Universidad De Zaragoza

Gas Detection of Different Polarity Molecules by Capacitive Sensors Based on Zeolites

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1. Introduction

The ability to sense different environmental parameters is extremely desirable in industry. Temperature, motion, humidity, pressure, sound and the presence of environmental molecules are just a few examples of important conditions many different commercial areas wish to detect and control. In particular, gas sensors are needed in the areas of industrial processing and the automotive industry [1]. Gas sensing in industry is important as increasing the control of gas flows and combustions can help to produce inexpensive, enhanced products. The automotive industry needed gas sensors due to the increase in restrictions in emissions [2]. Other industries that require gas sensors include but are not limited to: chemical processing, food, electronics, pharmaceuticals and textiles [1]. Gas sensors are also important for everyday human comfort technologies and in toxic environments for health and safety purposes.

There is a huge drive for research into different techniques for improving gas sensing equipment because of these needs. Traditionally the aim of gas sensor research has been to improve selectivity, sensibility, response and recovery times. Currently, the research drive is focused specifically on the improvement of selectivity as other parameters are deeply studied. As well as these parameters there is a particular interest in sensor miniaturization for cost and performance purposes [3]. By reducing the size of the sensors, fewer materials are used and therefore the output costs can be reduced.

When working with gas sensing the presence of natural moisture is very important. This is because moisture can appear near enough everywhere. The amounts and the effects of moisture need to be taken into account when detecting certain chemical species. This is to limit the interference effects that can take place while attempting to sense specific analytes [1].

1.1 What is a gas sensor?

Sensing devices are generally made up of three main parts. These are: a sensing material, a transducer and a signal processor. The sensing material is sensitive to a certain environmental stimulus. When this stimulus is introduced to the sensing material its properties are altered in a specific way. The job of the transducer is to detect the change in the sensing material properties and convert this change into an electrical signal. The signal processor receives this electrical signal and quantifies it into results which are comprehendible.

Fig. 1: Parts of a gas sensing device

Transducers

The transducer is probably the most important part of the sensor. It is used to convert one type of energy to another. There are two types: thr input and the output transducer. The input transducer converts a physical signal to an electronic current and the output transducer does the opposite. The types of transducer used in sensors are input transducers. Their function is to convert some sort of physical input, detected by a sensing material, into an electric signal. This can then be processed into something understandable to a user by a signal processor. The electrical signal, which the transducer outputs, is proportional to the strength or intensity of the physical quantity detected. A common example of an input transducer can be seen as the microphone. This converts vibrational energy into an electrical signal. Other examples of devices which use input transducers include motion detectors, touch screen devices and electronic weighing devices.
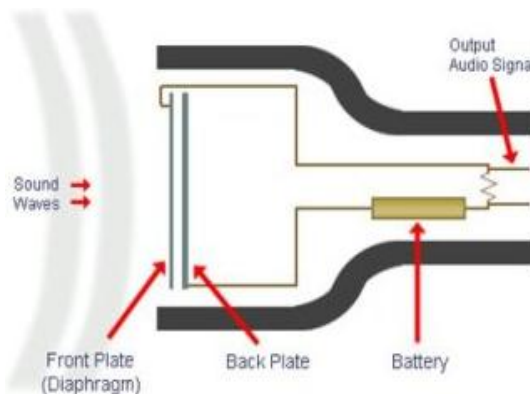
Fig. 2: The transducer of a condenser microphone [4]

- An electronically charged diaphragm is the sensing material part of the microphone

- A current is passed through the back plate and a capacitance is created across the gap

- The sound waves travel towards the diaphragm and this makes it vibrate

- The change in distance between the back plate and the diaphragm changes the capacitance

- This can then be quantified by a signal processor

The microphone is an example of a capacitive transducer. The concept of using a change in capacitance as a sensing device is commonly used. Around 75% of the humidity sensors are based on capacitive techniques [1]. This is due to the parameters that can cause a change in the capacitance of a device.

$$C = \epsilon_o \epsilon_r \ \frac{A}{D} \qquad Eq.1$$

Eq.1 shows the capacitance of a device, where C is the capacitance, A is the surface area, D is the distance between the electrodes, ϵ_o is the permittivity of the air and ϵ_r is the permittivity of the material in-between. The equation shows that the capacitance of a device can be affected by the surface area of the electrodes, the permittivity of the air and the material and the distance in between the two plates. Any external source that can alter these parameters can be detected using a capacitive transducer. This results in capacitive transducers having a wide variety of applications as sensing devices. To complete the sensing device, the transducer requires a signal processor and a sensing material.

Signal processors

The signal processor is important in a sensing device to show and record sensed changes in a comprehensible way. Their job is to receive the electronic signals given by the transducer and to quantify them into something that can be measured and understood. It is important that the signal processing method is produced and calibrated in the most accurate way possible to help avoid noise and other interference factors. For example if the signal processing's quantified values are too big then large amounts of information can be lost. The smaller these values are the more information can be saved.

Sensing materials

The sensing material is the part of the sensor that initially detects the environmental conditions. These conditions affect the properties of the sensing material in a way which can be measured. A sensor's ability has a high dependence on the type of sensing material used. For the most effective sensor, a sensing material is needed that is strongly affected by the desired conditions; also it is important that these conditions are easy to measure. There are many examples of materials that have been used for sensing such as: polymers, carbon and tin oxide nanotubes, anodic alumina and porous materials [1].

The nature of polymers makes them good sensing materials. They are used in sensing devices as they have a great variation of flexibility in use; they are cheap and because of their functional groups. Carbon and tin oxide nanotubes have been used due to their improved electrical and chemical characteristics at the nano scale. Porous materials have been used as sensing materials especially in gas sensing as their internal properties can be affected when molecules enter inside them. They also have selectivity properties and because of this they are possibly the material with the most potential. A good example of this type of material is zeolite.

1.2. Zeolites

As previously mentioned the majority of research into sensing devices is based upon large improvements in sensibility and selectivity for specific analytes. The problem is that for a lot of these cases the sensing devices are limited to ideal conditions. There is also research into materials that can be used as sensors and are also easier to manipulate for several different purposes; an example of these materials are zeolites.

Zeolites are materials that have become valuable in sensing equipment due to their internal frameworks, their ion change properties and their control in synthesis. They are natural occurring materials but can also be synthesised with high control over their internal structure, framework and ionic properties. This makes them an excellent material for mass manufacturing and industry. To date, there are approximately 34 different types of natural occurring zeolites known [5]. Zeolites that can be artificially synthesised in a lab have greater control over framework and properties. Nowadays there is estimated to be over 150 different artificially synthesised zeolite frameworks with exact channel and pore sizes inside of the crystals [1].

Zeolites are aluminiumsilicates crystalline porous materials. The chemical composition for zeolites can be written as [3,5];

$$Me_{xin}(AlO_2)_x(SiO_2)_y * mH_2O$$
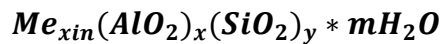
They are made up of AlO_4 and SiO_4 tetrahedral blocks formed in a three-dimensional formation via the oxygen atoms [6]. The tetrahedral blocks are linked together to form ring like structures [7]. This leads to crystal lattices with very small channels, pores and cages.
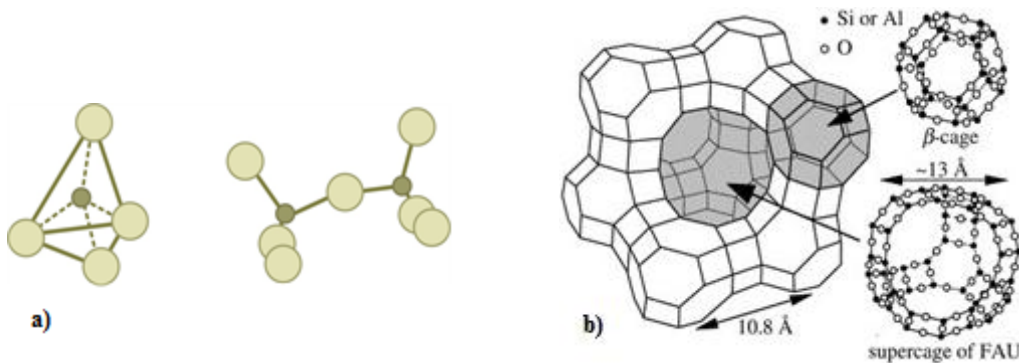
Fig. 3a and 3b: The basic building blocks of zeolite [8] *(left).* image of a zeolite with FAU framework [9] (*right*).

In a complete siliceous structure with SiO_2 tetrahedral, silica with a neutral charge is created. In zeolites the aluminium atoms replace some of the silicon ones and are alternatively bound between shared oxygen atoms. SiO_2 has a +4 charge. When the +3 charge of aluminium is introduced to replace the silicon it creates a negative charge inside the framework [8]. Extra framework cations electrostatically bound to the host are allowed to move along the channel to compensate and create an overall natural framework [7].

Properties of zeolites

The zeolites pores give a large surface to volume ratio which means that they are excellent at adsorbing. The channels that are created inside of the material can be used to trap, adsorb and filter different molecules. The pores have a uniform sub-nano size throughout the entire crystal [1, 6] and because of this they have been given the name "*molecular sieves*" [5].

Due to the uniformity of the small channel sizes in zeolites, only molecules with certain diameters that are smaller than the pore entrance may enter. This is not possible for larger molecules. F.S Stone et al. [12] show an example of this where zeolites were used to hydrate isopropanol. This can be used for processes where specific selectivity is needed. For example, the pores can be used to dry liquids or to separate gases by trapping molecules inside of the pores [6]. Specific zeolites can be carefully chosen to improve selectivity processes. This can be seen when comparing zeolite A and ZSM-5. Molecules between 4-6Å diameters in size can enter the pores of ZSM-5 (*4Å*) but not zeolite A (*6Å*). For adsorption, zeolite A has a bigger cubic capacity when compared to ZSM-5 although the amount of adsorption can be affected by other parameters such as the molecules polarity.

The extra framework cations inside of the crystals allow for ion exchange to take place inside the material. This is due to the negative charge created by the aluminium ions. In catalysis, the exchangeable cations allow for numerous applications [6]. This property has been used in the oil and gas industry to crack hydrocarbons. Currently around 95% of all cracking processes in the oil industry are done using zeolite material [5]. The amount of ion exchange to take place can be dependent on the amount of cations. For example zeolite A is greater for ion exchange then ZSM-5.

The electrostatically bound extraframework cations motion in zeolites can be interfered with the addition of guest molecules. This property allows them to be used in sensors based on transducers with electrical behaviour, detecting changes in impedance (resistance) and

capacitance when a guest molecule is introduced [13]. By measuring the changes in these properties, information about the amount of analytes being adsorbed into the structure and therefore environment can be obtained.

As well as this, zeolites can create selectivity by control of the pore sizes, structure and adsorption characteristics [1]. There are several characteristics that can affect the process of adsorption in zeolite materials. These are pressure, temperature, the nature of the gas and the nature of the zeolite.

Adsorption is greatest in zeolites when there is high pressure and low temperature. This is because both pressure and temperature affect the differential heat of a process. All adsorption processes are exothermic as energy is released when attracting the adsorbate to the adsorbent. Therefore negative change in the free energy is needed for adsorption to take place [5].

$$\Delta G = \Delta H - T\Delta S \qquad Eq.\ 2$$

(Where ΔH is the differential heat, ΔS is the change in entropy and ΔG is the free energy)

As the free energy is negative and the differential heat is negative so is the change in entropy. At low temperatures and high pressure a negative differential heat is more probable. This results in when the pressure is high and temperature is low the rate of adsorption is increased.

