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Investigation of zeolite acid sites for 2,5-dimethylfuran conversion

Master's thesis in Chemical Engineering

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DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING

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Abstract

Finding new routes for chemical valorisation of biological feedstocks is an essential part for developing a biobased economy and reducing the use of fossil fuels. This project tailor's new zeolite-based catalytic materials over which green aromatics, i.e., benzene, toluene, and xylenes (BTX), can be produced from 2,5-dimethylfuran (2,5-dmf), which can be obtained from pre-processed low-cost hemicellulose.

The acid sites present in different zeolite samples have been quantified and differentiated under several experimental conditions to better understand the role of the acid sites in zeolites. The samples studied are silica powder, alumina spheres and 3 HZSM-5 zeolites ranging different SiO_2/Al_2O_3 (SAR), 27, 55 and 330.

The experiments have been performed in a continuous flow reactor whose final stream has been analysed by infrared and mass spectrometry in parallel. A, diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS experiment has also been performed to analyse the in-situ evolution of acid sites and products formed on the surface of the zeolite during a reaction.

The experiments revealed a decrease on the total amount of acid sites before and after the reaction with 2,5-dmf. Differences were found between the different types of acid sites, Brønsted acid sites (BAS) and Lewis acid sites (LAS). BAS are the most abundant types of acid sites on HZSM-5-SAR55 zeolite but are easily deactivated with time on stream, while LAS showed the opposite behaviour, allowing the production of compounds for longer periods of time and at higher temperatures.

Different group compounds such as olefins, aromatics or isomers have different production trends over time. Aromatics production decreases faster with time on stream, compared to olefins and isomer production, which decreases at slower pace over time. Coke formation, as well as the production of compounds such as naphthalene, ethylene and toluene increase with temperature. Compounds such as p-xylene, which has a high value and was not obtained during continuous reaction, was only produced when adsorbing 2,5-dmf on the zeolite at low temperatures and then slowly increasing the temperature. This is an indicator of different reaction mechanism compared to continuous production.

Keywords: acid sites, BTX, catalyst, zeolite, 2,5-dimethylfuran.

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Notation

BAS	Brønsted acid sites
BTX	Benzene, Toluene and Xylenes
dmf	Dimethylfuran
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
FT-IR	Fourier transform infrared spectroscopy
LAS	Lewis acid sites
m/z	Mass to charge ratio
MFC	Mass flow controller
MS	Mass spectrometry
SAR	SiO_2 to Al_2O_3 ratio
TPD	Temperature programmed desorption
ZSM-5	Zeolite Socony Mobil-5

Contents

1. Introduction

Nowadays, the rapidly growing global population, climate change, warming of the earth, and therefore, loss of biodiversity caused by human activities are reaching the limits for our ecosystem to handle, becoming a real threat to the world.

A major actor in this environmental deterioration is the use of fossil fuels such as petroleum, natural gas, and coal as the main resources of energy and fuel. Not only burning of these chemicals which produce emissions of greenhouse gases are a threat [1], but its use as a primary source in almost all carbon-based materials.

Action needs to be taken, and it needs to be fast to match our needs as an always developing economy and society. A change of scope is needed to keep developing from a sustainable point of view. This idea has been around the political spheres for some time, but nowadays it escalated to a top priority in most developed countries. One example of this is the United Nations Framework Convention on Climate Change, also known as the "European Green Deal", where the EU strives for a 55% reduction of net greenhouse gas emissions by 2030 compared to 1990 levels, and no net emissions of greenhouse gases by 2050 [2]. A driving force is needed to fulfil these goals, and catalysts can be the material of change.

A catalyst is a material that accelerates a chemical reaction. It does so by forming chemical bonds with the reacting molecules. Later, these molecules detach from the catalyst leaving this last one unaltered. Catalysts not only help to accelerate the rate of a reaction, but also reduce de energy consumption and the formation of undesired products. It does that by increasing the efficiency and selectivity of the reaction. Therefore, catalysts might be the key player in accelerating the change our society need to a sustainable and greener future.

As stated before, almost all carbon-based materials are derived from fossil fuels, and catalysts are involved in the efficient transformation of all these compounds to produce energy sources such as petrol or diesel, but also building blocks for the chemical industry. Part of these building-blocks are known as the BTX aromatics, benzene, toluene and xylenes [3]. To help the transition to a greener future, the use of waste and biomass forest products can be a substitute carbon source of fossil fuels. It is important to make the change responsibly, the local ecosystems need to be protected and the harvest heavily controlled and regulated.

1.1. Motivation of this work

In our modern society, the transition from old fashioned fossil-based feedstocks to more sustainable and renewable sources is not a choice but an obligation. Our world has reached an extreme state of contamination, raw materials use and depletion. New chemical pathways must be explored and made industrially viable. Using renewable feedstocks such as wooden biomass or biomass waste from other processes gives independence from oil-based products and adds value for the manufacture of chemicals. The need of closing the loop motivates the shift from non-renewable fossil products to a bio-based circular economy. This is the driving force towards the research on how catalysts can be applied and designed for the efficient conversion of biomass into valuable chemicals for the industry.

2. Background

This chapter consists of a brief explanation of the scope of the project and an introduction to all the key parts to which this study is based on. These different parts are 2,5-dimethylfuran as the starting source, zeolites as the catalysts and aromatic hydrocarbons as the final products.

2.1. 2,5-dimethylfuran

In the pursuit of sustainable production of chemicals, using biomass-derived feedstock is a renewable and sustainable way of producing biobased chemicals to meet the growing demand for energy. Development of new technologies with the desired specificity to transform bioresources is key to keep up with global demand. These technologies will need to fulfil sustainable concerns such as environmental impacts and energy efficiency while replacing the previous production rate of fossil fuels. [4]

Furans, a class of 5-membered cyclic hydrocarbons, are a model platform molecule from which other compounds can be produced and later fed into several production processes. These compounds can be derived from the cellulosic feedstock, which consists of cellulose, hemicellulose, and lignin. All these compounds need to go through some upgrade processes to become the aromatic building blocks, furans. [5]

2,5-dimethylfuran (2,5-dmf), our starting raw material, can be obtained in several ways. One method to obtain it is described by Román-Leshkov et al. [6], and consists of a two-step catalytic process to convert fructose into 2,5-dmf. The first step is an acid-catalysed dehydration of fructose to produce 5-hydroxymethylfurfural in a biphasic reactor, subsequently, this product is then extracted from the reactor and converted to 2,5-dmf by hydrogenation of the C-O bonds over a copper-ruthenium catalyst. [6]

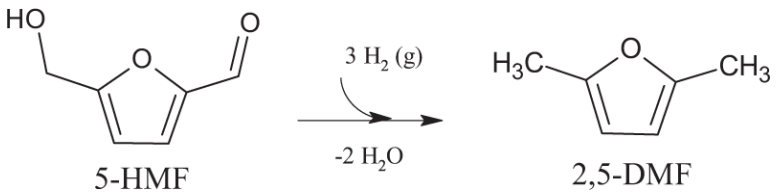


Figure 1 The hydrogenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF). [7]

2.2. Zeolites

Zeolites are crystalline, hydrated aluminosilicates with a framework structure [8]. The term “zeolite” was given to this kind of materials by the Swedish mineralogist Axel Fredrik Cronstedt in 1756 when he observed that certain minerals began to bubble on strong heating, and therefore the name came from the Greek *zeo*: to boil and *lithos*: stone. [9]

The three-dimensional polyanionic structure of this materials is constructed with SiO_4 and AlO_4 tetrahedra linked through oxygen atoms. Depending on the framework of the zeolite it can contain regular channels or interlinked voids in the range of micropores, and these pores contain water molecules as well as the cations, which are mobile and can be exchanged, necessary to balance the negative charge of the network. The negative charge appears when an Aluminium molecule replaces a Silicon in the framework, the charge can be balanced by metals, like Na or K, making it a Lewis acid site, or by hydrogen, making it a Brønsted acid site. The principal characteristic which all zeolite structures share is being a well-defined system of regular cavities or channels, which makes them the perfect material to act as molecular sieves. [8]

Zeolites are very versatile due to their great stability and selectivity. Zeolites have a higher selectivity to molecules of certain shape and size depending on the dimension of its channels and cavities. Furthermore, zeolites have a great thermal stability and are non-corrosive and not toxic [10]. The thermal stability of these materials varies depending on the structure type as well as on the SiO_2/Al_2O_3 ratio (SAR) and the nature of the cations [8]. Differences can be experimentally observed, low silica zeolites collapsed at temperature above 660ºC, while another sample of the same structure zeolite but with higher SiO_2/Al_2O_3 ratio collapsed above 700ºC. [11]

A unique feature of zeolites when using them as catalysts is that the reaction happening can be shape-selective. This phenomenon occurs when molecules have similar dimensions as the ones from the pores of the catalyst, this way, the catalyst exhibits a molecular-sieve effect on the reacting molecules. In this type of reactions, only reactant molecules that can fit through the catalyst cavities and channels are able to reach the active sites, where they can react and diffuse off the zeolite. Shape-selectivity has been observed specially in reactions where ZSM-5 is the catalyst. [8]

The channels of the catalyst can be uniform in size or may consist of interconnecting supercages, they also can have a wide variety in size, shape and the connectivity of the porous channels giving the possibility to produce different and very selective chemical reactions through its design. By adjusting the design of the catalyst, we can take advantage of the acid sites to better enhance the selectivity to a compound or group of compounds of interest. This can be done by many manners, for example taking

advantage of the principle of molecular exclusion or by the difference in the diffusivity of molecules in the zeolite channels. [12]

2.3. Aromatic BTX

Benzene, Toluene and Xylenes (BTX) aromatics are one of the most abundant products obtained from fossil fuels via petroleum refining and catalytic reforming, this process is highly energy and resource demanding [13]. Benzene is one of the most important hydrocarbons, it is the precursor for many other chemicals that may be used as intermediates or end products, almost all derived compounds are directly converted into other chemicals and polymers.

