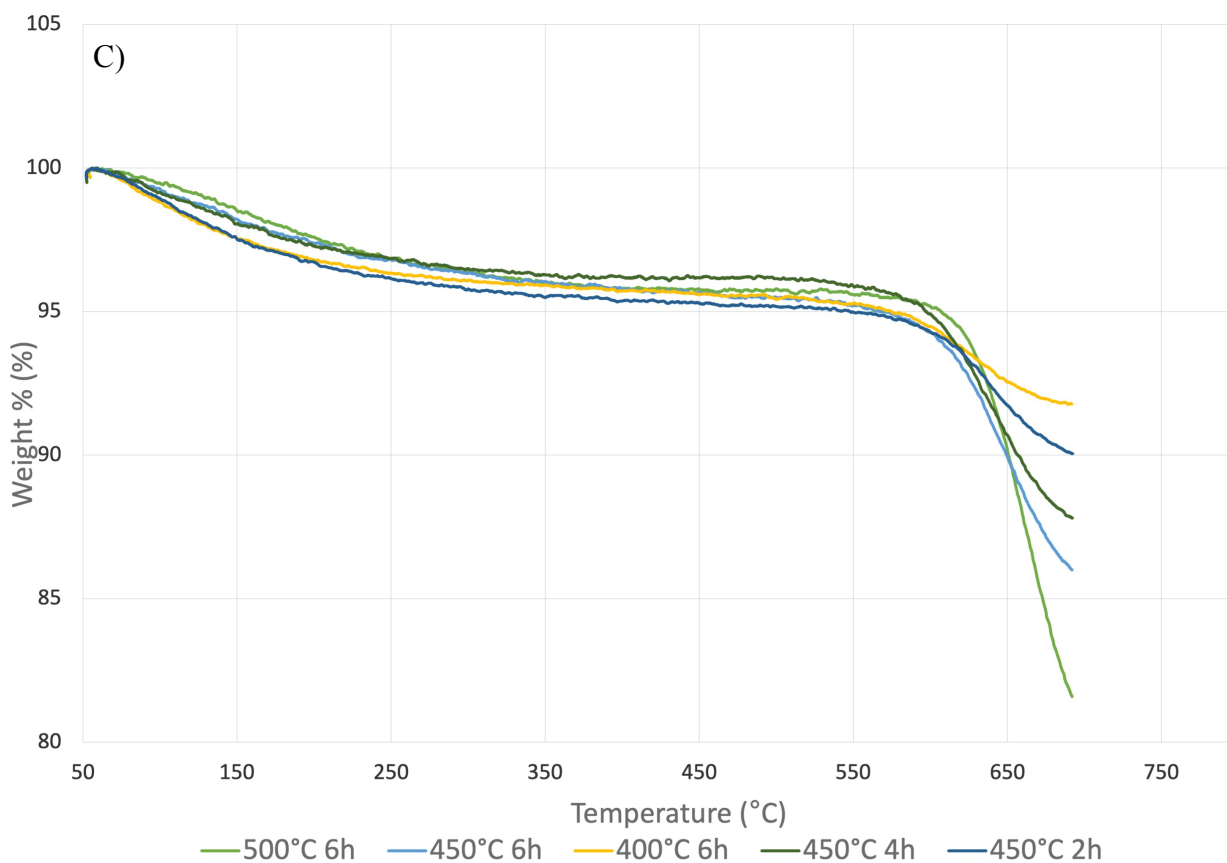
Figure 6: A) Total weight loss percentage vs. Reactor temperature; B) Total weight loss percentage vs. TOS; C) TGA curves for samples obtained from all runs

3.2 Product distribution

The product distribution from each 6 hours long run was examined by collecting one gaseous and one liquid samples every two hours.