The probability of zeolites to adsorb a guest molecule is determined by its adsorption affinity. This characteristic is determined by the relative ratio of Si/Al. This is due to the intrinsic charge compensation ions [1]. By controlling the Si/Al ratio, molecule selectivity can be improved. This is due to the polarity of the molecules and the reduction of charge from the Al atoms. When the zeolites are dried, the remaining cations are left inside of the channel walls or intersections and can seriously affect the rate of diffusion of most molecules [5]. As the cations are largely located near the pore openings, they can change the affective aperture size. When determining the effectiveness of a molecule to adsorb into a zeolite the important characteristic is the kinetic diameter. This is "*the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy*" [5]. This determines whether or not a molecule is small enough to enter inside the zeolite.

Therefore due to their adsorptivity, high surface area and porosity, presence of mobile ions and catalytic behaviour, zeolites are attractive candidates for chemical sensors [7].

Types of zeolites

Due to the huge amount of zeolites and the many different properties they possess, there are several different ways in which they can be classified. Some examples of zeolite classifications are: framework type, framework density, ionic properties and channel and pore size. The formation of frameworks is dependent on the way and the amount in which the Al and Si atoms are bound together. Depending on this, the size and shape of the channels are controlled. Some of the most common types of frameworks are LTA, MFI and FAU where the zeolite MFI framework is probably the most studied of all zeolite frameworks [8].

When choosing different zeolites it is important to understand the individual properties that they offer. This work has been focused on zeolites with LTA and MFI frameworks.

LTA structured zeolites (zeolite A) are built up of two types of arrangements; 8 tetrahedra in a cubic shape and 24 tetrahedra in an octahedron shape. The framework is built up by every cube corner connecting to the octahedrons creating caged cavities in-between. Zeolite A is a low-silica based zeolite and therefore has a high cation concentration to compensate for the reduction in charge [8]. The Si/Al ratio is around 1. This makes Zeolite A a fairly hydrophilic material. The pore sizes are around 4Å and a cage diameter of 11.5Å. The pore volumes are around 0.30cc/g [5].

Fig. 4: Image of LTA structure [10]

Example of MFI structured zeolites can be seen as silicalite and ZSM-5. Silicalite has a pure silica zeolite. The Si/Al ratio is infinite meaning it is very hydrophobic. ZSM-5 is also a high-silica zeolite resulting in low cation content [8]. The Si/Al ratio can range between 2.5-100; meaning that it is less hydrophilic than zeolite A but more than silicalite. The pore sizes are around 6Å and have pore volumes of about 0.10cc/g [5].
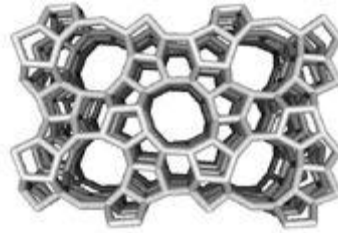
Fig. 5: Image of MFI [11]

1.3. Zeolites as gas sensors

As far as sensing goes; zeolites have obvious benefits over other materials. Zeolites can be used to improve the selectivity of sensors systems and also as a sensing medium itself. [1,14-15]. The characteristics of zeolites present us with an excellent material for creating gas sensing devices with a large control over their properties.

Zeolite sensors on Interdigital capacitance boards have been proposed to be used in on-board-diagnostic system in vehicles. *G. Hagen et al. [2]*. The zeolite sensors can be placed in car exhausts to detect the components of the engines exhaust gases. Using this information advanced engine controls can reduce emissions and fuel consumption.

Using zeolite IDC sensors for humidity sensing is another area zeolites have been combined with sensors to improve performance. *M. Urbiztondo et al. [1]*. As humidity is a frequently desired physical quantity, zeolite enhanced humidity sensors with improvements in selectivity and sensitivity could be used for many purposes; the main area being control of industrial processing.

Zeolites have also been used as a filter to separate methane or hexane in ethanol with a tin oxide sensor. *O. Hugon et al [6]*. This was done with several applications in mind. This include: fire detectors, carbon monoxide detectors, gas-leak detection in industry and domestic uses.

Zeolites are currently being used in many types of sensing devices to help improve the sensors abilities. These types of sensors include IDC, QCMS and cantilevers [1].

2. Project Aim

The aim of this project was to build gas sensors based on zeolites as sensing materials. As transducers, Interdigital Capacitors (IDC) have been selected and electrically characterized. The gas testing was carried out following the changes in capacitance and resistance for increasing concentrations of different analytes (water, toluene and ethanol). Moreover, the sensor design was changed completely, instead of depositing zeolites over IDCs, the IDCs were fabricated over an individual zeolite crystal. This sensor, called NanoIDC, was also characterized in the same conditions.

To achieve this aim, several objectives will need to be completed, including:

- Synthesis of zeolites, MFI and LTA type zeolites with different sizes and their characterization (SEM, XRD).

- Microfabrication of IDCs and the incorporation of the zeolites.

- Fabrication of the NanoIDC.

- Design and create an experimental set-up for the electrical characterization and gas testing.

- Electrical characterisation of different sensors.

- Testing zeolite sensors in presence of different analytes.

3. Experimental

3.1. Interdigital capacitors as transducers

Interdigital capacitors are capacitors with the electrodes in a comb-like interlocking finger shape [3]. This approach allows for a large electrode surface area over very small dimensions. The capacitance of a capacitive device can be found using Eq. 1 previously mentioned. The equation shows that by increasing the surface area of the electrodes, greater capacitances can be created over a smaller overall area.

The IDC chips used in the project were created using the reverse baking method of photolithography. This was done in a clean room with a class of 100.

The process was done, starting with Pyrex SiO_2 substrate. A photoresist was spin coated on top of the wafer. The wafer was then placed into a mask aligner and it was then exposed to UV to harden the resist. A mask of the corresponded design was placed over the wafer and a reverse bake was done to harden the parts which were uncovered. Then the mask was removed and a flood exposure was done. This was then developed. This reversed the hardened parts of the wafer. Aluminium was then deposited over the wafer using metal evaporation. A lift-off process was done to remove all the unwanted aluminium and leaving only the required designs. The individual chips were then cut to separate. Chips were designed with several different spacing between the electrodes. The optimum distance chosen for the electrode spacing was 10 micros.
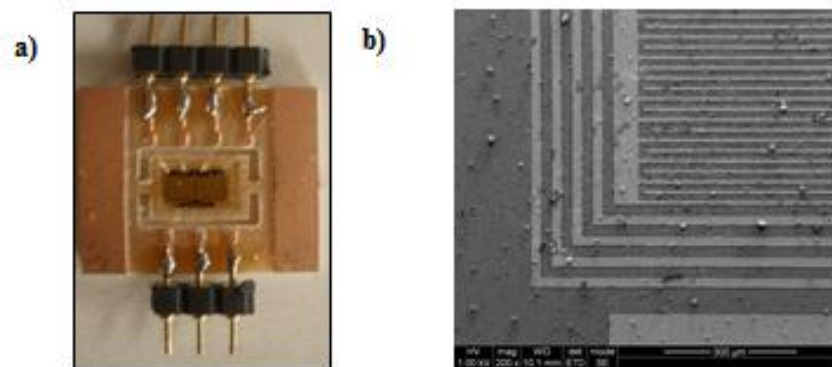
Fig. 6a and 6b: The zeolite IDC chip *(left)* and a SEM image of the chip *(right)*

IDC sensors, with zeolite crystals on top of an IDC chip, are sensors that have previously shown a high potential for gas sensors [1]. These sensors were produced with different zeolite types to show the effect of the different types of crystals on the sensibility of the IDC.

IDCs were first used with zeolites in [3] where they were used as dielectric gas sensors. This technique allows for the creation of sensor systems on single chips aiding towards miniaturization.

The sensor was created by attaching the IDC chips to a circuit board. The connections were made using micro contacts. Further connections were made to the circuit board to allow for easy access to the measuring device.

The theory behind Zeolite IDCs as gas sensing devices is based on the chips working as both the sensing material and the transducer needed to detect gas changes. When a current is passed though the IDC chips a capacitance is created across the interlocking electrodes.

As seen in Eq. 1 the amount of capacitance across the electrodes can be determined by the permittivity of the air and the material in between. When an analyte is introduced to the IDC chip the air permittivity can change and therefore affecting the electronic signal and the amount of capacitance across the chip. This theoretically can be used as a sensing device as the changes in capacitance can be related to the amount of analyte introduced. The problem is that in the case of an IDC chip in air there is a relatively low change in permittivity (unless high amounts of the analyte are introduced directly into the capacitor) this results in a very low sensitivity.
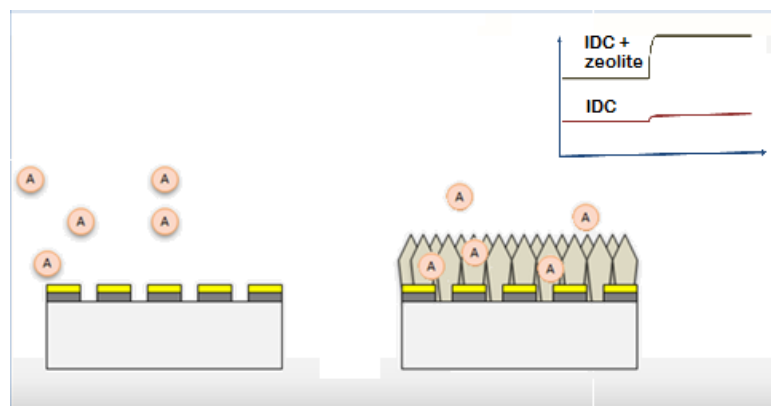
Fig. 7: Image of increased permutation close to the IDC with the use of zeolites

By depositing zeolites over the top of the IDC; when the analyte is introduced the pores of the zeolite help to trap more of the analyte closer to the electrodes. This results in an increase in change of permittivity and therefore a more sensitive sensing device. Zeolites also have the benefit over other materials, as previously mentioned, that they can be highly selective.

A problem with this configuration is that the change in capacitance is limited only to the area above the capacitor. This is because the analyte is not able to change the capacitive of the substrate effectively. To further increase the sensitivity of the sensor it was proposed to change the substrate for a sensing material, zeolite in this case. By doing this, a change of capacitance can be achieved by, not only the top layer of zeolite but also, the changes in the substrate. Moreover, to get further sensitivity a nanocapacitor could be created on top of a zeolite crystal. This idea gives nano scale benefits as well as the increase in sensitivity.
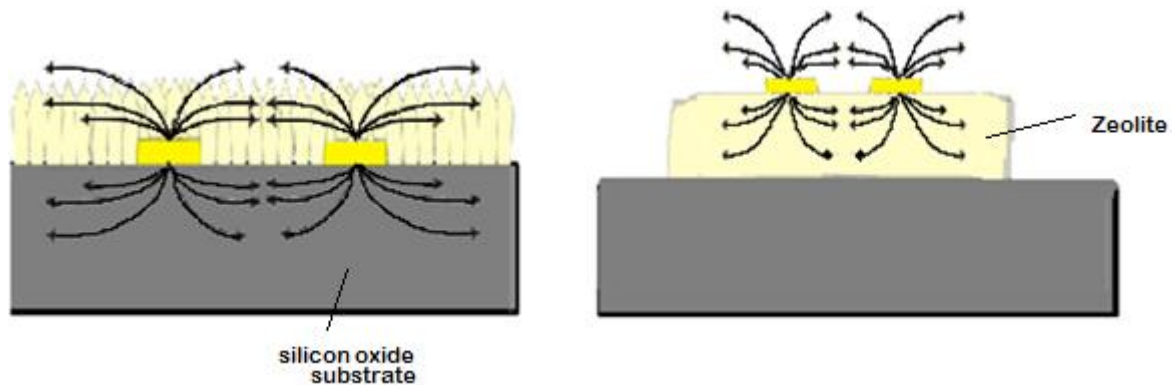
Fig. 8: Capacitive effect in IDC chips and nano capacitor

Zeolite nanocapacitors

With the use of nano sized technology, sensing equipment can be developed with improved characteristics. This is due to such benefits as increased surface area/ volume ratios, electrical and mechanical properties and also molecule selectivity [16-18].

