Preparation and Characterisation of Hierarchical Zeolite Catalysts

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Abstract

Diesel fuel is one of the most important fuels, given its high combustion efficiency (it has a strong tendency to auto-ignite). The blendstock for this type of fuels are middle distillates obtained from hydrocracking, thus the need to improve the efficiency of hydrocracking catalysts in terms of selectivity.

Zeolite Y is the most widely used catalyst for these processes, due to its high thermal stability, density of acid sites and rather high acid strength. However, it also produces a large amount of light distillates. Hence, modifying zeolite Y to increase the mesoporosity can improve the yield of middle distillates: with bigger pores, more middle distillates can be obtained.

The main goal of this work was create hierarchical mesoporosity in zeolite Y. The starting material was zeolite Y in the NaY form, and two different routes were experimented: Route 1, where the zeolite was ion exchanged to NH4Y form and then suffered an acid treatment to create mesopores and Route 2, where the zeolite suffered the acid treatment and was ion exchanged subsequently. In the end of both routes, a calcination step took place to remove the formed NH3.

The following characterisation techniques have been used: N2 sorption, XRD, FTIR and SEM/EDS. In FTIR, two experiences were made: pyridine was used to characterise the acid sites in zeolite Y (number and type) and different probe molecules were used to test pore accessibility.

Results have shown that Route 2 is preferable, since the loss of crystallinity was smaller and the amount of acid sites was higher.

SEM/EDS results showed an increase in the Si/Al ratio, as expected, due to dealumination and a slight desilication by the acid treatment.

Keywords: zeolite, FAU, characterization, modification, preparation, mesoporous, catalyst, biodiesel

1. Introduction

Diesel fuel is an important fuel, given its high combustion efficiency: ignition is simpler, since it does not need a spark; diesel is denser than petrol which means that it releases more energy; diesel fuel has much more lubrication. In the last few years, diesel fuel has been in short supply, and its demand has been increasing significantly. Therefore, there is an urge to increase the yield of diesel fuels to meet the market's current demand. [1]

Middle distillates, obtained from hydrocracking, are treated and blended into diesel fuels. Hence the need to improve the efficiency of hydrocracking catalysts.

The most widely used catalyst for hydrocracking processes is zeolite Y [2], because of its rather high acid strength, higher hydrothermal stability, density of acid sites and large hydrogen-transfer capacity. Although it has better performance than other materials, it is not enough to satisfy the maximum yield of middle distillates, since it also produces a large amount of light distillates. Besides, zeolite Y is scarce in mesopores, there is no point in trying to enhance the conversion of large molecules because of diffusion limitations. [1]

Modifying zeolite Y to create mesopores can improve the yield of middle distillates in the hydrocracking process. However, to allow middle distillates to enter the pores, the mesopores need to be accessible from the external surface. This is the main difference from the commercial existing mesoporous zeolites, since they only have mesopores inside the framework. The process of creating mesopores is complicated because the modifying conditions have to be very strict, and even so the zeolite loses crystallinity. [1]

The effect of zeolite Y crystallite size on the hydrocracking activity has been studied, and it was concluded that the catalyst with a smaller crystallite size (bigger pore size) Y zeolite exhibits higher middle distillate selectivity. Usually, the hydrocracking activity is related to the number of acid sites. Yet, a smaller crystallite size of zeolite Y has less acid sites. What improves the hydrocracking activity is the larger amount of available acid sites due to higher surface area and creation of mesopores.

Zeolites are crystalline aluminosilicates based on an infinite extending three-dimensional, four-connected framework consisting of AlO4 and SiO4 tetrahedra linked to each other by sharing one oxygen atom. Each AlO4 in the framework bears a net negative charge which is balanced by extra-framework cations of hydrogen or of alkali or alkali-earth metals, such as sodium, potassium, magnesium or calcium or even transition metal entities. [4] [5] The resulting structure is highly porous and contains channels and cavities of molecular dimensions that are occupied by cations and water – the zeolite's pores.