3.2.1 Temperature

As it appears from the liquid samples' GC results (Figure 8), temperature can indeed affect the product distribution of the MTH reaction. For instance, the amount of poly-substituted aromatics detected tends to decrease as the temperature is increased, while the selectivity for p-xylene increases together with the reactor's temperature. Gas chromatography on gaseous samples (Figure 7) showed, in accordance with literature[1], that the only detectable hydrocarbon gaseous products are methane, propane, ethane, propylene and ethylene. The distribution of these is also affected by the reactor's temperature, with an increasing selectivity for methane and alkenes as temperature grows, as previously determined by Teketel et al.[28,29,30]

The consequences of increased temperatures are easily explained via the phenomenon of hydrocarbon cracking: this mechanism can elucidate the reason for the lower concentration of poly-substituted aromatics, which has been observed in previous publications[28,29] as well. Furthermore, hydrocarbon cracking is clearly the cause of the increased methane content in samples obtained from high-temperature runs, since the breakage of C-C bonds and their rearrangement into double bonds is more likely. This therefore also shines a light over the predilection for alkenes rather than alkanes at higher temperature.

Catalyst dealumination, already identified through TPD analysis and enhanced by higher temperatures, is said[9] to partially explain a higher olefins (especially propylene) production at higher temperatures due to weaker acid sites. This increase in propylene selectivity was not observed in this publication (Figure 7E), likely implying a more complex mechanism, which might involve catalyst quantity and WHSV variations as well as temperature.

3.2.2 Time on stream

Comparing GC results at different times of reaction shows that poly-substituted aromatics are less and less detected as the reaction proceeds. It also appears that the selectivity for p-xylene increases with increasing TOS (Figure 8E), which can be explained by the previously introduced catalyst dealumination, which weakens the acid sites and leads to the rearrangement of meta-xylene to para-xylene[32,33]. From the gaseous samples' GC results, it looks like the relative selectivity for each product remains about constant throughout the reactions, with a preference for the alkenes in respect to their alkane form in all runs.

Although cracking plays a role in influencing the products' distribution away from poly-substituted aromatics and alkanes, it is not alone in this: in fact, the extent of coking at a certain reaction time can also impact the product selectivity. As confirmed by TGA analysis, catalysts present more extensive clogging of the pores at higher reaction times, which then impede the passage of slightly bigger molecules such as poly-substituted aromatics. Although the difference in size between BTX aromatics and poly-substituted rings is quite small, it has to be taken into account especially at long TOS, when the extent of catalyst coking is close to leading to complete deactivation.