Current research based around nanosensors is aimed at making use of singly synthesised nano structures that can be manipulated to work as a sensing device; the sensing material and the transducer. The sensors take advantage of the nano properties of increased sensitivity to parameters such as capacitance and resistance which can be transferred to the sensor's sensitivity [16]. The nano aspect of the project also can aid towards miniaturisation and as less material is used the product can be lower-cost [17]. By taking advantage of these nano characteristics and using them with the zeolite characteristics, the sensor should have an improved sensibility and selectivity.

3.2 Synthesis of sensing material: zeolite

For this project different types of zeolite crystals are required to test their different sensing capabilities. The parameters that will be compared will be: a difference in structure, changes in Si/Al ratios and variation in crystal size.

The difference in structure will change the pore size of the zeolites. This should affect the types of analytes that can be adsorbed, the rate of adsorption and the capacity of adsorption. The types of structures that will be produced will be MFI and LTA.

By producing zeolite sensors with different Si/Al ratios, an understanding of the effect of polarity can be obtained. This should affect the sensing abilities of different analytes in different ways. The crystals that will be synthesised will be: silicalite (*Si/Al = ∞*), ZSM-5 (*Si/Al= 100*) and zeolite A (*Si/Al = 2*)

A variation in crystal size will allow different sizes of sensors to be created. With small crystals sensors will be made with IDCs and with large crystals nano sensors. By creating different sizes in sensors it will be able to compare the sensing ability from the micro to the nano scale.

Zeolite crystal growth

To synthesise zeolite in a hydrothermal process there are several different reagents needed; a source of silica, a source of alumina and a mineralizing agent such as OH-. Also for a high Si/Al ratio zeolite such as silicalite, organic molecules may be required to help create the structure. The molecules can be used to fill voids, balance charge and/or as structural templates to create high-silica zeolites [8]. To create crystals the process moves from a meta-stable phase where the reactants are mixed, to ion transportation where monomers are produced, to a final stable phase where crystallization takes place.
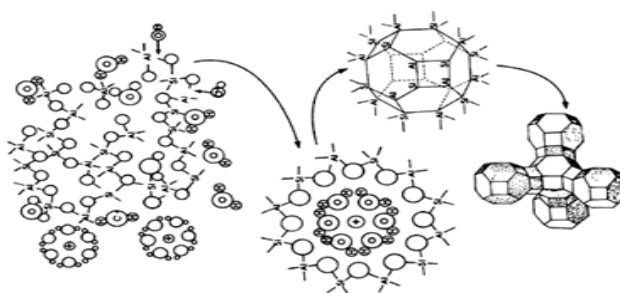
Fig. 9: The growth of zeolite crystals

Material type	Molar ratio	Method	Temperature	Synthesis time	Ref.
Silicalite	$9TPAOH: 25SiO_2: 480 H_2O: 100EtOH$	Oven	100ºC	15 hours	[21]
ZSM-5	$Na_2Al_2O_4{:}200SiO_2{:}14 Na_2O{:}9.5TPAOH{:}9400 H_2O$	Microwave	180ºC	15min	[21]
Zeolite A	$13.4(TMA)_2O: 0.3\ Na_2O: 1.8\ Al_2\ O_3 : 11.25\ SiO_2 : 700\ H_2O$	Rotatory oil bath	100ºC	8-12hours	[20]

Table 1: Small zeolite crystals

Silicalite

The small silicalite crystals were created using an oven method. To create the silicalite 48.6g of H_2O and 0.27g TPAOH were mixed together until homogenous. Then 1.12g of TEOS was added to the mixture drop by drop. The mixture was stirred for 8 hours until completely homogenous. The mixture was then placed in to a vessel and into the oven for 15 hours at 100ºC. Once completed the mixture was centrifuged at 8500rpm for 45 minutes. The seeds were then cleaned. This process was repeated 3 times.

ZSM-5

The ZSM-5 crystals were created using a microwave method. The process was done starting with 0.2737g of NaOH mixed with 38.9607g H_2O. 2.5770g of TRAOH were added to this mixture and stirred for an hour until homogenous. Then 0.0513g of aluminium $Na_2Al_2O_4$ were added and again stirred for an hour until homogenous. Finally 8.1373g of LUDOX solution were added and this was then stirred for 24 hours. The crystals were then produced in the microwave. This method was done at 180ºC at 300W. For the small crystals the synthesis time was 15 minutes.

Zeolite A

The small zeolite A crystals were grown in a rotating oil bath. The process was done by creating two solutions; the silica part (solution 1) and the aluminium part (solution 2). Solution 1 was made using 6.39g of silicon Ludox diluted in 5.68g of H_2O. Solution 2 was made using 2.13g isoprapoxide aluminium mixed with 14.20g TMAOH and 19.88g H_2O

which were stirred till homogenous. Solution 2 was mixed with 2.8g of 1 mole NaOH and 70ml of H_2O. Solution 2 was then added over solution 1 and was left to mix for 48 hours. The solution was placed in a rotating oil bath at 100ºC until it turned white. A centrifuge was then used to purify the samples. This was done at 400rpm for 10 minutes. The supernatant was then removed, replaced with water and then mixed in a sonic bath. After completing 3 times the crystals were then dried in an oven at 80ºC for 24 hours.

Synthesis of large crystals of zeolites

Material type	Molar ratio	Method	Temperature	Synthesis time	Ref.
Silicalite	$40SiO_2$: 9TPAOH: $9500H_2O$	Oven	130 ºC	12 hours	[22]
ZSM-5	$Na_2Al_2O_4$:200SiO$_2$:14 Na$_2$O:9.5TPAOH:9400 H$_2$O	Microwave	180ºC	90min	[21]
Zeolite A	$1.7Na_2O$: $Al_2\,O_3$: $0.7\,SiO_2$: $165H_2O$: 6.1TEA	Oven	85ºC	4 days	[19]

Table 2: Large zeolite crystals

Silicalite

Large silicalite crystals were synthesised using an oven method. 11.80g TEOS and 9.02g of water were added drop by drop into a vessel and stirred at room temperature. They were left to stir for 1 hour and then 11.38g TPAOH 1M were added and stirring was continued for another 3hours. (aging time of the gel)

When the aging was finalized a highly diluted gel was obtained. The gel was introduced into a Teflon autoclave with a steel casing as the process produces high temperatures. The autoclave is introduced into the oven at 130ºC for 12 hours. After this time the autoclave was cooled to complete the growing process. The mixer was then centrifuged at 2750rpm and 20 minutes to separate the crystals from the gel.

ZSM-5

The synthesis process for the large ZSM-5 crystals was the same as for the small ZSM-5 crystals only changing the synthesis time. For the large crystals the synthesis time as 90 min.
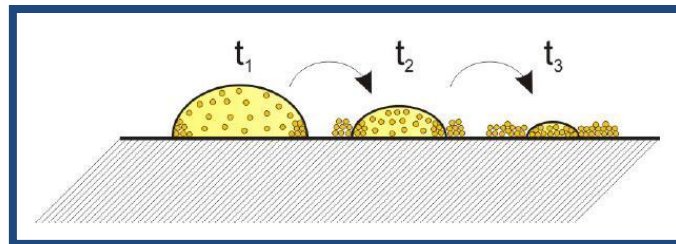
Zeolite A

Large zeolite A crystals were synthesised in an oven. To prepare the synthesis gel, 0.99 g of NaOH were diluted with 4.95g of H_2O in a vessel. During continuous stirring, 0.66g of aluminium flakes were added slowly and heated up to 90ºC for 2 hours. Once the aluminium was completely dissolved, 1.16g of sodium metasilicate, 5.52g of triethanolamine (TEA) and 12.82g of water were added. While this solution was under stirring, solution 2 could be prepared. For that purpose, 5.58g of TEA with 17.78 g of H_2O were mixing in a vessel and 0.58 g. of TEOS were added under continuous stirring until a homogeneous solution was obtained. After 2 hours mixing, solution 2 was poured over solution 1 and stirred for 6 hours. The final solution was introduced into an autoclave at 85ºC for 4 days. After several centrifugations at 4500 rpm for 15 min followed by a sonication step, the zeolite A crystals with the appropriate size had been achieved.

3.3. Incorporation of sensing material and final sensor preparation

The final part of creating the zeolite sensors was to introduce the zeolite crystals on to the chips. Due to the different types of sensors, different methods were proposal for introducing the zeolites to the different types of chips.

Standard Interdigital capacitor (IDC)

The IDC and zeolite sensors were prepared using micro-drop deposition. The process involved the suspension of the crystals in ethanol. This was done by placing 0.015g of the crystals with 3ml of absolute ethanol into different vessels. These vessels were then placed into a sonic bath for 10 minutes. This was done to make the suspension homogenous, allowing agglomerations to sink to the bottom of the vessel leaving single crystals dispersed. Using a micro-syringe, a single droplet (*10ul*) of the solution was carefully deposited on to the chip. This was left for 10mins. Over this time the ethanol evaporated and the crystals adhered to IDC surface by electrostatic forces. The process was repeated until around 50ul was achieved (*usually repeated 5 times*).


Fig. 10: Micro deposition of zeolite crystals

Zeolite nano capacitors

Sensors were created with nano capacitors on top of crystals to show the sensing properties on the nano scale. The nano capacitor was created using a focused ion beam (FIB) in a clean room of 10 000.