The global market aromatic value was estimated to be $185.9 billion in 2017 being Asia-Pacific the largest geographic region with 40.3% of the total share [14]. The use of this type of chemicals will be increasing as its role as building blocks for other industries such as the pharmaceutical is key. It is estimated that the global market value of this type of chemical compounds will reach the value of $323.9 billion dollars by 2027. [15]

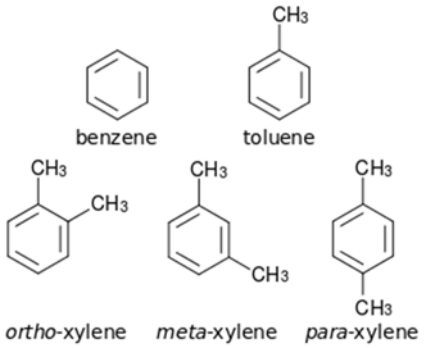


Figure 2. Representation of BTX aromatics.[25]

2.4. Objective of the thesis

The objective of the thesis is to apply several methods and procedures to better understand the behaviour and characteristics of the conversion of the biomass model compound 2,5-dimethylfuran to obtain valuable aromatic compounds such as BTX (benzene, toluene and xylenes). An on-line analysis of the hydrocarbon stream is carried out using Fourier transform infrared spectroscopy (FTIR) and mass spectrometry in parallel to validate the results obtained, both techniques are chosen for their capacity to obtain the data in high time resolution. The outcome of this analysis is to better comprehend the complex reaction mechanisms of the zeolite catalyst with organic molecules and the influence of the acid sites in the conversion of these compounds. This information would be essential when designing future catalysts for biomass conversion.

3. Methodology

Two analytical techniques have been used to carry out the on-line analysis of the furan conversion during this work. These techniques are infrared spectroscopy and mass spectrometry which are used to identify and quantify different compounds inside a complex hydrocarbon's gas stream. Further analysis of the surface behaviour of zeolites have also been conducted with Diffusive reflectance infrared Fourier transform spectroscopy. In this chapter an introduction to the different analytical techniques can be found as well as details about the catalyst material and preparation, reactor setup and the procedure used to study the catalyst.

3.1. Infrared spectroscopy

Infrared spectroscopy has become one of the most important analytical tools in research and technical fields. It has its origin in the year 1800, when William Herschel discovered the infrared region of the electromagnetic spectrum. Over a century later, William W. Coblentz [16] ran the first infrared spectrum and finally, in the 1970s, the appearance of the first research-grade Fourier transform infrared (FT-IR) initiated a revolution in this field. Today's infrared spectroscopy instruments are very versatile and are used for simple, routine identity and purity examinations, as well as for quantitative analysis, process measurements or identification of unknown compounds. [8]

The main goal of infrared spectroscopy is to identify chemical substances or their functional groups. It can be applied to gases, liquids and solids. To achieve this goal, it measures the absorption and transmission, or reflectance, of the incident infrared light interacting with matter. The absorbance can be approximated by the Beer-Lambert law (Equation 1), this equation relates the absorbance and the concentration in a linear way, being ϵ the molecule specific extinction coefficient, l the sample thickness and c the sample concentration.

$$A = \epsilon l c$$

Equation 1. Beer-Lambert law

Absorption occurs when the frequency of the light source matches the frequency of the molecular vibration. This vibration of the chemical bonds inside a molecule can have several vibrational modes and their frequencies are affected by the shape of the molecule and the mass of the atoms involved in the chemical bond. [3]

For the on-line analysis of the complex hydrocarbons stream studied in this work, a gas phase FT-IR spectrometer (MKS MultiGas2030) was used. The quantification of the concentration of compounds in

the stream was approximated by the linear relationship between the absorbance and the concentration.

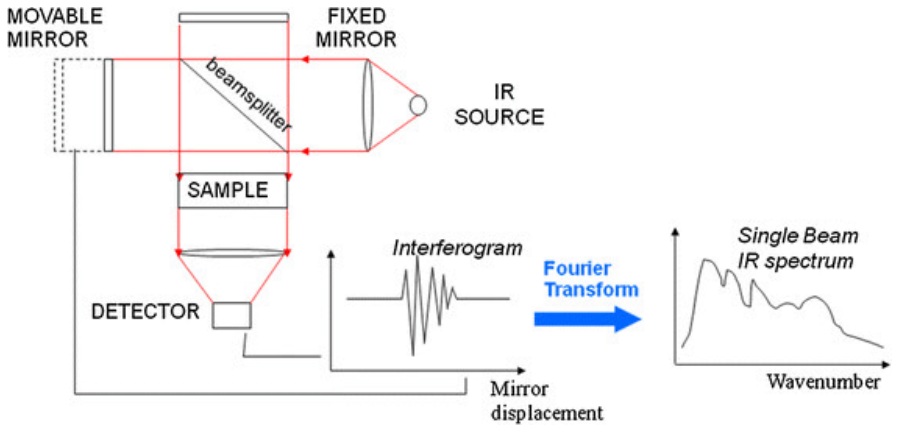


Figure 3. Scheme of FTIR spectrometer. [17]

3.1.1. Group frequencies

To better understand the vibrational spectrum and the way infrared spectroscopy is used to identify chemical groups, there is an analogy where you can compare a diatomic molecule with two-point masses connected by a massless spring, which represents the interatomic bond. Then, the behaviour of the system is described by Hooke's law, deducing that the vibrational frequency between the two atoms increase when the bonding of the two atoms is stronger. Furthermore, the frequency would be smaller when the vibrational mass is heavier. [8]

The vibrational modes are a characteristic of common types of chemical bonds and functional groups and can be distinguished by the frequency to which they appear in the spectrum. Therefore, certain molecules can be distinguished inside a hydrocarbon stream by looking at the wavelengths in which their functional groups appear. This can be a complex task when dealing with streams with a wide variety of hydrocarbons. Different molecules can have overlapping absorbance bands, a good selection and comparison of the absorption bands is required to avoid misjudging the spectrum obtained.

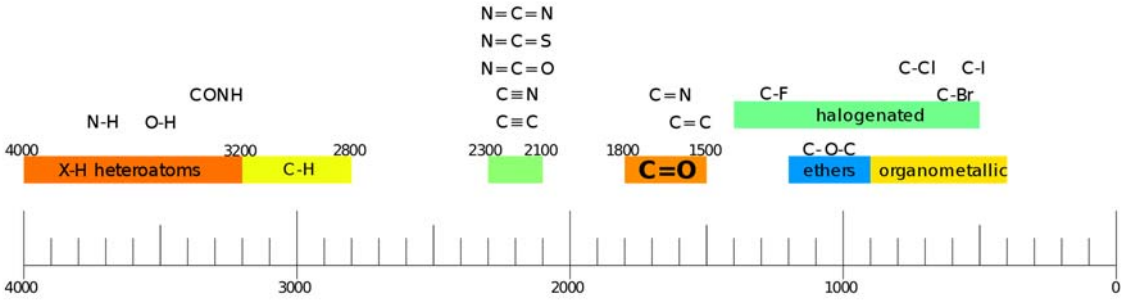


Figure 4. Characteristic infrared spectroscopy bands. [18]

3.1.2. Diffuse reflectance

Diffuse reflection is produced when the incident light is reflected in all directions by the rough surface of a material, this phenomenon can be observed for finely ordered materials such as powders. The distribution of rays can then be collected by parabolic mirrors and molecular surface species can then be studied, making this technique ideal for *in-situ* experiments. This technique can be referred to as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). [3]

The zeolite studied with this technique is HZSM-5-SAR55 sieved to have a particle size in the range of 80-40 µm. The sample powder is also diluted in KBr, which is a non-absorbing powder, to reduce the specular reflection and ensure a better penetration of the incident light to obtain a better signal [8]. Before each experiment, the sample is calcined in the DRIFTS machine at 307ºC and 20% O_2.