As temperature also plays a role in catalyst deactivation, the most extreme effects on product selectivity can be seen at high TOS in the run carried out at 500°C, when the extent of pore clogging is at his maximum.
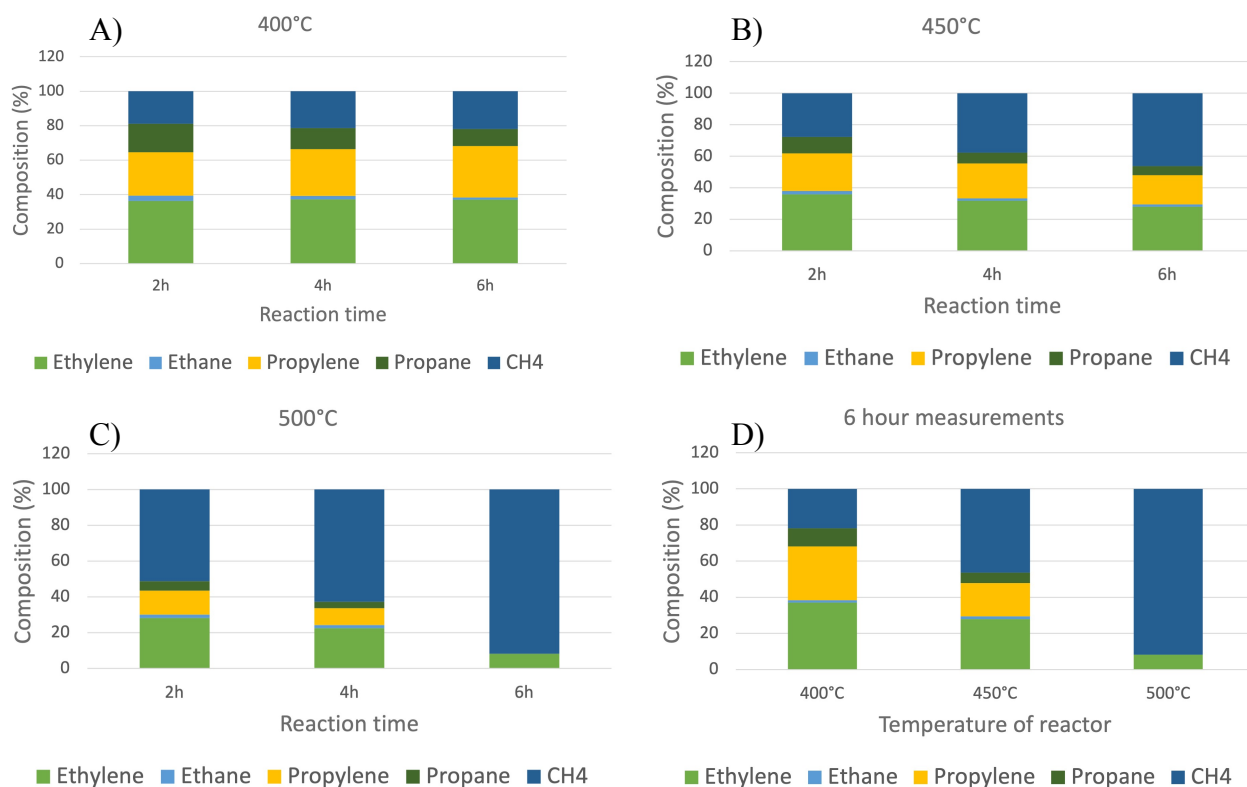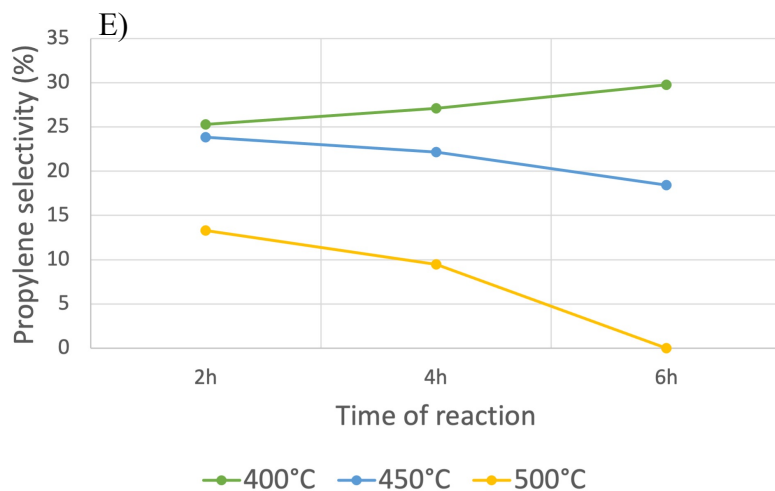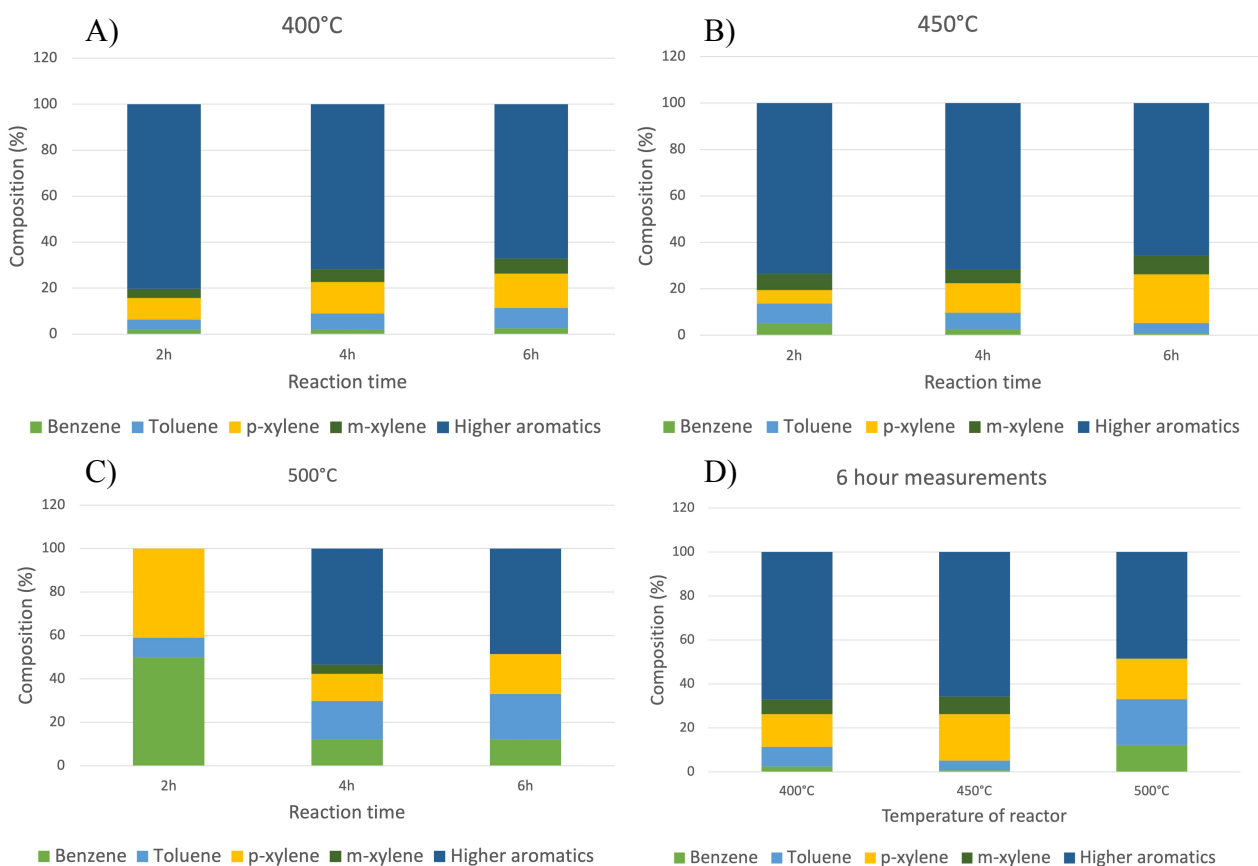
Figure 7: Gas GC results from runs carried out at A) 400°C, B) 450°C and C) 500°C. D) Shows the samples' composition at the same moment in time at different reactor's temperatures and