The process for creating the nano capacitors started using the micro-drop deposition as previously discussed with the IDC sensors but with further dilution. This was done to deposit fewer crystals and to give a better chance of having single crystals deposited in the horizontal plane. The chip used in this case was a simple 4 line micro adapter. These chips where made of Si with a thin layer of SiO_2.
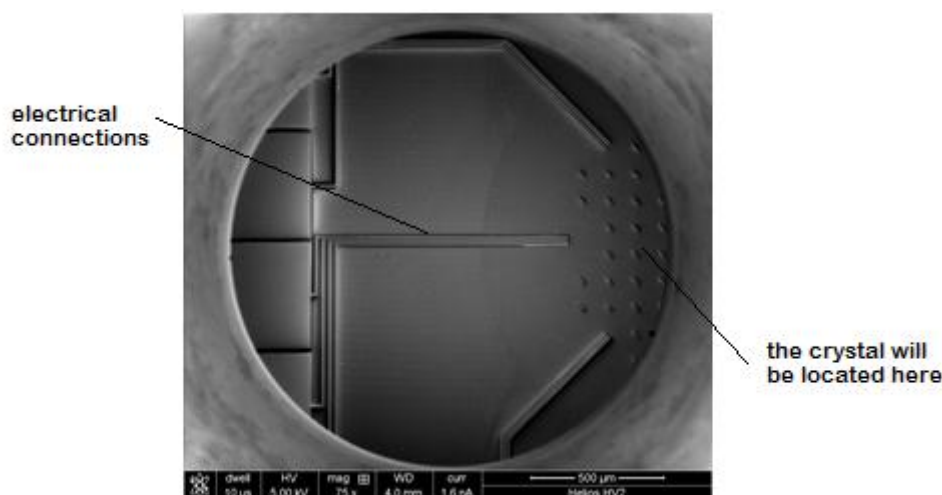
**Fig. 11**: SEM image of simple 4 line micro adapter

The FIB has the capability of drawing lines of palladium over this type of material with a minimum width of 200nm. Due to the limitations of the ion beam width crystals of micro size were needed to create a capacitor which was several electrodes thick. It was also important that the surfaces were planer to improve the accuracy of the capacitor.

In the clean room, the chip was introduced to the FIB vacuum chamber and pressurized. In the process the first step was to examine the chip to find a suitable crystal. A capacitor pattern was placed on top of the crystal and the ion beam was turned on to create it. An ion beam is used to ionise a palladium precursor on to the samples surface. Three types of materials were used for the nano sensors. These were: silicalite, Zeolite A and ZSM5 crystals.

Wires were drawn from one of the four way connections to the single crystal. The wires and the capacitor were then connected by creating lines up the vertical axis of the crystal. A capacitor was also drawn on the opposite side over the substrate. This was done to create and test a blank reference.

3.4. Experimental set up

To test the sensors features an experimental system was designed. The idea was to test the changes in capacitance and resistance when introduced into certain environments. To do this the sensors were placed inside a gas chamber. The gas chamber was connected to several mass flow-meters which were in turn connected to several different types of analytes. The mass flow-meters were controlled by a computer system. The sensor itself was connected to an impedance analyser that could measure the output.
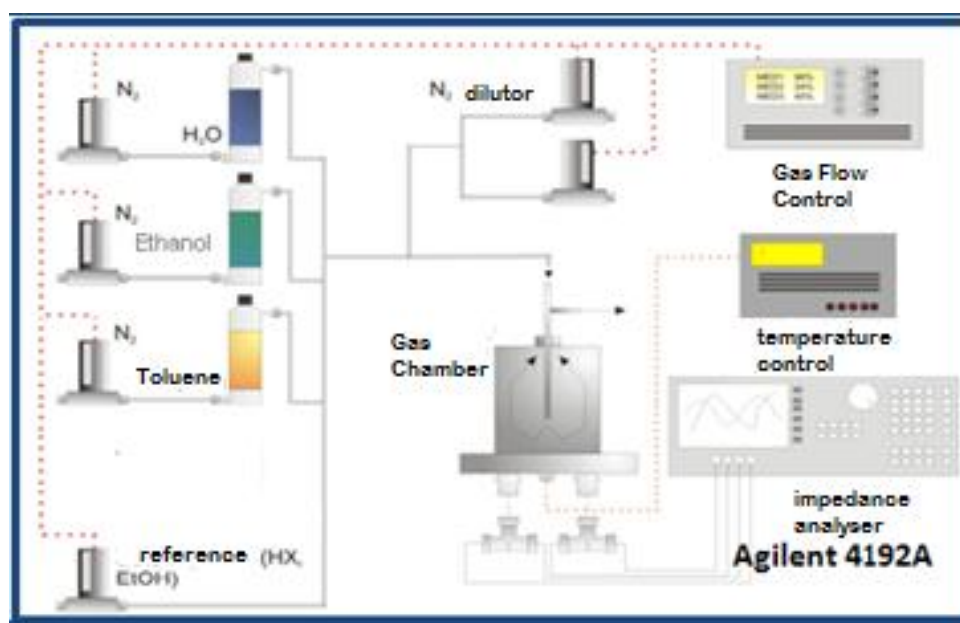
Fig. 12: Experimental set-up

Using this set up an accurately controlled environment could be created inside the gas chamber under automated control. There were three main analytes used to test the sensors parameters. These were; ethanol, toluene and water. These were chosen because of their known variations in behaviour with zeolite material. Water and ethanol are known polar molecules and toluene not. Therefore the analytes should produce different results when coming into contact with hydrophobic or hydrophilic zeolite crystals.

As well as this, nitrogen was connected to build an inert atmosphere and as a reference point. To produce the analytes in gas form a controlled nitrogen flow was passed through a saturator containing the desired analyte. This flow then passed out to the gas chamber. The gas chamber was made of steel and had a cubic capacity of $200cm^3$

A 4294A precision impedance analyser was used to measure the sensors response to different analytes. The impedance analyser works with a frequency range of 40Hz - 110MHz with a resolution of 1mHz. It works by taking sweeped measurements of voltages and frequencies to see the behaviour of a load. It was connected to the sensors using 4 different wires. This was used to cancel out large parasitic effects. The voltage and frequencies were introduced into the sensor and the response is recorded.
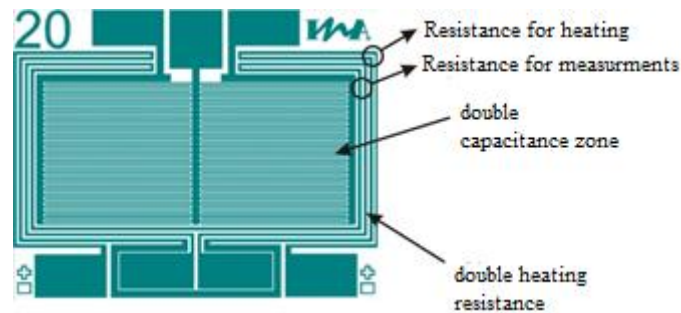
4. Results

4.1. Electrical behaviour of sensors

Description and behaviour of the IDC

The IDC was made over Pyrex (SiO2) with an aluminium thickness of 100 nm. The design has two capacitive and two resistant zones. Different separations between electrodes from 3, 5, 10 and 20 microns were produced.


Fig. 13: Scheme of 20 microns IDC with double capacitor and resistance

For the sensor tests, it was very important to have control over the temperature. This is because as temperature increases, the ionic current between the OH groups improves. This produces an improved response in capacitance and resistance. As temperatures continue to rise, up to 500ºC, the cations inside of the zeolites have increased mobility and therefore there is an increased current flow [1].

There are two problems with this temperature though. The first problem is that, as previously mentioned, as the temperature increases the adsorption affinity decreases. The second problem that occurs is that it is practically difficult to experiment using these temperatures. Due to these factors, 150ºC was chosen.

This was done using the IDC resistance; one resistance was used for monitoring the temperature while the other was used for heating. This was found by heating the IDC chip inside an oven and measuring the resistances at different temperatures. Afterwards, a voltage was introduced to IDC and the resistance was measured. From this a voltage to temperature ratio could be calibrated. (*For further results a trend line was used*). This type of heating was done to show how a heating process could be achieved in a commercial point of view.
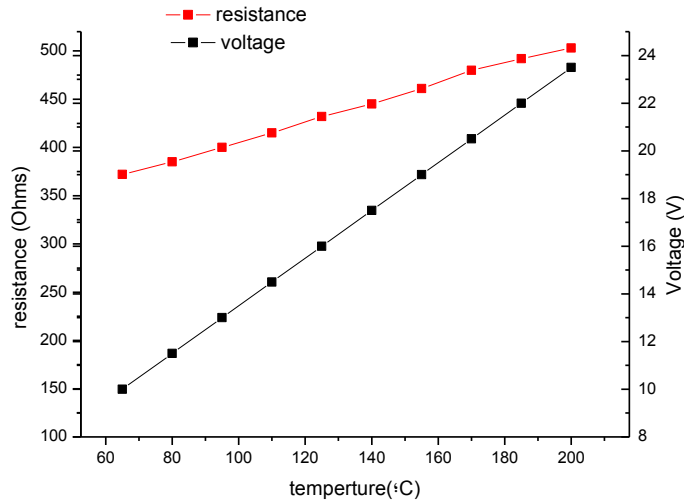
Fig. 14: Calibration of voltage/temperature

Before testing the different sensors with different analyte amounts it was important to do some preliminary tests. The capacitance and resistance of different chips were measured with the intensions of calculating the impedances.

$$Z = \sqrt{R^2 + x^2} \qquad Eq.\ 3$$

Eq.3 shows how to calculate impedance where Z is the impedance, R is the resistance and x is the capacitance. This impedance was measured over a range of different frequencies. Using the results from these experiments an equivalent circuit of how the sensors behave could be found. These results could then be used to analyse the sensors capabilities.

The capacitances and resistances at different frequencies were measured in the blank IDC (*without any sensing material*). The impedances were then calculated and graphed in Nyquist and Bode diagrams. These measurements were taken under heat to improve the sensors response and in a pure nitrogen environment to cancel out atmospheric effects. The results can be seen in Fig. 15a and 15b.
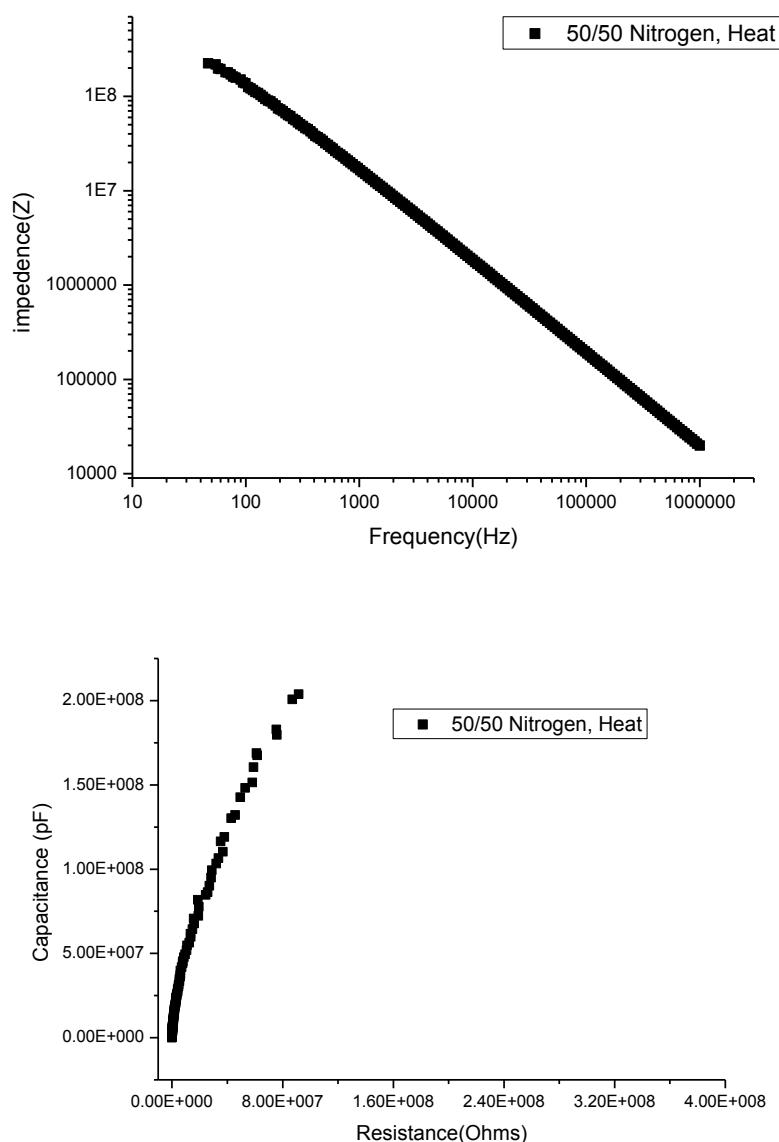
Fig. 15a and 15b: Response of Blank IDC with, Bode diagram (*top*), Nyquist diagram (*bottom*)