In this work, a Bruker Vertex 70 FT-IR spectrometer was used in diffuse reflectance mode to study surface species for *in-situ* experiments, to better comprehend the behaviour of the zeolites and the characteristics of their acid sites. This is done by observing changes in the nature of the OH vibrations of the acid sites that would happen upon different environmental conditions of the reacting chamber. By observing the 3600 nm region of the spectrum at different times it is possible to observe any modification in the nature of the acid sites like the deactivation or formation of coke on the surface of the catalyst. [19]

3.2. Mass spectrometry

Mass spectrometry was historically designed to separate atoms and to determine the masses of isotopes. The first signs of this type of instrumentation were recorded in 1918 when Dempster [20] build a predecessor of magnetic sector field mass spectrometers. Years later, some of the first analytical instruments were used in refineries to identify hydrocarbons [8]. The combination of this technique with infrared spectrometry was reported shortly after. [21]

A mass spectrometer is an analytical instrument used for identification and monitoring of pure samples and complex mixtures, this is done by producing ions from neutral species and using the mass-to-charge ratio (m/z) [8]. The procedure used in this device consist of vaporizing the sample, in case it is in liquid form, and ionizing it to form charged particles. Several techniques can be used to carry out this step, electron ionization is one of them considered a hard ionization technique, and it uses an electron beam to break down the chemical bonds of the sample molecules, obtaining a high degree of fragmentation. All the fragments obtained are directed through a magnetic field that makes them pass through a filter to sort them by the mass-to-charge ratio. The final step of the mass spectrometer is a

detector that analyses the selected ions. These ions induce a charge to produce a current which is correlated to the abundance of each species. [3]

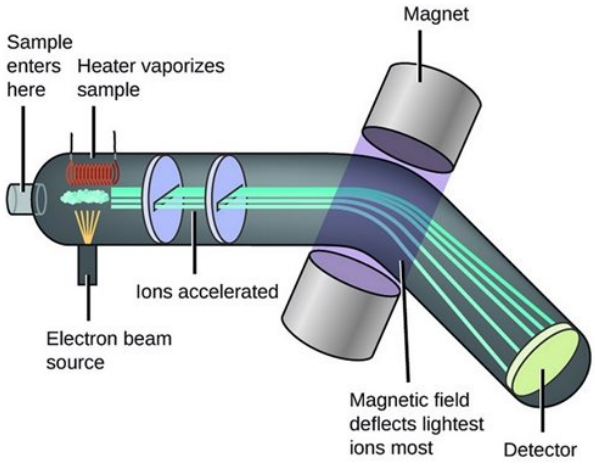


Figure 5. Schematic of mass spectrometer. [22]

3.3. Catalyst preparation

Five different types of catalysts have been studied in this work. Mainly ZSM-5 of the MFI type have been used to continuously study the conversion of furans to aromatics due to their shape selectivity towards BTX yields.

The selection ranges different types of acidities in relationship with its SiO_2/Al_2O_3 ratios (SAR), to study the behaviour and amount of acid sites present in each type of zeolite. Two out of the five catalysts studied are pure SiO_2 powder and Al_2O_3 spheres of 1 mm of diameter, the other three samples correspond to SAR 27, 55 and 330 of the HZSM-5 zeolite.

The three ZSM-5 samples as well as the pure SiO_2 sample are a fine powder not suitable to be used in the reactor, since it would produce overpressure in the system. To avoid this, the samples where pressed in pellets and then grinded and sieved between the range of 300 µm – 350 µm of particle size. The sieved samples then, are introduced inside a quartz glass reactor tube between two clogs of quartz glass wool to prevent any sample loss. The amount of sample used in each reactor tube is around 65 mg.

The zeolite also underwent a calcination process to regenerate its properties and remove coke and other substances that may be attached to the surface of the catalyst before and after starting any experiment. This step consists of flowing a gas stream of argon with a 20% content of pure oxygen for 75 minutes, while keeping the temperature constant at 630 ºC.

3.4. Reactor setup

The continuous flow reactor used in the experiments of this work consists of different inlet gasses whose flow rates are controlled with mass flow controllers (MFC). Each MFC is connected to a different gas source and with the help of Argon, which is used as a balance gas to obtain an inert environment free of oxygen and water, the concentration of a specific gas inside the reactor can be easily monitored.

The inlet of the reactant gas, 2,5-dimethylfuran, is controlled by a gasifier setup. This consists of an MFC that controls the flow rate of argon gas through a gasifier filled with the liquid reactant. The carrier gas and the liquid reactant mix inside the gasifier, forming a saturated vaporized gas, which is assumed to be in equilibrium. This stream is then continuously feed into the system to finally reach the reactor cell. The gasifier used is made of glassware and has an inner volume of 4 mL.

A system of stainless steel tubing guides the different gases from their designated MFC to the reactor cell. In the case of the tubing coming from the gasifier it is heated and thermally isolated to avoid the condensation of the hydrocarbons in the pipes. Before entering the reactor cell, the line from the gasifier goes through an electrically controlled switch that diverges the stream to the reactor cell or to the exhaust line. By having this gadget it is easier to control the overshoot when first flowing gas through the line, being able to redirect the stream to the catalyst when the flow rate and concentration of the reactant is stable.

The reactor cell consists of a quartz glass tube with the catalyst powder inside. To control the temperature, the reactor tube is surrounded by a heating coil and an insulator, two thermocouples are inserted inside the reactor tube, one of them is placed inside the catalytic bed, and the other one at the beginning of the reactor cell, to keep better control of the catalyst and reactor temperature.

Finally, after going through the reactor cell, the gas stream is directed to the analysis instrumentation which operate in parallel in order to validate the results obtained. This instrumentation consists of an ion-molecule reaction mass spectrometer (Airsense Compact, V&F) and a gas phase FT-IR analyser (MKS MultiGas 2030).

3.5. Ammonia temperature programmed desorption

There are several methods to study the properties of a solid acid. These methods can be used to determine the concentration, strength and type of acid sites present in the surface of a zeolite. The information obtained by characterizing the acid sites of a specific catalyst can be used to optimize and improve its design to obtain a better performance of a specific reaction.

Ammonia temperature programmed desorption (NH3-TPD) is a common method when studying the surface acidity of porous materials, like zeolites, because of its simplicity and unexpensive costs. Integration of the TPD-profile to obtain the total amount of acid sites on the catalyst is the easiest part of the analysis, whereas interpretation of the peaks' shape and position is complicated and depends on the experimental conditions. [23]

Experiments of NH3-TPD with zeolites usually show two peaks on the desorption curves, corresponding to at least two different types of acid sites present on the catalyst. These acid sites are Brønsted (BAS) and Lewis (LAS) acid sites.

On one hand, the first ones are formed by the species Al-O(H)-Al [3]. This site is believed to be the main catalytic center and it can bind to basic molecules by hydrogen bonds. By increasing the Al content in the framework, the amount of BAS will increase as well. [23]

On the other hand, LAS are composed of aluminium with low coordination and can be generated by using metals as counter ions such as Na^{+} and Ga^{3+} [3]. These sites have importance acting as electron pair acceptors in many catalytic reactions giving rise to charge transfer processes. [23]

Luz Rodríguez et al. [23] studied the acid properties of HZSM-5 zeolites with different silica to alumina ratios (30, 50, 80, 150, 280 and 1000) by means of NH3-TPD. While performing the experiments, they distinguished between two different peaks, one in the range of 443-553 K they called the low temperature one, which was attributed to the desorption of weakly bound ammonia and showed no catalytic importance [24], and a high temperature one on the range of 643-713 K which was attributed to the desorption of ammonia from the BAS.

Luz Rodríguez et al. [23] observed that purging with water seemed to lead to the selective desorption of the ammonia bound on weak acid sites without any influence on the BAS. Also, some flattening of peaks behind the BAS peak was observed when purging with water saturated helium.

In this work, the NH3-TPD procedure is performed as follows. First, it is important to clarify the argon is used as the balance gas, hence, if the total flow set for the reactor is 400 mL/min and another gas is introduced, the difference between that gas and the total flow will correspond to the flow of argon through the system. During the first step of the procedure the temperature is set to 100 ºC while flowing Argon to purge the reactor for 30 minutes. As soon as this step is over, ammonia is introduced to the gas stream with a flow of 3 mL/min for 30 minutes. The next step consists of maintaining the temperature at 100 ºC and stop the flow of ammonia, which is assumed to be completely adsorbed to the catalyst surface. Then, argon is flowed through the system for 90 minutes to completely purge it from the ammonia molecules that didn't get adsorbed. Finally, the temperature is increased with a temperature ramp of 10 ºC/min until 600 ºC for 50 minutes in order to desorb the ammonia molecules.

Usually, after all the steps are completed, argon is flowed through the reactor for 90 more minutes and the temperature of the reactor is cooled to reach the desired value for the following step in the experiment.