E) presents the propylene selectivity percentage at different reaction times during each run.
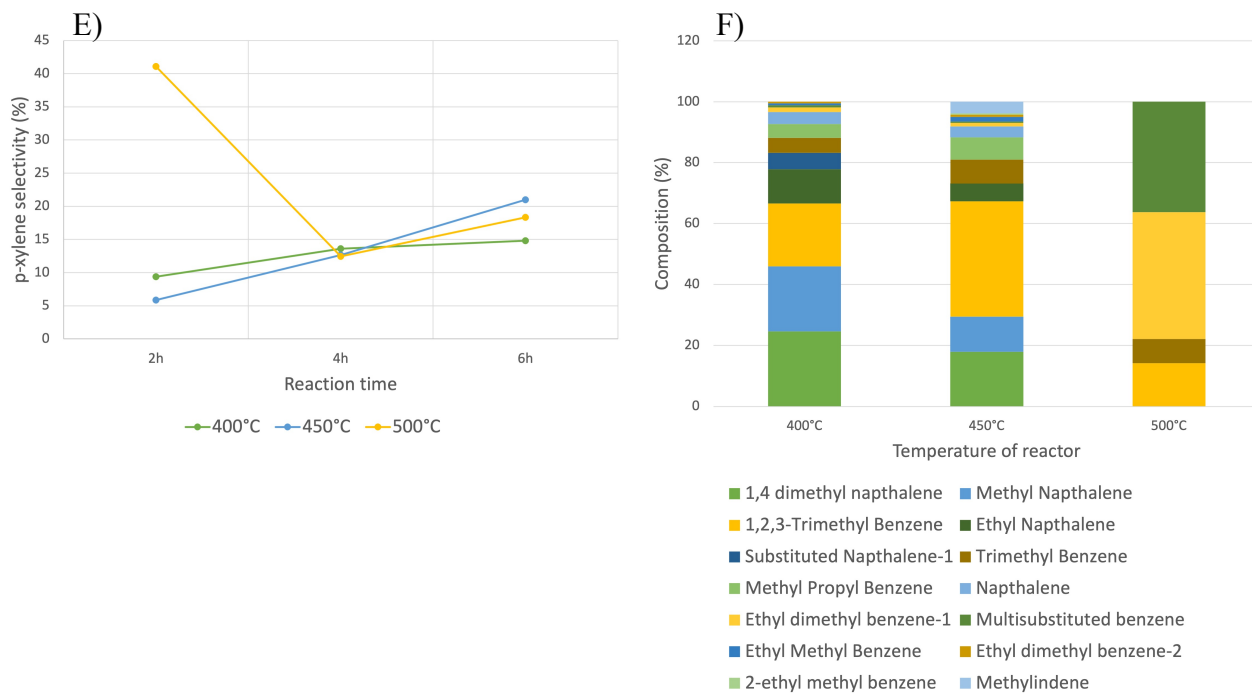
Figure 8: Liquid GC results from runs carried out at A) 400°C, B) 450°C and C) 500°C. D) Shows the samples' composition at the same moment in time at different reactor's temperatures; E) presents the p-xylene selectivity percentage at different TOS during each run; while F) shows the poly-substituted aromatics' distribution at the same moment in time at different reactor's temperatures.