The blank IDC showed signs of a capacitance response. This can be seen in the Fig.15a where there is a negatively linear relationship between frequency and impedance just like in a capacitor. The capacitance has greater impedance as the frequency becomes lower and it is more like an open circuit. This is due to the fact that the increased current switching time allows more charge to build up on the capacitive plates. This reduces the amount of available charge and therefore increases the impedance. Eventually, if the frequency was too low the capacitor would become fully charged and the impedance would become infinite. This can be seen in the formula for impedance:

$$X_{c = \frac{1}{2\pi FC}} \qquad Eq.\ 4$$

*Where X_c is impedance, F is the frequency and C is the capacitances.*

The Nyquest diagram in Fig.15b also shows that it is likely to be a capacitive response. For a pure capacitive response there is expected to be a straight line as can be seen in Fig 16. The results in Fig.15b produce a slightly curved line. The reason for this not being completely straight is due to noise in the measuring process.
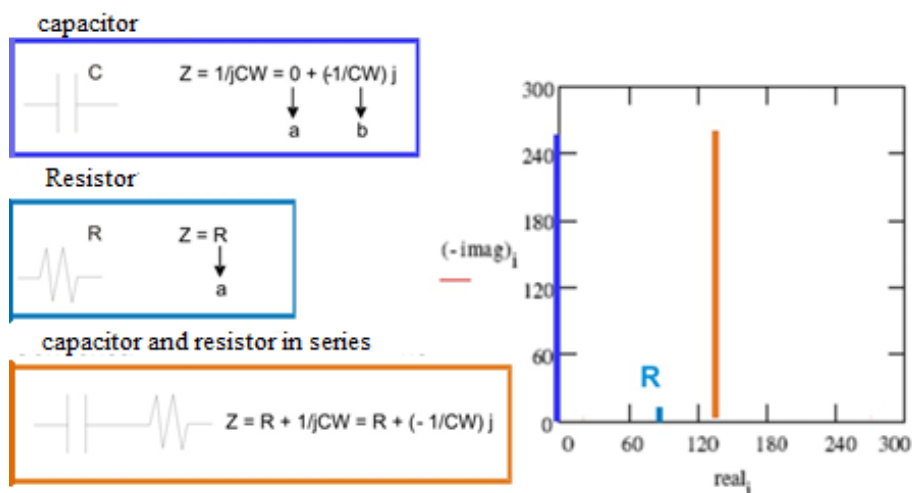
Fig. 16: Typical response of resistances and capacitances

"Nano" interdigital capacitors (NanoIDC)

Following the same procedure as for the IDC, a nano single electrode circuit was fabricated over a 4 line micro adaptor. This was done using the exact same design as for the single crystals. The capacitances and resistances were tested over a frequency range under heat in a pure nitrogen environment.
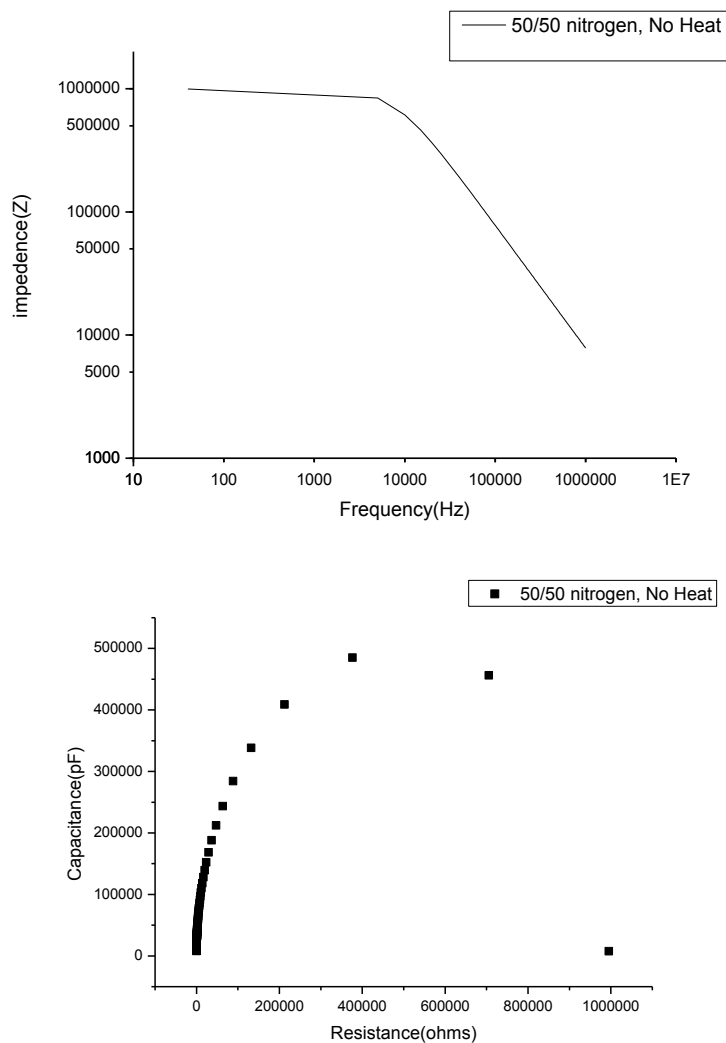
Fig 17a and 17b.: Bode diagram of blank nanoIDC (*top*) Nyquest diagram of blank nanoIDC (*bottom*)

The results from the blank nanoIDC show a different response than the IDC chips. As well as the capacitor behaviour it had an extra element at low frequencies. Due to this extra response it was deemed that the nanoIDC's behaviour was the equivalent of an RC circuit. In the Bode diagram, Fig. 17a, there appears a straight and horizontal line corresponding with a resistance contribution followed by a slope of -1
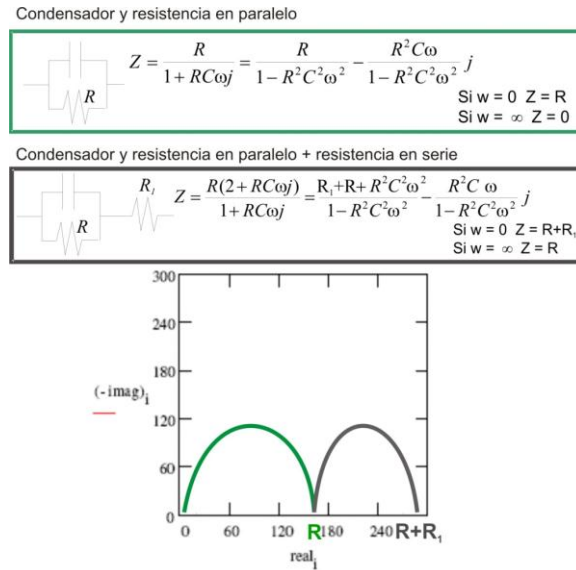
Fig. 18: Response of RC circuits

An RC circuit is a circuit that consists of a resistance and a capacitor in parallel. This can be seen in Fig. 17b as when plotting resistance with capacitance both components feature and produced a semi-circle. These results match the theory which can be seen in Fig. 18 also in the impedances graph the resistance can be seen by the horizontal line and the capacitance by the more sloped line, a typical RC response.

This extra resistance element in the chip is due to the difference in substrates. In the IDC the Pyrex SiO_2 base was fairly non-conductive therefore the sensor response was only produced by the electrodes capacitance. The nanoIDC substrate was a thin layer of SiO_2 and Si. At low frequencies the capacitor produced very high impedance. The Si base gave the current an easier path to flow and this is what took place when the impedance was high enough. This resulted in a resistance at low frequencies.

4.2. Synthesis of sensing material: zeolite

The crystals were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

XRD is used to show what type of material a substance is made of. This is done by firing X-rays into the material and collecting them after. By knowing how much the x-rays were deflected and at what speed were lost or gained, an idea of the internal parameters of the crystals can be assumed. This information is then compared with previous material knowledge to show what material is present.

SEM is a high vacuum method for imagining materials in the nano scale. It works by firing an electron beam, in a vacuum, into what is required to be imaged. By collecting the deflected particles an image can be built up. This technique is important for measuring the size of the crystals and also for seeing the shape and distribution.

Synthesis of Small crystals of zeolite

Silicalite
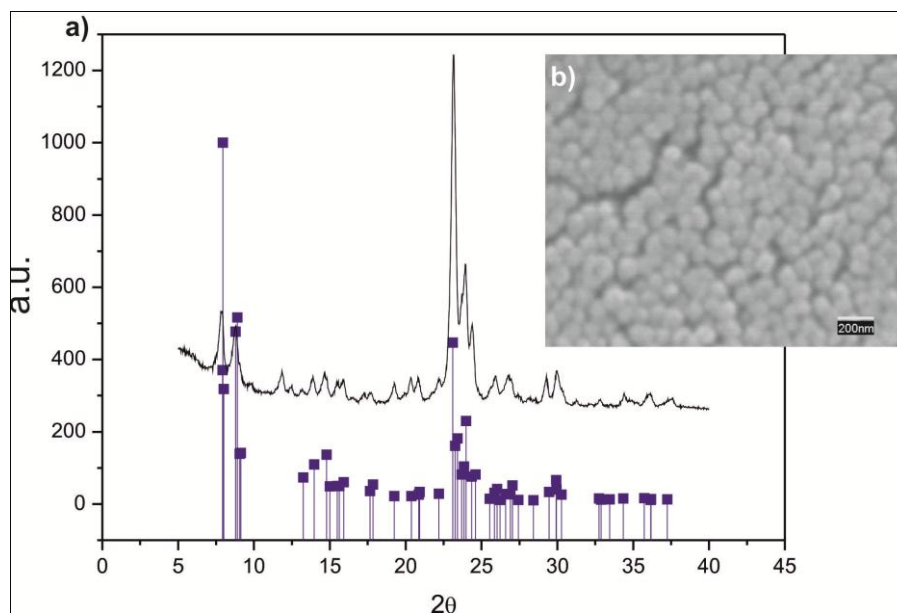
Fig. 19a and 19b: Small silicalite crystals XRD (*left*) and SEM (*right*)

The XRD and SEM images of this synthesis show that the material is silicalite. This can be seen in the XRD as all the peaks are in the same places and visually in the SEM. The SEM also shows that uniformed crystals were produced around the size of 1μm.