4. Results and discussion

To obtain the results described in this chapter, some work has been done previously to speciate the conversion products in the stream due to the complexity of the hydrocarbons stream analysed. This has been done with the help of the commercial FT-IR library and the extension and enrichment of this library carried out by previous researchers in the same field as done by C. Sauer et. al. [3] where he used pure gas samples with known concentrations of different compounds typically formed in 2,5-dimethylfuran conversion reactions and matched them to form the extension of the FT-IR library.

This chapter will include the findings on the catalyst properties and deactivation when exposed to long term reactions times without its regeneration. It will also include the observations made to the acid sites when exposed to the model compound 2,5-dimethylfuran (2,5-dmf). Finally, some interesting results were obtained when exposing the catalyst to the model compound and then performing a temperature programmed desorption of the molecules trapped inside the zeolite structure.

4.1. 2,5-dimethylfuran influence on the acid sites

The first analysis consists of performing an NH3-TPD before and after a 2,5-dimethylfuran pulse of 2 hours at high temperature. By doing this, it can be determined the amount of acid sites available on the catalyst before and after the reaction.

Different results are obtained for the SiO_2 pure sample, alumina spheres and the HZSM-5 zeolite. The first two were tested with an experimental procedure with two different temperatures during the 2,5-dmf pulse, at 400 ºC and 500 ºC, while for the zeolite the temperature was maintained at 450 ºC. The results obtained show that the pure silica sample, apparently, does not have accessible acid sites where the ammonia molecules could be attached to. The other two samples tested showed a decrease in the total amount of acid sites available between the first and the second NH3-TPD, but no difference when testing different temperatures. The alumina spheres accounted for 0.320 and 0.316 mmol of acid sites per gram of catalyst [mmol/g cat] before the model compound pulse and 0.180 and 0.164 mmol/g cat after it at 500ºC and 400ºC respectively, in the case of the HZSM-5-SAR55 the amount of acid sites is 0.486 mmol/g cat before and 0.300 mmol/g cat after the 2,5-dmf pulse.

The same experimental procedure has been performed on the HZSM-5 zeolite (SAR 27 and 55) with a 2,5-dmf adsorption step at lower temperature, 100 ºC. The concentrations of acid sites in this case are 0.767 and 0.417 mmol/g cat before the 2,5-dmf pulse and 0.306 and 0.042 mmol/g cat after the pulse for SAR27 and SAR55 respectively. The amount of acid sites available before and after the 2,5-dmf adsorption step are very different from at high temperatures for the SAR55 sample. Apparently, when

adsorbing at low temperatures, almost all acid sites are deactivated, the reason to this behaviour is related to the 2,5-dmf molecules getting adsorbed on the surface of the catalyst, impeding the ammonia molecules to occupy the acid sites. This will be further explained in chapter 4.3.

A graphical representation of the results obtained can be seen on Figure 6, where the ammonia, 2,5-dmf and CO signal (ppm) has been plotted over time (minutes). The ammonia desorption peak maintains its shape, but with a smaller signal. The CO signal has been plotted as an indicator of coke formation during the experiment, in this case, when increasing the temperature during the second NH3-TPD and on the final calcination step to regenerate the zeolite, two small CO peaks appear. The reduction of acid sites available before and after the 2,5-dmf pulse can be related to the deactivation of this acid sites due the formation of coke on the surface of the catalyst.

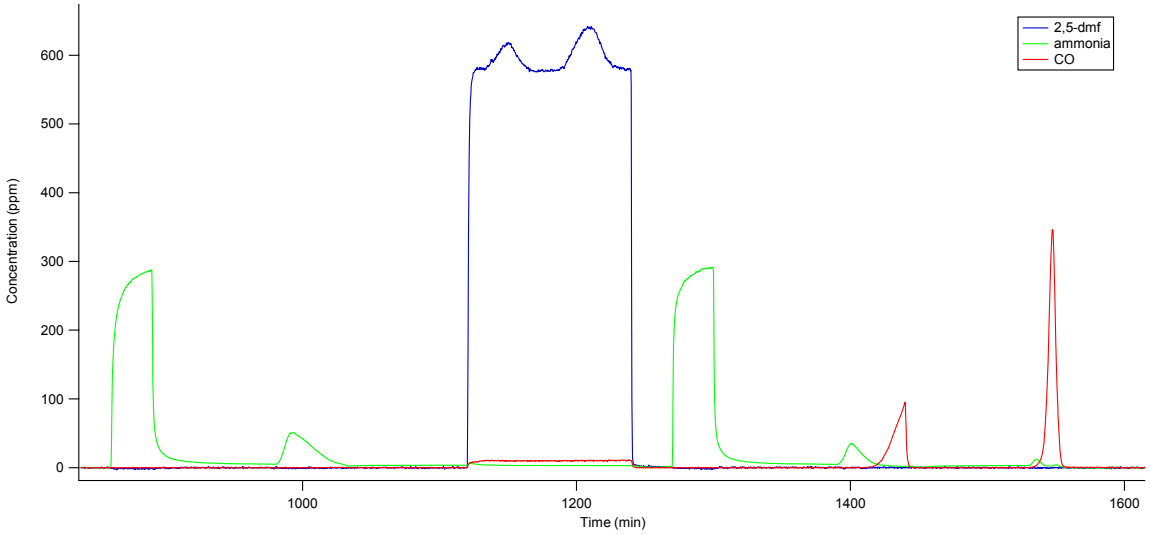


Figure 6. Concentration of species of interest on alumina spheres

It is of great interest to analyse the ammonia desorption peaks in detail. With the help of a Multifitting software tool, several peaks can be identified inside the desorption signal of the NH3-TPD. By doing this, not only the total amount of acid sites can be quantified, but also the amount of acid sites corresponding to different types or classes. In this case, acid sites have been correlated to weak acid sites or Lewis acid sites (LAS) and strong acid sites or Brønsted acid sites (BAS).

In Figure 7, there is a graphical representation of the analysis conducted. That desorption signal corresponds to the experiment done with the zeolite HZSM-5-SAR27 before the 2,5-dmf pulse at 100 ºC. The upper graph represents the residue obtained between the amonia signal (red values in the middle graph) and the fitted function (blue values in the middle graph). The green signal represents the background taken in order to avoid errors in the raw data. Finally, in the bottom part, there is an enumeration of the three peaks identified on the desorption profile of ammonia. The first peak correspond to the LAS, since the ammonia molecules are more loosely attached to this sites, these are

the first to get desorbed from the surface when increasing the temperature. The range of temperature where this desorption happens is around 110 ºC and 240 ºC, having the maximum desorption at approximately 190 ºC. On the other hand, the two other peaks correspond to the BAS, where the ammonia molecules are strongly attached to the acid sites, needing high temperatures to get desorbed. An aproximate range of temperature where this happens is around 240 ºC and 520 ºC, with the maximum desorption at around 360 ºC.

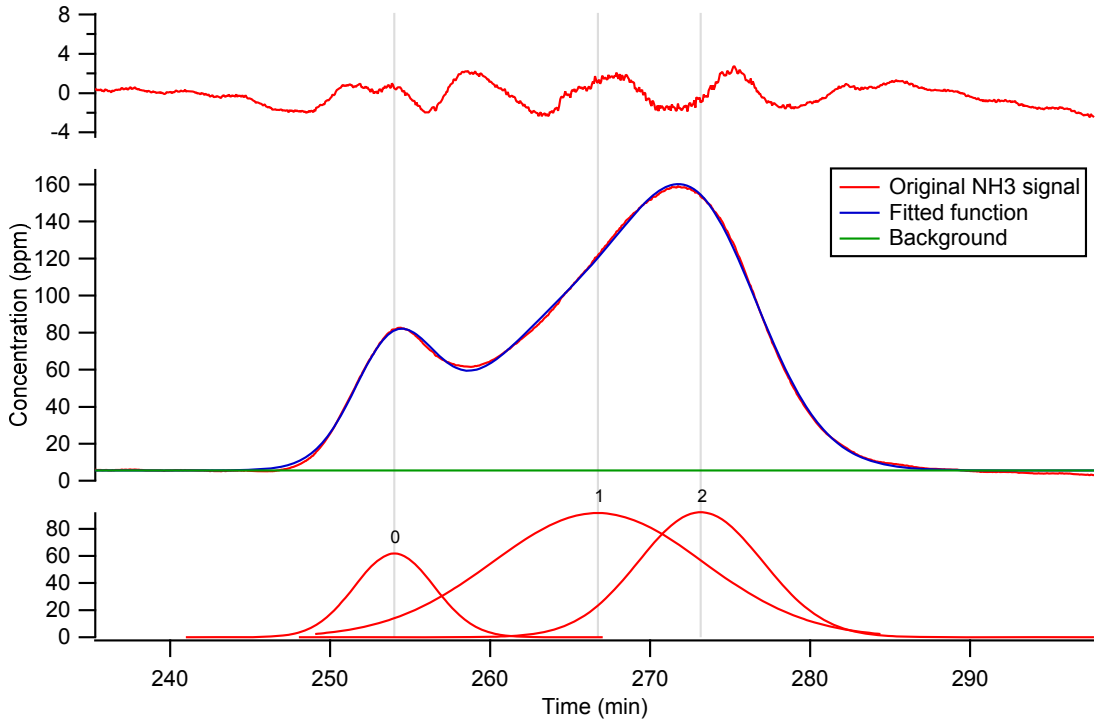


Figure 7. Analysis of the desorption signal of ammonia during NH3-TPD on HZSM-5-SAR55.