4. Conclusion and outlook

The catalytic conversion of methanol to hydrocarbons was investigated using an home-made setup while using different reactor temperatures and times on stream (TOS). It was observed how coking modifies the catalyst and how TOS and temperature can affect the products' distribution. Through TGA, it was possible to observe that high reactor temperatures lead to a more abundant formation of coke, trend that was also observed for increasing TOS. TPD, XRD and N_2 physisorption elucidated how the catalyst changes after use, but due to the abundant amount of catalyst needed per analysis it was not possible to build trends for increasing temperatures and TOS. It was however observed that the number of acid sites and their acidity decreases drastically during use, as seen by comparing TPD results of a pristine and used catalyst at 450°C for 6 hours. Strong acid sites are virtually eliminated and weak acid sites loose activity and decrease in number. Furthermore, it appears that the crystalline structure of the H-ZSM-5 framework is not severely affected by its use in the reactor setup for 6 hours at 400°C, which allows for the possibility of catalyst regeneration, as previously observed by other publications[1,9,33,34,35]. As N_2 physisorption showed, the catalyst was completely deactivated after 6 hours at 500°C. It was not possible to investigate via this analysis whether lower temperatures would allow for a longer lifetime, but TGA analysis and previous studies[9] would suggest so. TGA showed a linear correlation between coke formation and temperature as well as TOS. More (1 hour, 3 hours) and longer TOS could be investigated in order to confirm this trend and discover if it continues past the 6 hours limit.