ZSM-5
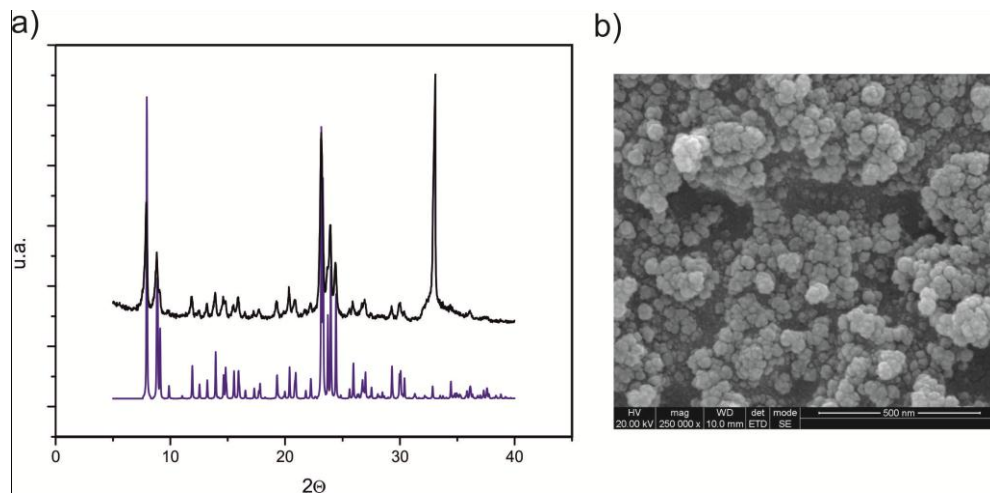
Fig. 20a and 20b: XRD (*left*) and SEM (*right*) images of small ZSM-5 crystals

The XRD shows that the crystalline structure fits with a MFI type material. With SEM images round shaped crystals could be observed. Their size was smaller than 200nm.

Zeolite A
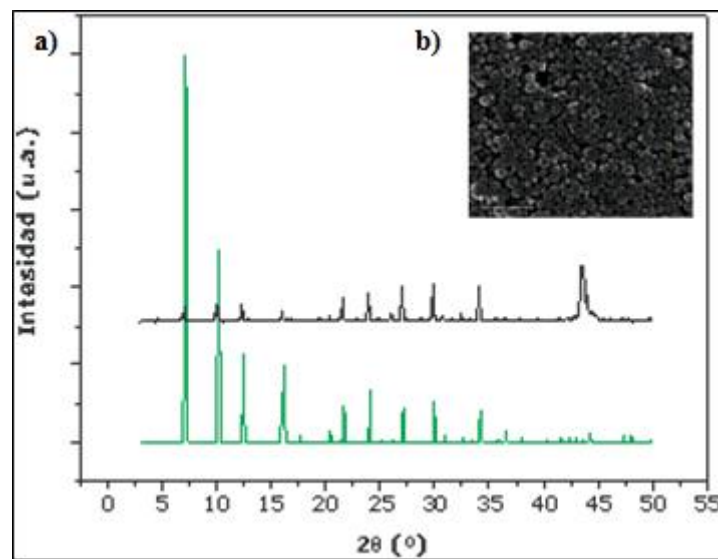
Fig. 21a and 21b: XRD (*left*) and SEM (*right*) image of zeolite A small crystals.

The XRD image shows that the material created is zeolite A. This is known from the fact the measured results have a strong match with previous known characteristics. It can be seen that there is a strong match in the peaks between the known sample and the sythesised sample.

The SEM image shows that there are some homogenous single crystals created. These have a slightly square shape with flat surfaces. The size of these crystals is just under 200nm.
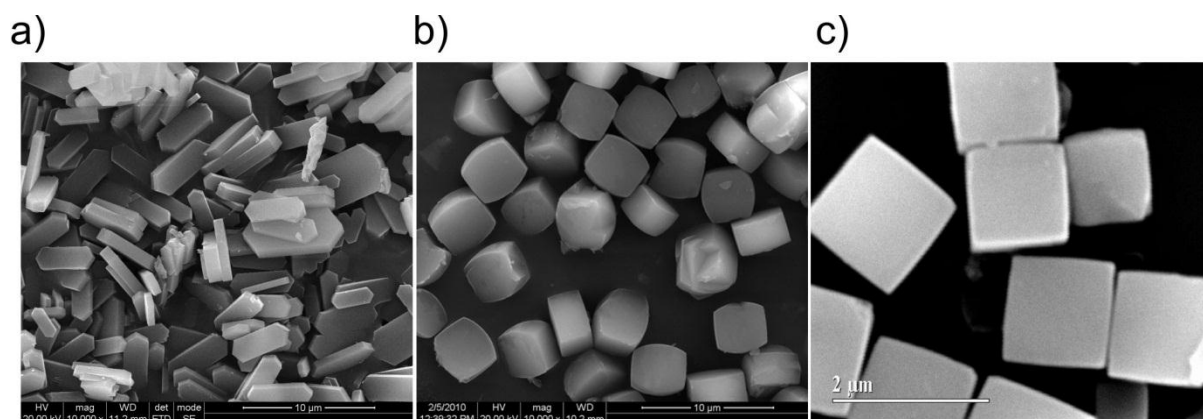
Fig. 22a, 22b and 22c: SEM of big silicalite (*left*), ZSM-5 (*centre*) and zeolite A (*right*) crystals

The large silicalite crystals can be seen in Fig. 22a. They have a coffin like shape and have a width of around 2μm and a length of around 5μm. A SEM image of the large ZSM-5 crystals synthesised can be seen in Fig.22b. The image shows that the crystals are fairly homogenous. The average size is around 4μm. Their shape is rectangular with flat surfaces. Fig. 22c is of the sythesised large zeolite A crystals. There are single square crystals with the size of around 2μm.

For using these crystals for the NanoIDC some agglomerations were needed to be removed. The crystals were mixed with ethanol and then placed in a sonic bath for 10mins. The sonication made the agglomerations sink to the bottom and therefore the single crystals were left floating. These were then removed and used in the deposition process.

4.3. Zeolite deposition

IDC deposition

The process of depositing the zeolite on to the IDC chip, as previously mentioned, was done by micro drop deposition.
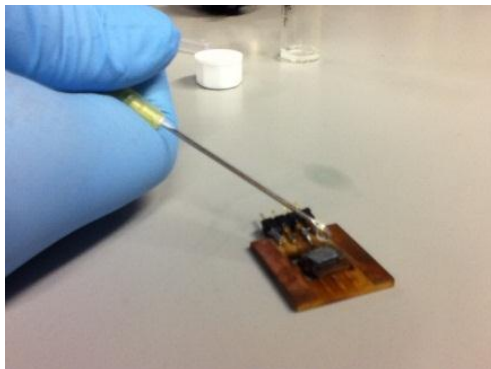
Figs. 23: Micro-drop deposition on to the IDC

Fig 23 shows the process of depositing the zeolites on to the IDC. It was done with a micro syringe and deposited slowly to produce the smallest drops possible. The drops were left for the ethanol to evaporate and this left the crystals distributed across the IDC. The step was repeated to increase the amount of zeolite crystals.
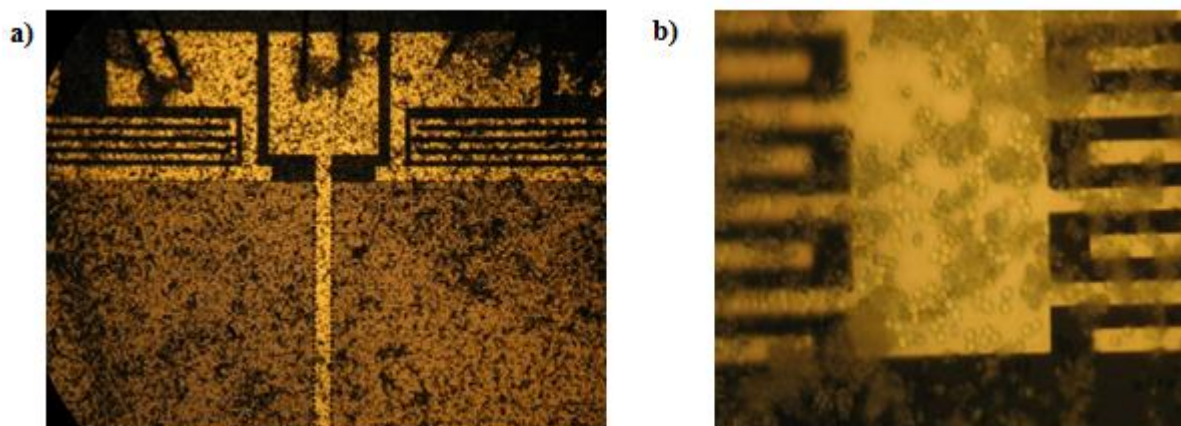
Fig. 24a and 24b: IDC with zeolites deposited on top.

Figure 24a and 24b show images of the IDC chips with the zeolites deposited on top of them. From the images it can be seen that crystals were spread across the IDC fairly homogeneously covering the IDC's electrodes equally. At the top of Fig. 24a the three double micro contacts can be seen. They were connected to wires to measure the responses.

"Nano" Interdigital capacitors (NanoIDC)

The NanoIDCs were produced by depositing a lesser amount of crystals onto the Si chip than the IDCs. This was then taken to the clean room and a nanocapacitor was drawn on top of the crystal and connected to micro contacts. As well as this the blank nanocapacitor was created as a reference (*as mentioned above*).
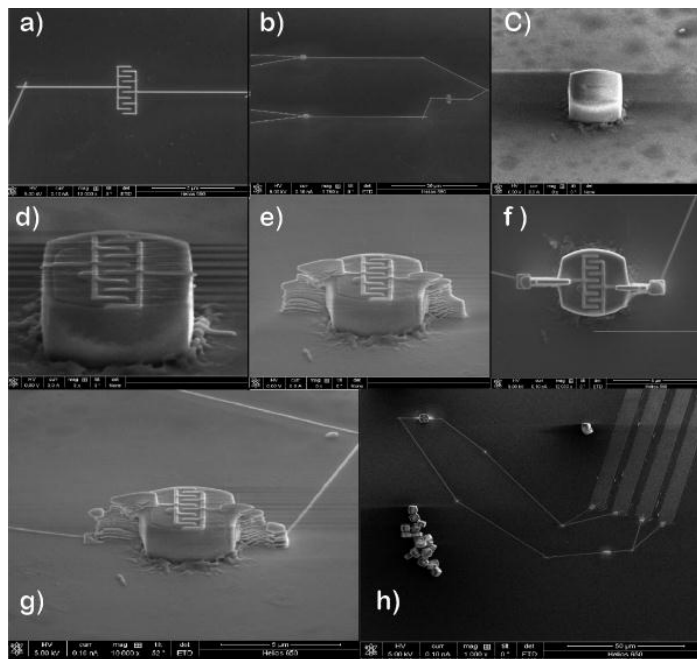

Fig 25a-h: Ion beam creation process of ZSM-5 nanoIDC and blank nanocapacitor

Fig. 25 shows the process of producing the nanocapacitor on top of the zeolite crystals. Firstly the blank nanocapacitor was created on top of the substrate. This was done by finding an area without crystals and then using the ion beam to create the capacitor. This can be seen in fig 25a. The capacitor was then connected to the micro contacts which can be seen in fig. 25b.

To create the nano capacitor first a suitable crystal was found. This consisted of finding a single crystal that was square in shape and that had a flat surface. It was also important that the crystal was in the horizontal plane. These parameters made the process of producing the nanocapacitor easier. A crystal was chosen that was close to the micro contacts to help reduce the time it took and the chance of error.

The capacitor design was created on top of the crystals. To connect the capacitor to the substrate, wires were created down the sides of the crystal. These were then connected in turn to the micro contacts.