The results obtained from these experiments can be summarized in Table 1. Although all the results show a decrease in the acid sites before and after the reaction has taken place, there are some differences between the two zeolites. On one hand, for the HZSM-5-SAR27, both BAS and LAS have a reduction of around 60 % of their total amounts. On the other hand, for the HZSM-5-SAR55, there is a difference between both acid site types, the reduction of the available acid sites is 70 % and 93 % for the LAS and BAS respectively.

This difference can be explained looking at the different nature of the zeolite framework, which depends on the SAR. More aluminium atoms in the framework makes it more likely that some acid sites get modified by an aluminium molecule, increasing its size to the point where ammonia molecules could easily fit but the larger 2,5-dmf molecules couldn't get adsorbed. That explains why HZSM-5-

SAR27 has a lower reduction of its acid sites after the adsorption step than HZSM-5-SAR55, some of these acid sites will always be available for the ammonia because 2,5-dmf can't access to them.

	HZSM-5-SAR27		***HZSM-5-SAR55***	
	Pre adsorption	Post adsorption	Pre adsorption	Post adsorption
1st peak	0,104	0,016	0,064	0,019
2nd peak	0,462	0,023	0,090	0,023
3rd peak	0,201	0,078	0,263	-
4th peak	-	0,188	-	-
Total LAS/BAS	0,104 / 0,663	0,039 / 0,266	0,064 / 0,353	0,019 / 0,023
Total	0,767	0,306	0,417	0,042

Table 1. Summary of concentration of acid sites in mmol/g cat

4.2. Performance of the catalyst over time

In this chapter the capacity of the catalyst to perform under long periods of time and repetitive exposures to the reactant.

The first test consists of performing 4 NH3-TPD consecutively without any regeneration step of the zeolite to check the reproducibility of the experiments, a decrease of the amount of acid sites would mean that some of them get deactivated during the NH3-TPD process due to insufficient temperature for the desorption of all the ammonia molecules. The amount of acid sites obtained chronologically were 0.435, 0.471, 0.477 and 0.486 mmol/g cat. All the values are similar, specially the last three, the difference between the first one and the rest can be explained looking at the graphical results, in that case, the ammonia line was empty from a previous purging, making it impossible to flow sufficient ammonia to saturate the zeolite, as can be seen in Figure 8.

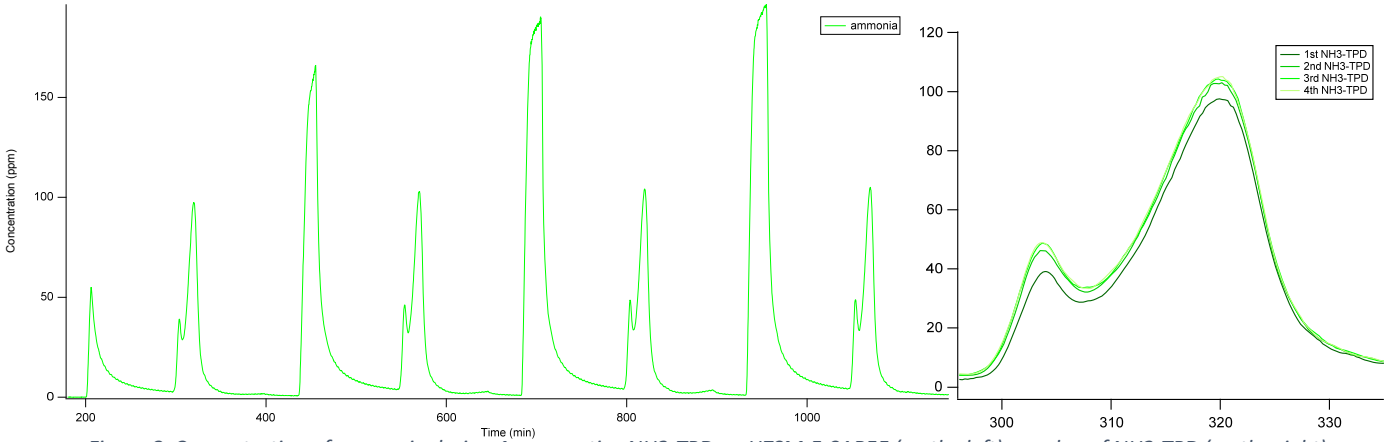


Figure 8. Concentration of ammonia during 4 consecutive NH3-TPD on HZSM-5-SAR55 (on the left), overlap of NH3-TPD (on the right).

4.2.1. Performance on discontinuous flow

The following experimental procedures consist of regenerating the catalyst with a calcination step and then performing four consecutive short 2,5-dmf pulses at 450 ºC for 20 minutes and one NH3-TPD after each dimethylfuran pulse. The zeolite HZSM-5 with different SiO_2/Al_2O_3 was tested. The amount of acid sites available after each pulse are 0.0126, 0.0134, 0.0137 and 0.0136 for the SAR27, 0.2477, 0.1975, 0.1885 and 0.1729 mmol/g cat for the SAR55 and finally 0.0199, 0.0141, 0.0104 and 0.0086 mmol/g cat for the SAR330. The trend for the last 2 samples is to decrease the amount of acid sites available after each reaction period, while for the first one, the amount of acid sites remained stable over the repetitions. The SAR330 shows the biggest decrease in acid sites in proportion.

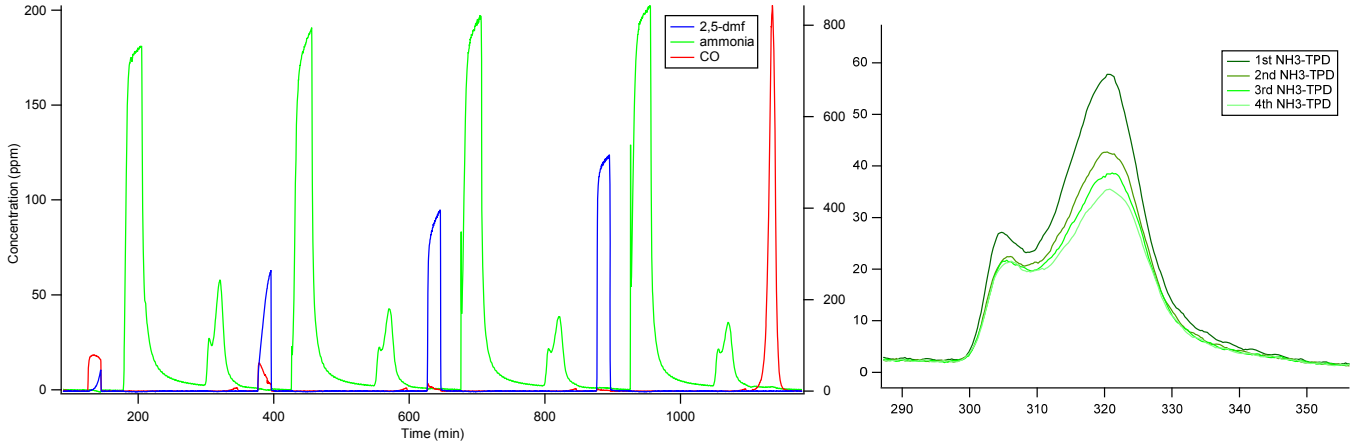


Figure 9.Overview during 4 consecutive NH3-TPD on HZSM-5-SAR55 (on the left), overlap of NH3-TPD (on the right).

As previously done in Figure 7, each ammonia desorption signal has been analysed in detail to determine the behaviour of the acid sites. The data of the ammonia signal collected for the samples HZSM-5-SAR27 and HZSM-5-SAR330 is not suitable for this analysis since the values are extremely low. The signal analysed is the one corresponding to the Figure 9, all the desorption peaks have similar shape, and the concentration decrease over time on the right. Three peaks can be easily identified, the first two correspond to LAS and the last one to BAS. Table 2 shows the concentration of acid sites for the different zeolites.

	HZSM-5-SAR27	***HZSM-5-SAR330***	**HZSM-5-SAR55**	
	Total	Total	LAS / BAS	Total
1st NH3-TPD	0.0126	0.0199	0.0479 / 0.1999	0.2477
2nd NH3-TPD	0.0134	0.0141	0.0420 / 0.1975	0.2395
3rd NH3-TPD	0.0137	0.0104	0.0414 / 0.1885	0.2299
4th NH3-TPD	0.0136	0.0086	0.0415 / 0.1729	0.2144

Table 2. Summary of concentration of acid sites in mmol/g cat.