The effects on products' distribution were analysed through GC. Results show that higher temperatures lead to lower concentrations of alkanes and poly-substituted aromatics. BTX aromatics tend to increase in concentration with increasing temperatures and TOS, which was explained with the contributions of hydrocarbon cracking, which becomes more influential with increasing temperatures, and catalyst deactivation by coking. Hydrocarbon cracking and catalyst deactivation would also explain the increased concentrations of ethylene with growing temperature, since broken C-C bonds rearrange into double bonds, making alkenes more abundant than their alkanes analogues. Methane concentration also grows with increasing TOS and temperature, which is thought to be caused by the soaring deactivation of the catalyst. Catalyst dealumination was first observed via TPD and can explain the increase in p-xylene selectivity with growing TOS.

As the setup made available did not allow for the quantification of the collected samples, calculating product yields was not possible. Other publications[1,9] present yields and mass balances in order to express the influence of catalyst modifications on products' distribution, but further improvements to the home-made setup would be needed in order to do the same, as the current arrangement does not allow to quantify the amount of product collected.

Repetition of the experiments at all tested temperatures and TOS or an upscaled setup would allow further data collection concerning catalyst characterisation, especially for TPD, XRD and N_2 physisorption. This would allow the observation of trends across different temperatures and TOS in regard to the effect that the variation of these parameters has over the catalyst's structure.

As such, this publication has provided insight in the influence that temperature and TOS have over product formation and catalyst deactivation. Modifications to the H-ZSM-5(23) catalyst would help in directing the product distribution to desired proportion and in increasing catalyst performance and lifetime[36,37]. The results have generally been in line with previous publications, excluding the propylene selectivity trend presented by Yarulina et al.[9]. Due to the complicated nature of the MTH reaction mechanism, this difference can be due to many factors, of which the main can be identified in the differences in the setup, such as pre-treatment of the catalyst, WHSV and reactor conditions, in respect to the mentioned publication.

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Appendix

Appendix A

A.1 Methanol volumetric flow calculations

Taking an average flow rate of nitrogen ($\phi_{V,tot}$) equal to 41 mL/min, a relative pressure for methanol (p_{MeOH}) equal to 354 mbar[38] and a total pressure (p_{tot}) of 1 bar, the total flow and pressure where defined as:

$$\phi_{V,tot} = \phi_{V,MeoH} + \phi_{V,N_2} \text{ and } p_{tot} = p_{MeOH} + p_{N_2}$$

In order to determine the volumetric flow of methanol, the following proportion was established:

$$\frac{\phi_{V,MeOH}}{\phi_{V,tot}} = \frac{p_{MeOH}}{p_{tot}} = \frac{\phi_{V,MeOH}}{41\ mL/min} = \frac{354\ bar}{1000\ bar} = 0.354$$

From which $\phi_{V,MeOH}$ was found equal to 14.51 mL/min.

A.2 Weight hourly space velocity (WHSV) calculations

As the methanol volumetric flow was found in mL/min, it was first converted to g/h by using the ideal gas law and molar mass, before calculating the WHSV as follows:

$$p \cdot \phi_V = \phi_{mol} \cdot R \cdot T \text{ with } p = 1\ bar,\ R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}\ and\ T = 40°C \text{ with p=1 bar,}$$
R=8.314 J·K⁻¹·mol⁻¹ and T=40°C

$$\phi_{mol,tot} = \frac{p \cdot \phi_{V,tot}}{R \cdot T} = \frac{10^5 \cdot 41 \cdot 10^{-6}}{8.314 \cdot 313.15} = 1.57\ mmol/min$$

$$\phi_{mol,MeOH} = \phi_{mol,tot} \cdot 0.354 = 55.75\ mmol/min$$

$$\phi_{m,MeOH} = \phi_{mol,MeOH} \cdot M_{MeOH} = 55.75\ (\frac{mmol}{min}) \cdot 32.04\ (\frac{g}{mol}) = 1.79 \cdot 10^{-2}\ g/min = 1.07\ g/h$$

$$WHSV = \frac{\phi_{m,MeOH}}{m_{catalyst}} = \frac{1.07(\frac{g}{h})}{200 \cdot 10^{-3}(g)} = 5.37\ h^{-1}$$