This technique was done for the three types of big crystals, Silicalite, ZSM-5, and zeolite A. Images from the creation of the zeolite A nanocapacitor can be seen in Fig. 26.
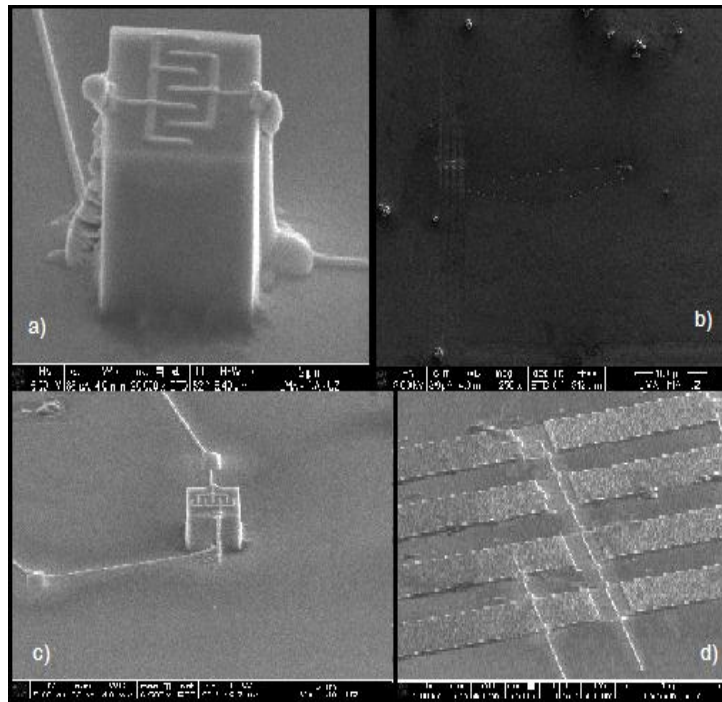
Fig 26: creation of Zeolite A nanocapacitor

Table 3 shows a summation of all the sensors prepared in this work stating their main characteristics;

Name	Zeolite	Si/Al	Fabrication method
Sil. IDC small	Silicalite	∞	Micro-drop
ZSM-5 IDC small	ZSM-5	100	Micro-drop
ZA IDC small	Zeolite A	2	Micro-drop
Sil. NanoIDC	Silicalite	∞	FIB
ZSM-5 NanoIDC	ZSM-5	100	FIB
ZA NanoIDC	Zeolite A	2	FIB

Table 3: classification of sensors

4.4. Zeolite sensor characterisation

When the zeolites were deposited on to the IDC chips their electrical behaviour had changed. Similar to the substrate in the nanocapacitors the zeolites had created an alternative path for the electric to flow through at low frequencies. Just like the nanocapacitors the IDCs behaviour could now be determined as a RC circuit. This can be seen in previous works such as [1].
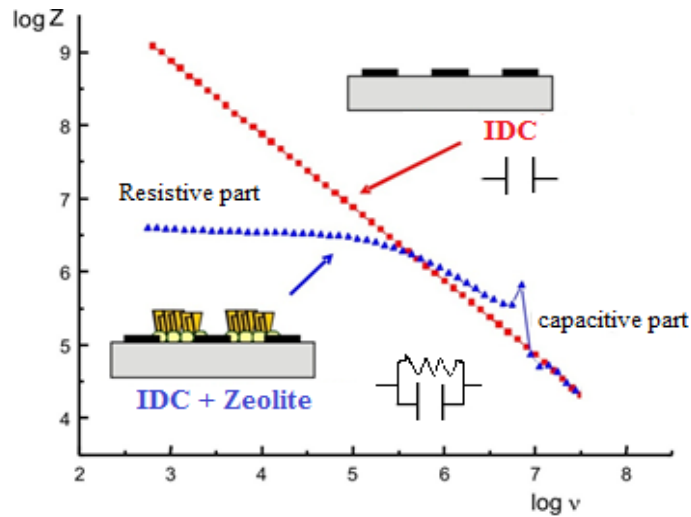

Fig. 27: RC circuit produced in IDC sensor

To increase the effectiveness sensors the ZSM5 IDC sensor was tested at different temperatures. By testing at different temperatures the optimum sensor characteristics could be found. The test was done under pure nitrogen at temperatures ranging from 25ºC- 150ºC.
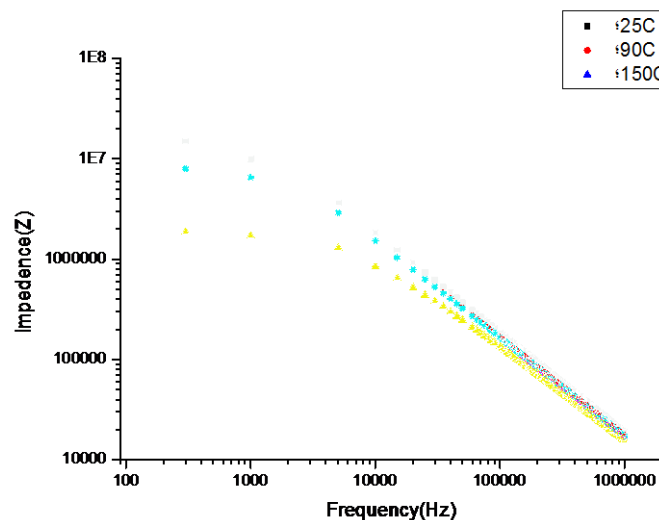
Fig. 28: Heat test of ZSM-5 of a IDC

The ZSM5 IDC tests at different temperatures showed that the device had a RC circuit response although this was more difficult to see at lower temperatures. This can be seen from the graph as when the voltage, and therefore heat is increased so did the resistant elements of the sensor. This can be seen in the impedances results were impedance is reduced when the temperature increases. The ideal temperature was chosen to be around 150ºC.

The preliminary tests showed the effect that temperature had on the sensing response but the response can also be affected by the presence of different analytes. Similar experiments, but under different atmospheres, have been carried out, where mainly changes in the resistance have been registered. From a more functional point of view, the optimal frequency (better signal/noise ratio) was found. The concept was to measure the changes in the capacitance and resistance of the system using this frequency over a longer period.

The optimal frequency was found by comparing the sensors response when introducing nitrogen to introducing water. The frequency was chosen which produced the biggest difference in impedance between the water and nitrogen results. The results for the preliminary tests showed that the best working frequency was 7.5KHz.

4.5. Dynamic gas characterisation

IDC gas characterisation

The different chips were then tested using an automatic program. This was done with the gases introduced in steps. The optimal temperature of 150ºC and a frequency of 7.5KHz were used. Firstly a flow of nitrogen was introduced to the sensor for 6 hours to create a referenced atmosphere. Then steps of the analyte were introduced changing the concentration of ppm depending on the composition of the analyte. With water it ranged from 4000-35000ppm, with ethanol 7500-62000ppm and with toluene 3200-25000ppm. Each step would last an hour with an hour gap in between of pure nitrogen to test the sensors ability to recovery.

As an example of this type of experiment the results for the ZA IDC are present in Fig. 29. Changes in the resistance and capacitance for the three analytes could then be deeply analysed.
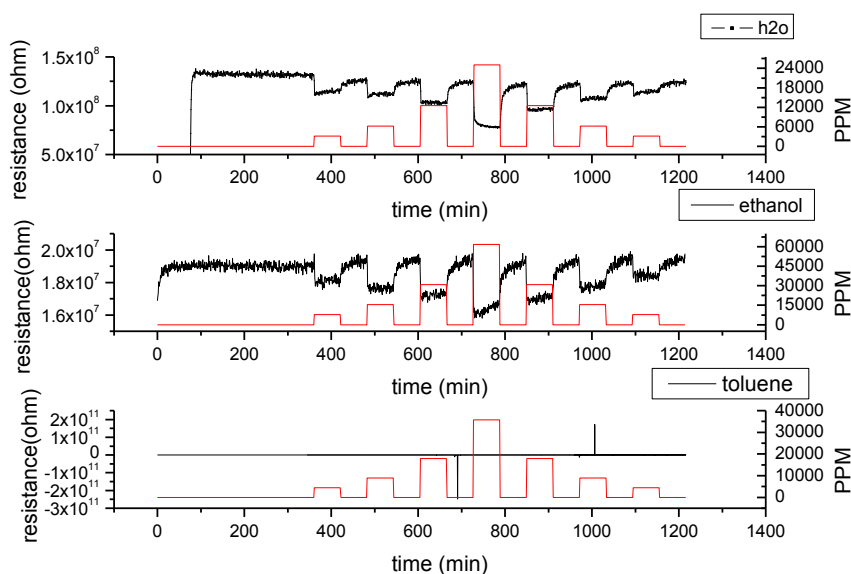
Fig. 29: Zeolite A small IDC resistance

(Where the red signal is the amount of analyte and black is the responses)
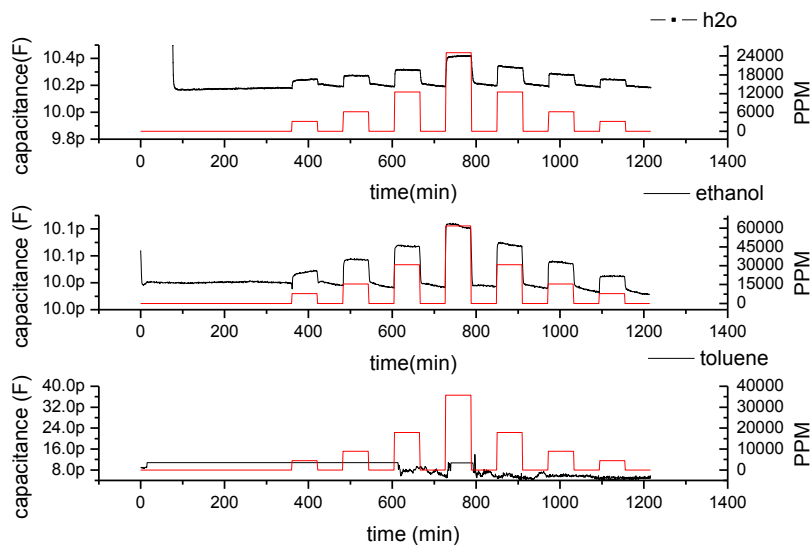
Fig. 30: Zeolite A small IDC capacitance

The results from the gas chamber experiment show that the increase of concentration of the different analytes cause a reduction in the resistance and an increase in capacitance in the small ZA IDC chip. This was expected as the analyte will be adsorbed into the zeolite increasing the permeability, which is directly related with the capacitance. On the other hand, an increment of water, for instance, could increase the ionic conductivity, making electron transport easier and therefore decreasing the resistance.

The resistance results of the ZA IDC showed that ethanol and water were the best suited for this chip. Toluene was insensible. This can be seen by the responses in steps in-line with the analyte steps. The capacitance results of the ZA IDC show that the most sensitive gas was ethanol then water. This can be seen by the large steps produced in the results due to the steps in analyte. Toluene showed little signs of sensibility and had a high signal to noise ratio.

These results are due to the fact the Zeolite A is a hydrophilic zeolite. This means that it has better attraction to the polar molecules water and ethanol. This also explains why toluene was insensible.