The analysis of the peaks reveals that there are more BAS available than LAS. The average reduction of acid sites is 6.19, 2.99 and 12.76 % for the three peaks consecutively, the average reduction of the first two peaks corresponds to the LAS, which is 4.5 %. The total reduction from the first desorption signal to the fourth one is 13.35 and 34.26 % for the LAS and BAS respectively. LAS are less abundant in the zeolite but are less easily deactivated, while BAS have the opposite behaviour. This trend can be explained by the formation of coke on the surface of the zeolite. This coke can deactivate the acid sites not only by occupying them but also by blocking the entrance for other molecules.

In Figure 10 there is a representation of the four consecutive 2,5-dmf pulses explained in Figure 9 but in this case, representing different species and its behaviour over time. The order of the pulses goes from the first one on the upper left to the fourth one on the bottom right. The first graphic has all the compounds represented on the left axis except ethylene, and for the other ones, the two dimethylfurans concentrations are also represented on the right axis.

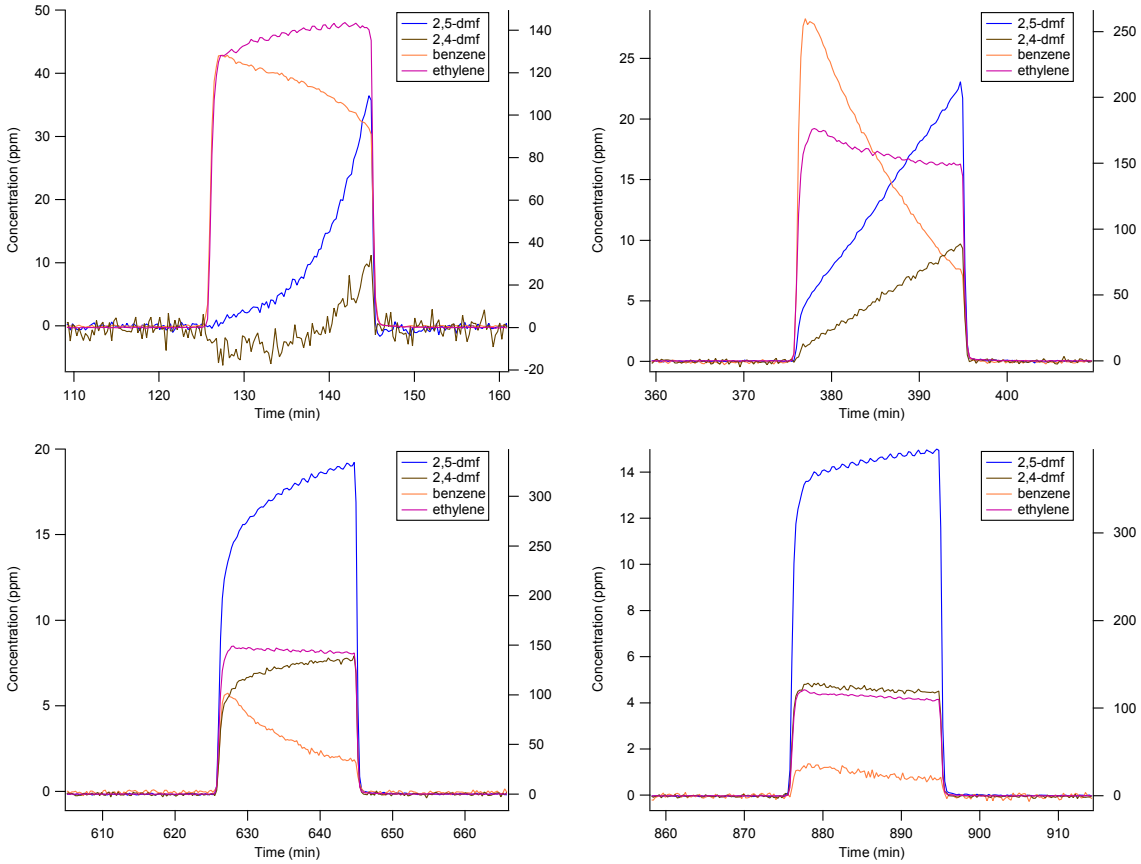


Figure 10. Concentration of different species during four consecutive pulses on HZSM-5-SAR55.

As it can be seen, each one of the selected compounds has a different trend representing all the different behaviours found during the analysis. Beginning with the aromatic molecule benzene, it has a high conversion during the first pulse, where the amount of 2,5-dmf is not enough to saturate the

system, but the amount produced is reduced gradually with time, each time a new pulse begins, the concentration of benzene is the same as it was at the end of the previous pulse. Another molecule with the same behaviour as benzene in this experiment is toluene. Ethylene, which is an olefin has a completely different behaviour. The concentration of the compound is high at the start, and it increases to reach a maximum at the end of the first 2,5-dmf pulse, once this maximum is reached, the concentration decreases very slowly with time. Finally, the isomerization of 2,5-dmf to produce 2,4-dmf has a different trend as the previous two, in this case, the concentration of 2,4-dmf increases in a similar way as the 2,5-dmf concentration does, until it reaches a maximum value where the system is saturated, at this point, the production of 2,4-dmf remains stable with time.

These results for the different compounds can be related to the evolution of the amount of acid sites represented in the Table 2. In that table, the amount of LAS decrease very slowly, while the amount of BAS decreases faster. The concentration of benzene decreases very fast, this could be related to the fact that more BAS are deactivated each reaction period. On the other hand, ethylene has a slower decrease in the concentration and 2,4-dmf production is stable in time, both compounds could be produced on the LAS that have a slow deactivation.

4.2.2. Performance on continuous flow

In long reaction time experiments, the catalyst gets deactivated due the formation of coke on the surface, stopping the different reaction pathways. For this case, it was decided to test how temperature would affect these long reactions. The experiment consists of flowing 2,5-dmf through the system for a given amount of time at low temperature (100 ºC), and then include a temperature ramp of 10 ºC/min from 100 ºC to 600 ºC for twice the time of the low temperature step. The experiment lasted 7.5 hours performing 5 oscillations of temperature.

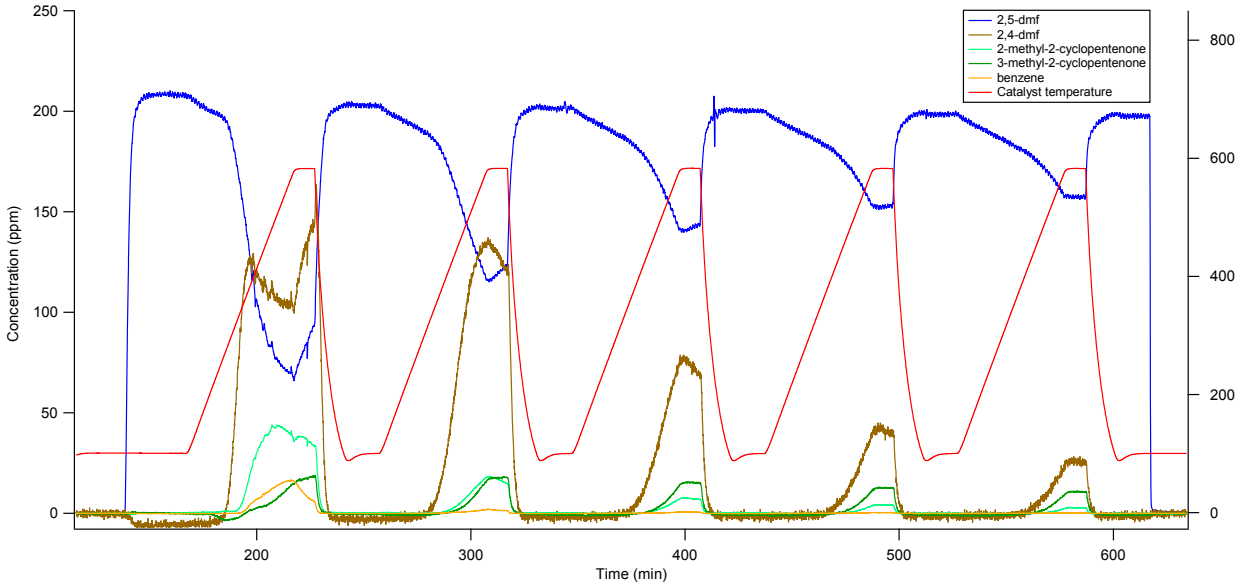


Figure 11. Concentration of different species during temperature oscillation on HZSM-5-SAR55.

The concentration of 2,5-dmf is higher during the low temperature step because at that temperature there are almost no species forming, when the temperature increases, several compounds start to appear. Some aromatic compounds like the BTX share a similar behaviour, there is some production during the first increase in temperature, but on the following ones the concentration gets drastically reduced, this can be seen on the benzene signal. Other compounds, like the ones formed due isomerization reactions, like 2,4-dmf or 2-methyl-2-cyclopentenone, also have a reduction of its production with time, but with a slower reduction than the aromatics group. A different trend than any other compound is observed on 3-methyl-2-cyclopentenone, that has a similar concentration production for all the oscillations.