Appendix B

B.1 HAZOP

Nr.	Guide word	Element	Deviation	Possible causes	Consequences	Safeguards	Comments	Actions required	Actions assigned to
1	No	Nitrogen	No nitrogen coming into the system	Empty nitrogen tank	Methanol is not carried through the catalyst bed and reaction doesn't proceed	Check nitrogen tank before each run	Leakages and excessive flows during nighttime are possible	Communicate to students to check the tank every day and note down anomalies	Students
2	Low	Nitrogen	Low nitrogen flow though the system	Leakage	Compromised results due to lower pressure and WHSV	Check for leakages by closing V-104 and nitrogen feed and keeping track of pressure via pressure indicator	Perform check before every run	Instruct students to preform the check	Students

3	Off	Water bath	Heating plate under water bath not turned on	Student forgetfulness	Methanol does not vaporise enough and presents low WHSV, compromising results	Check plate temperature before each run	The student should know how a heating plate works	Instruct student to perform check	Students
4	Off	Heated line	Heated line not turned on	Student forgetfulness	Methanol/ nitrogen mixture condenses before entering the reactor	Check heated line generator before each run	The heated line can be assumed to be working if turned on	Instruct student to perform check	Students
5	Released	Gaseous products	Crack in glass reactor	Improper handling while cleaning and placement	Reaction products are released in reactor. Danger arises due to high flammability of gasses	Check reactor's state before each run and handle with care	New reactors can be provided	Instruct student to perform check and how to clean the glass reactor	Students
6	Off	Product mixture	Cooling tower not turned on	Student forgetfulness	Aromatic products can not condense. Liquid samples can not be collected	Check cooling machine before each run	The machine takes approximately an hour to reach -10°C	Instruct student to perform check	Students
7	Over	Pressure	Over-pressurisation of the system	Clogging of lines due to reaction mixture's deposit	Reactor and lines can be damaged	Check pressure indicator periodically, stop reaction if value is deemed too high	The system can be cleaned	Instruct student to perform check and periodically clean the system	Students, apparatus technician

Appendix C
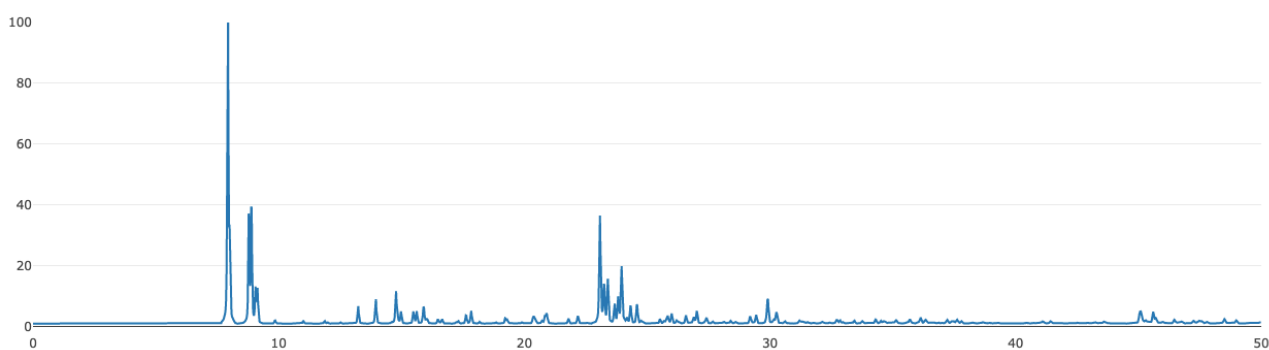## C.1 XPD generated plot for H-ZSM-5

Figure C.1: Generated XPD plot for calculated ZSM-5 catalyst. Plot generated using the website "Database of Zeolite Structures. http://www.iza-structure.org/databases/". X-axis: °2θ; Y-axis: Intensity