Using these types of experiments, (*dynamic gas testing)*, the calculation of the sensitivity, selectivity, response time and recovery time could be calculated. The sensitivities of the sensors were calculated by dividing the change in capacitance or resistance by the amount of ppmV of each analyte. The limit of detection (LOD) was calculated by dividing three times the noise in the response by the sensitivity. The noise was calculated by taking enough random points during the first 6 hours of testing and finding the standard deviation.

These experiments were done for all the different chips and the important results were calculated. The results can be seen in tables 4-6.

H2O								
	Capacitance ($\epsilon r = 1.85D$)				Resistance			
	Sensitivity (pF/ppm)	LOD (ppm)	Response time (min)	Recovery time (min)	Sensitivity (Ohm/ppm)	LOD (ppm)	Response time (min)	Recovery time (min)
Sil. IDC small	1.16E-06	1900	8.3	10.2	n/a	n/a	n/a	n/a
ZSM-5 IDC small	1.16E-05	530	1.9	2.5	19952	580	2	2
ZA IDC small	1.94E-5	340	1.6	21.8	381141	8.95	2.6	2.6

Table 4: IDC water results

Ethanol								
	Capacitance ($\epsilon r = 24D$)				Resistance			
	Sensitivity (pF/ppm)	LOD (ppm)	Response time (min)	Recovery time (min)	Sensitivity (Ohm/ppm)	LOD (ppm)	Response time (min)	Recovery time (min)
Sil. IDC small	1.48E-06	1490	8.4	8.3	n/a	n/a	n/a	n/a
ZSM-5 IDC small	2.8E-03	2.2	6.5	24.8	12323	820	4,4	8.8
ZA IDC small	2.3E-6	520	1	1.9	118	4900	0.4	9.3

Table 5: IDC ethanol results

Toluene								
	Capacitance ($\epsilon r = 2.3D$)				Resistance			
	Sensitivity (pF/ppm)	LOD (ppm)	Response time (min)	Recovery time (min)	Sensitivity (Ohm/ppm)	LOD (ppm)	Response time (min)	Recovery time (min)
Sil. IDC small	4.17E-06	520	4.3	5.5	n/a	n/a	n/a	n/a
ZSM-5 IDC small	8.4E-03	0.62	6.4	23	362629	50	1.45	16.2
ZA IDC small	1.24E-4	25	1.6	3.2	n/a	n/a	n/a	n/a

Table 6: IDC toluene results

Using these results, observations could be made about the different sensors abilities. Firstly, this was done, focusing on the capacitance results:

At a glance, it would be easy to think that zeolite A would adsorb more water and ethanol (polar molecules) than other zeolites due to its hydrophilic behaviour. However, the response was not as expected. This is because these zeolites need a more intense drying process, 150º C is not enough. Due to this, the zeolite had all its pores blocked by previously adsorbed ambient water. This resulted in less increases in sensitivity when the concentrated water was introduced.

Silicalite and ZSM-5, both MFI type zeolites, present different Si/Al ratios. This will have an effect in specific adsorption; but always with more preference for the non-polar molecules. Both zeolites present more affinity for the toluene than for other analytes.

In the particular case of the ZSM-5 with ethanol, the adsorption is quite a lot higher, but it has to be considered that the permittivity of this analyte is 10 times more than that of the toluene. This means for the same amount of analyte adsorbed into the zeolite there will be a change, 10 times higher than the change for the ethanol.

Then focusing in the resistance result, generally, the results show an improvement in the sensors performance having a lower limit of detection and response and recovery times.

The silicalite based sensor did not present any change in the resistance. Silicalite has an infinite Si/Al ratio; therefore no presence of aluminium is in its structure. Due to this the silicalite couldn't produce ionic conductivity.

In the case of water and ethanol, zeolite A presented more variation in the response than ZSM-5. This is opposed to the response obtained in the capacitance. In this case, the resistance benefited from the ambient water previously adsorbed into the zeolite A. When the concentrated steps of water and ethanol were introduced to the chamber the ambient water helped to increase the sensors response. This effect is based on ionic conductivity. The combination of a hydrophilic zeolite and polar molecules, with the possibility of hydrogen bonding, maximised the conductivity; resulting in a strong reduction in the resistance. The consequence of this was a sensor with high sensitivity to ethanol and water.

As could be expected, the zeolite A sensor did not present any response for the toluene, making this sensor fully selective to the polar molecules.

An array of these sensors could be prepared to detect the three analytes separately. Following resistance changes, toluene could be discarded with a sensor based on zeolite A. Moreover, with a sensor based on ZSM-5 and analysing the changes in the capacitance, water versus ethanol could be distinguish, as the selectivity of ethanol is 220 times higher than water in this zeolite.

NanoIDC gas characterization

As previously mentioned temperature had an effect on the sensing abilities of the IDCs. To see if this was also true for the NanoIDCs, the response of the Sil. NanoIDC was tested at room temperature and at higher temperatures (up to 150ºC). This showed the effect that heat has on the NanoIDCs. This can be seen in Fig. 31
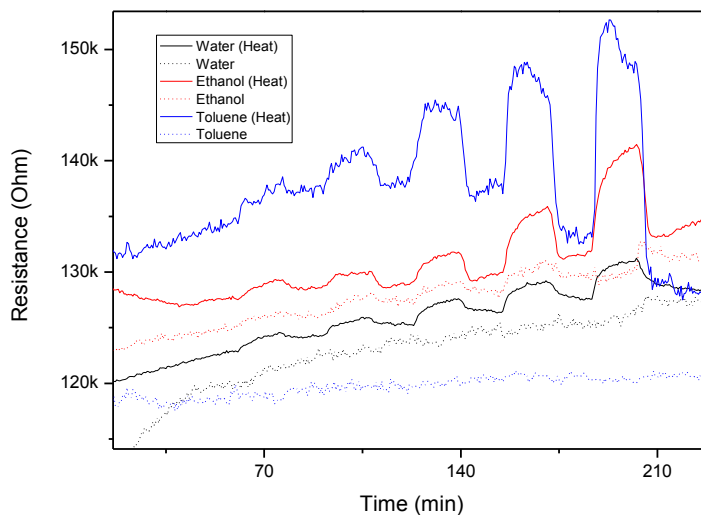
Fig. 31: Heat effect on silicalite nanocapacitor

The test clearly shows that the NanoIDC was highly affected by the changing in temperature. The higher the temperature the better the response was just like in the IDCs. This means that for the best results the NanoIDC were tested under the same heat as the IDCs (*150ºC*).

As the preliminary results showed that the IDC and the nanocapacitor had different behaviours without the crystals, it was important to take this in to account when analysing the results. To avoid this inconsistency, the blank capacitors were tested with the different analytes.
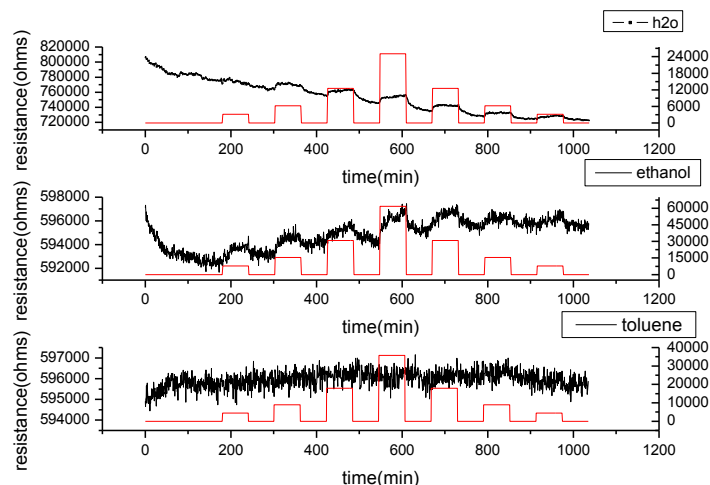
Fig. 32: Results of blank nanocapacitor with different analytes.

These results were then subtracted from the results with the zeolites to show the real effect the zeolites and nano scale had on the sensors capabilities. The results from the NanoIDC testing can be seen in tables 7-9.

	H2o							
	Capacitance				Resistance			
	Sensitivity	LOD	Response	Recovery	Sensitivity	LOD	Response	Recovery
Sil. Nano IDC	n/a	n/a	n/a	n/a	O,44	600	4.1	3.8
Zsm-5 Nano IDC	n/a	n/a	n/a	n/a	0.034	5700	9.3	18.7
ZA Nano IDC	2.81E-6	6600	15.36	33.73	n/a	n/a	n/a	n/a

Table 7: NanoIDC water results

	Ethanol							
	Capacitance				Resistance			
	Sensitivity	LOD	Response	Recovery	Sensitivity	LOD	Response	Recovery
Sil. Nano IDC	n/a	n/a	n/a	n/a	0.35	745.57	2.5	1.8
Zsm-5 Nano IDC	n/a	n/a	n/a	n/a	0.32	6300	40.1	4.2
ZA Nano IDC	2.76E-5	2900	21.51	31.20	19.55	253.988	36.64	6.25

Table 8: NanoIDC ethanol results

	Toluene							
	Capacitance				Resistance			
	Sensitivity	LOD	Response	Recovery	Sensitivity	LOD	Response	Recovery
Sil. Nano IDC	n/a	n/a	n/a	n/a	1.26	200	3.3	4.1
ZSM-5 Nano IDC	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
ZA Nano IDC	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table 9: NanoIDC toluene results

With these results some observations can be made about the NanoIDCs;

In general, the main features of these sensors were less effective than the features of the IDCs. The strengths of the NanoIDCs may be seen as their response and recovery times. Although due to the limitations of the equipment, the acquisition time, the results were not as enhanced as expected.

This said; it is important to take into account the amount of sensing material used in the case of each sensor. The sensitivity was calculated using the change in magnitude for each ppm of analyte but not considering the amount of sensing material.

If this consideration was introduced to the values for sensitivity it could be seen that the NanoIDC sensors are $20.8x10^6$ higher than normal IDC (*per amount of sensing material*). Consequently this would also affect the LOD.

Looking at the capacitance results of the NanoIDCs it shows that zeolite A like in the IDCs, due to its hydrophilic behaviour, presents more affinity for the ethanol and the water. This higher affinity could be translated into a higher adsorption amount of analyte. Therefore higher responses were obtained in the capacitance than in the cases of the other sensors.

Focusing onto the resistance the character of the hydrophilic zeolites once again appears. For instance, with ethanol, higher changes were obtained for zeolite A than obtained for the ZSM-5 and the silicalite. Their results were quite similar.

Comparing the silicalite NanoIDC responses with different analytes, the affinity for the non-polar molecules is clear. The sensibility of this zeolite for toluene is three times higher when compared with other analytes.

5. Conclusions

It has been shown that several IDC capacitive gas sensors; using zeolites as a sensing material, can be prepared to detect the presents of different gas analytes. The main factor affecting the capability of these sensors were based on their and the analytes polarity. NanoIDC were created and gave both measurable capacitive and resistant sensing responses with similar polarity effects as with the IDC sensors. This shows that it was possible to create selective sensing devices using single zeolite crystals.

Further work

The results presented in this work suggest that there are opportunities to develop the work further. There are several directions that this could be done.

For example there could be an increase in variation of zeolites used as sensors to see their response to different analytes. There also is the option of using different analytes with the current sensors to test their detection ability.

The experiment set up could be change to enhance the results. Instead of using an impedance analyser there are specifically made micro controllers that can be used to take faster results, improving response times. These types of equipment can also help lower the SNR using wires specially for connecting to the sensors.

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