Looking into detail on the first temperature oscillation, the 2,4-dmf production has a convex form at the top of the peak, in this same pulse there is some benzene signal. On the other temperature oscillations, the 2,4-dmf pulses have a concave form at the top, and there is no benzene production. This relationship could be attributed to both species being produced on the same acid sites, when benzene is producing the reaction is dominant and 2,4-dmf can not be produced in those acid sites, while for the following temperature oscillation, these acid sites are deactivated and the production of 2,4-dmf is not interrupted by any benzene forming on the zeolite.

In Figure 10 it seemed like 2,4-dmf production would be stable over time during the 4 pulses, with this experiment it can be seen how long enough periods of time would end up with the reduction of isomerization reactions due the deactivation of the acid sites of the catalyst.

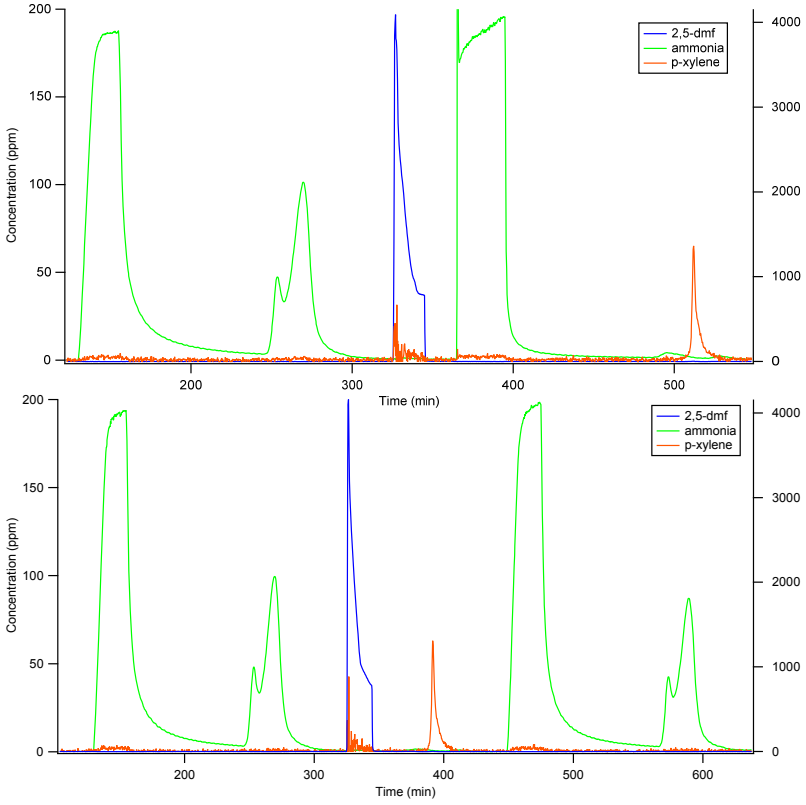
The main reason to the reduction of the concentration of products with time is coke formation on the surface of the catalyst. By looking at the 2,5-dmf signal on Figure 11 it is clear that the total amount of

species produced is reduced each time the temperature increases, since the difference from the signal at low temperature and at high temperature is less each time.

4.3. Characteristics of 2,5-dimethylfuran desorption

When performing the experiments described in chapter 4.2.1, the formation of p-xylene during the temperature ramp was observed corresponding to the NH3-TPD performed after the 2,5-dmf pulse. That compound is not produced in significant amounts when flowing the model compound through the system at higher temperatures. Adsorbing 2,5-dmf to the surface of the zeolite at low temperature (100 ºC) and then increasing the temperature will promote the reaction mechanisms to produce p-xylene and desorb it from the catalyst. Several experiments have been done to better comprehend the mechanism of the reaction.

Adsorbing 2,5-dmf onto the zeolite at low temperature and then performing a TPD, with a temperature ramp from 100 to 600 ºC at a rate of 10 ºC/min, is enough to produce p-xylene. By doing this experiment, it is possible to determine the temperature of maximum production of p-xylene, which is estimated at around 360 ºC. It is noteworthy that this temperature is similar to the optimal temperature for BAS desorption when performing NH3-TPD analysis.



The upper graph in Figure 12 corresponds to an experimental procedure were 2,5-dmf is adsorbed onto the surface of the zeolite for a short period of time, 20 minutes, and at 100 ºC, and two NH3-TPD are performed, one before and one after the 2,5-dmf pulse. The graph below has a similar procedure, but before performing the second NH3-TPD, a temperature ramp from 100 to 600 ºC is added.

Figure 12. p-xylene production with two different procedures on HZSM-5-5SAR55.

It can be observed how on the first scenario, during the NH3-TPD there is almost no ammonia desorption, while p-xylene is produced. On the counterpart, on the second case, during the temperature ramp p-xylene is formed and after that, NH3-TPD gives similar values of available acid sites that those obtained before the 2,5-dmf pulse.

On the first experiment, the amount of acid sites available before and after the 2,5-dmf pulse are 0.463 and 0.033 mmol/g cat. For the second experiment, the values obtained are 0.460 and 0.410 mmol/ g cat. By looking at these values, almost all acid sites are occupied on the first experiment and are reactivated during the temperature ramp of the second one. The small reduction of the total amount of acid sites on the second experiment can be related to the formation of coke on the surface of the catalyst during the temperature ramp after the 2,5-dmf pulse.

Performing a 2,5-dmf pulse at low temperature has an effect of adsorption of the molecules to the acid sites, and when increasing gradually the temperature the acid sites get activated and produce different species such as p-xylene, which then can get diffused to the environment. That is why on the first experiments ammonia molecules couldn't get attached to the zeolite during the second NH3-TPD, but on the second one, the acid sites previously occupied are available.

To increase the amount of p-xylene produced, some experiments were designed using ethylene as a driving molecule to enhance the total production. Different procedures were tested, they consisted of pre-adsorbing ethylene on the catalyst before the 2,5-dmf pulse and flowing ethylene during the temperature ramp where the p-xylene is produced. None of those practices made a difference on the amount of p-xylene produced, furthermore, ethylene seemed to not be suitable for adsorbing on the HZSM-5 zeolite with SAR27 and SAR55.

Related to the previous explanations, the acid sites of the zeolite would behave differently depending on the reaction temperature. The experimental procedure designed to test the performance of the zeolite at different temperatures consisted in five short 2,5-dmf pulses of 20 minutes at different temperatures (250, 300, 350, 400 and 450 ºC), followed by a temperature ramp from 100 to 600 ºC and finally a calcination step to regenerate the zeolite before the following pulse.

In Figure 13 there is a graphical representation of the 2,5-dmf pulses with some other species to see the different trends. CO peaks are an indicator of the amount of coke released when performing the calcination step. Two other species are represented to show the different behaviours depending on the nature of the compound. As it can be seen, ethylene signal during the temperature ramp is high at lower temperatures, but as the temperature increases, that amount decreases, and the amount of

ethylene produced during the 2,5-dmf flow increases, benzene has a similar behaviour to the one of ethylene. On the other hand, naphthalene, which is often considered a precursor of coke formation, is only produced during the 2,5-dmf pulse, and its production increases with the temperature, other compounds that have similar behaviour are 1,3-butadiene, toluene and 2-methylfuran. The amount of coke produced on the surface of the catalyst increases when increasing the temperature of reaction, coke forming on the surface of the zeolite could affect its acid sites by deactivating them, impeding 2,5-dmf molecules to get adsorbed and therefore reducing the amount produced during the temperature ramp step.

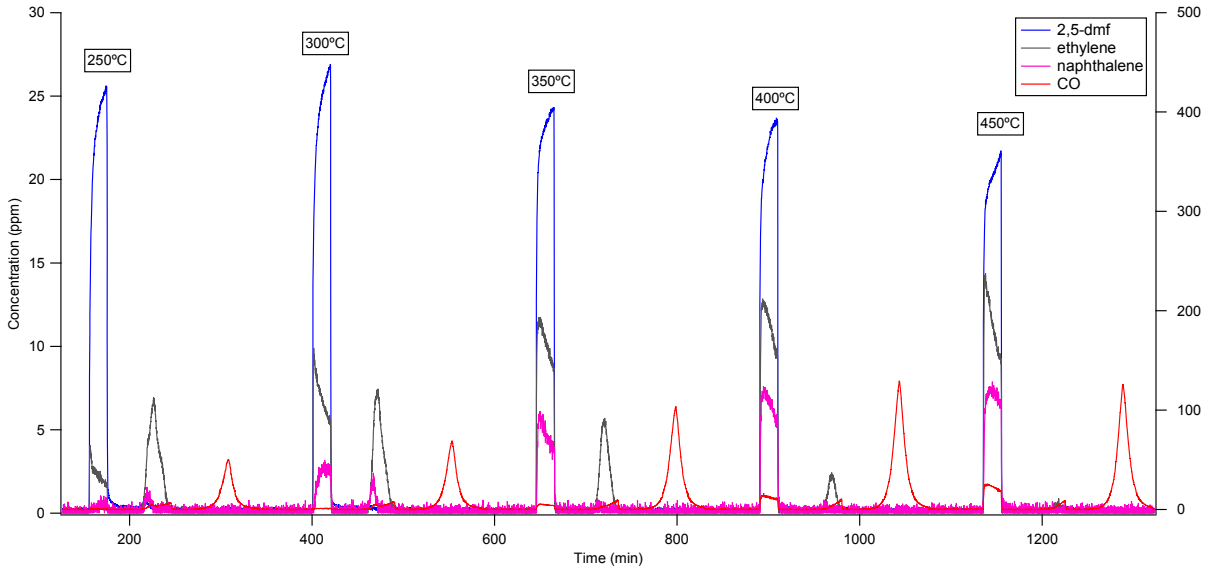


Figure 13. 2,5-dmf pulses at different temperatures on HZSM-5-SAR55.

4.4. DRIFTS analysis

The experimental procedure conducted on DRIFTS consisted of a calcination step where the temperature was maintained at 307 ºC, the maximum temperature the chamber could reach, while flowing 20 % O_2 into the system. This step is necessary to have the zeolite ready for the experiment. The zeolite selected was HZSM-5-SAR55 with a particle size between 80-40 µm. As previously mentioned on the methodology, it was used KBr to obtain a better signal during the experiment.

After the calcination step, the chamber is purged with Argon. When the signal is stable and there is no oxygen in the system a background is taken. Finally, 2,5-dmf is flown into the system and spectra are collected every few seconds to appreciate changes on the surface of the catalyst while reaction is happening.

In Figure 14 an overview of all the signals obtained during the 2,5-dmf reaction inside the region of interest can be seen. Chronologically the signals go from blue to red and finally green. Some peaks of interest are at around 3000 cm^{-1} which corresponds to the vibration of the CH bond and at 3600 cm^{-1} which corresponds to the vibration of the OH bond.

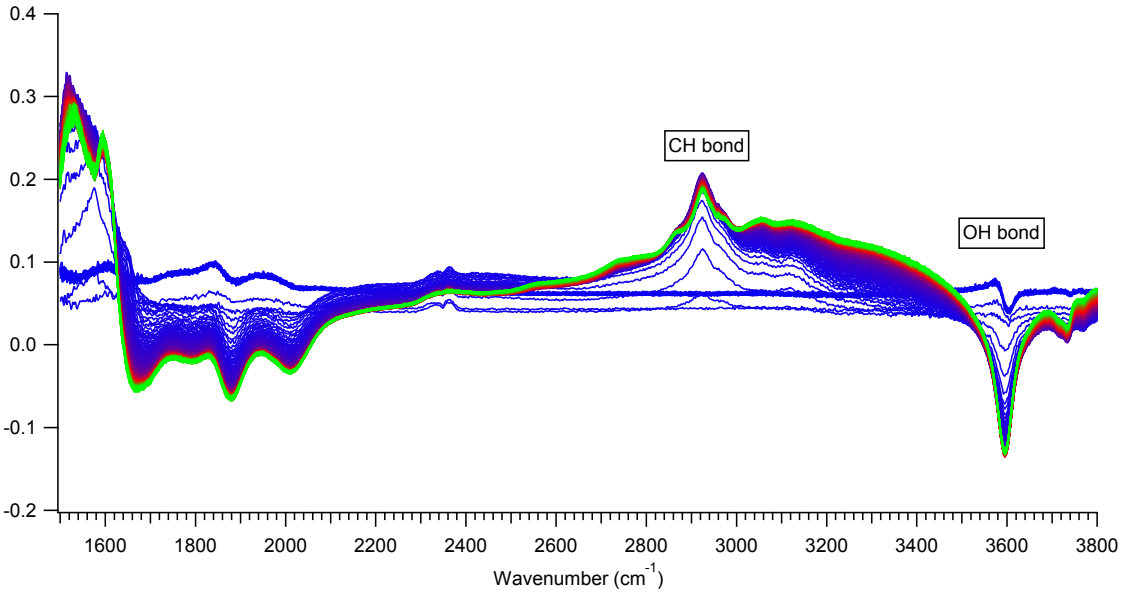


Figure 14. Overview of all the signals obtained during 2,5-dmf reaction.

Looking into detail into these areas we can see how the CH-vibration increases while the OH-vibration decreases. The OH bonds correspond to the bonds inside the zeolite framework. The decrease of these bonds can be interpreted as the reduction of the amount of acid sites available on the catalyst. On the other hand, the CH bonds can be attributed to the hydrocarbons formed around the catalyst, this is in line with the results, that show an increase of the CH signal with the reaction time.

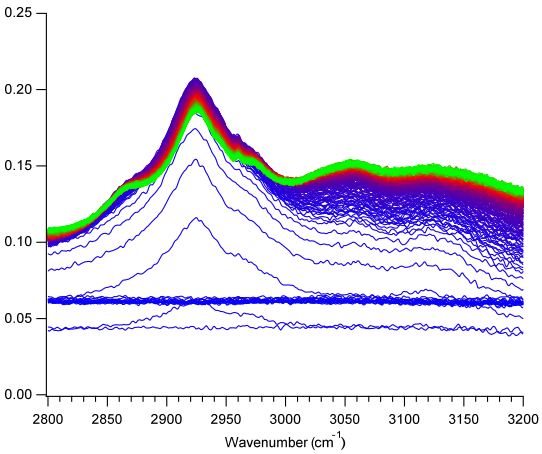


Figure 165. CH bond signal.

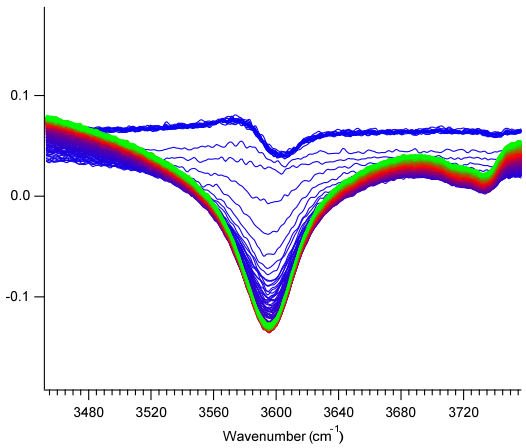


Figure 156. OH bond signal

Looking at Figure 156 there is a big peak around 3600 cm^{-1} and one smaller peak at around 3720 cm^{-1}, as discussed by other researchers the bands at lower frequencies are expected to involve weaker OH group bonds, which means that are more acidic [26]. Therefore, this signal could correspond to the acid sites behaving as BAS while the other peak corresponds to LAS. Taking this into account, there are more BAS in the zeolite, also, these sites are the ones that deactivate faster during the reaction for the zeolite studied. These results are in line with the experimental observations made in previous experiments during this project.

5. Conclusions and future work

As a conclusion of the thesis, all the techniques used during the development of this project contributed to obtain quality data for the quantification and analysis of the acid sites of the zeolites in different scenarios. The acid sites have been differentiated and its behaviour and characteristics can be related to the production of different compounds.

Performing reactions for long periods of time or at elevated temperatures resulted on the faster deactivation of the acid sites due coke formation on the zeolite. Increasing the reaction temperature will also increase the total amount of coke formed around the zeolite, affecting specially the BAS that deactivate faster than LAS.

Different groups of compounds such as olefins, aromatics or isomers have their own reaction pathways, which means that their production can be optimized by design of the catalyst or the conditions of the experiment. The production trend of the different compounds can be associated to the acid sites of the zeolite, for example, benzene production has a decrease in time similar to that of the BAS available on the zeolite. On the other hand, isomerization reactions and olefins production are more stable over time, having a decrease in a much slower pace, this behaviour is like for the LAS, which are harder to deactivate over time.

An interesting observation was made when adsorbing 2,5-dmf on the zeolite at low temperatures. Other reactions mechanisms are enhanced allowing to produce valuable compounds such as p-xylene, which is not produced at higher temperatures or different conditions.

Finally, about the different types of acid sites of the zeolite. BAS showed to be the most abundant type of acid sites on the samples studied but are easily deactivated over time. On the other hand, LAS are less abundant but are harder to deactivate, allowing the production of compounds for longer periods of time or at higher temperatures.

Future work can be performed on the analysis of the coke formation. Temperature programmed oxidation is an experimental method similar to the NH3-TPD that can help improve our knowledge on coke formation. What type of coke is formed, where and when are some of the questions that may be answered. The information of this project together with the analysis of the coke can lead to a better understanding of the reaction's mechanisms and characteristics of the acid sites.

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