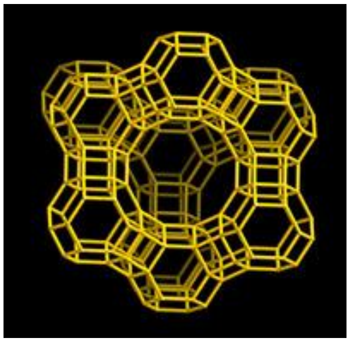

Figure 1 – Zeolite (Faujasite) structure

Based on the possible variations in the framework of zeolites, a "structure code" has been assigned to each one of them, for the sake of simplicity in their identification. These structure codes have been proposed by the Structure Commission of the International Zeolite Association (IZA-SC) and consists of a three-letter code derived from the name of the zeolite or "type material", e.g. FAU is for Faujasite. A detailed compilation of framework types can be found in the Atlas of Zeolite Framework Types. [7] [8]

Besides the structure type, zeolites can also be classified by the number of oxygen atoms in the pore openings. By definition, zeolites are microporous materials. A material can be defined as microporous if its pores are up to 2nm, mesoporous when the pore diameters are between 2 and 50nm, while the materials having larger pore openings than 50nm are defined as macroporous. [6]

The most general physical property of zeolites is the existence of a regular microporous system, due to their crystallinity. High thermal and hydrothermal stability allows them to be used as catalysts under severe temperature conditions. [8]

Zeolites can also be used as ion exchangers, due to their capacity to replace the cations in the framework by ions present in external solutions. Ion exchanging zeolites has been widely used to modify the catalytic or sieving actions of the original zeolite. [3]

Moreover, zeolites have a large internal surface area, due to their microporous structure of channels and cavities. Hence, there is a high concentration of active sites inside the framework, whose strength and number can be modified to meet the desired experimental conditions. Since catalytic reactions over zeolites occur within their intracrystalline cages and channels, the stability, activity and selectivity of all the reactions carried out over zeolite catalysts depend on the shape and size of the cages and channels. Thus shape selectivity is a general characteristic of zeolite catalysed reactions. It is the impossibility of certain molecules entering or exiting the zeolite's pores. [9] The zeolites of a specific pore size on their external surface can allow diffusion of molecules of smaller size or shape into their internal pores. Some cations are too large to enter the internal pores and consequently they are adsorbed in the surface pores of zeolites. [8] Due to the restricted space of the pores, confinement effects may appear which make zeolites behave like solid solvents. Molecules can be physisorbed in zeolite pores due to this effect, and in a confined and restricted environment the actual concentrations of the reactants are higher than in bulk. [6]

Furthermore, Si/Al ratio is an important parameter, which can influence such adsorption by zeolites. The higher the Si/Al ratio, the smaller the framework charge and the higher the number of water molecules present. [3]

One of the most important properties of zeolites is the surface acidity. Zeolites can present two types of acidity: Brønsted acidity and Lewis acidity. In Brønsted's view, an acid is defined as a proton donor, whereas in Lewis's theory an acid is an electron acceptor. A Brønsted acid has an extra proton to give to other species, while a Lewis acid has a vacant orbital that can accept a pair of electrons. Ergo, the acidic nature of a zeolite can be described by the characteristics of containing Brønsted and Lewis acid sites. [4]

Brønsted acid sites correspond to bridging OH (hydroxyl) groups linking Si to Al, formed by a proton directly bonded to a framework oxygen atom connecting one Al and one Si atom: Si-O(H)-Al.

It is possible for some of the Si atoms at tetrahedral sites of the zeolite framework to be substituted by Al atoms. Then, the fourfold coordinated Al atom has a negative charge which is balanced by a nearby extra framework cation. [10] Seeing that, in the case where this cation is a proton, a Brønsted acid site is formed, the number of cations depends on the overall charge of the AlO4 tetrahedra. Hence, the maximum number of protons in the acid sites equals the number of framework Al atoms. [3]

Besides bridging OH groups, there are other types of hydroxyl groups, such as silanol groups (SiOH) and extra-framework Al (EFAL) hydroxyls - AlOH. However, Brønsted's OH groups are much more acidic than silanol's OH groups. Regarding EFAL groups, these are produced by mild steaming leading to partial dealumination, therefore reducing the number of Brønsted sites by converting them into Lewis sites. [11]

Lewis acid sites in zeolites can be due to charge-balancing extra-framework cations (such as Na, K, Cs, Cu, Co, Zn, Ga), extra-framework aluminium species and heteroatoms substituted at framework T position. [11]

The acidity of aluminosilicates depends on the coordination number of aluminium and on the chemical nature of its neighbours. Dehydroxylation, steaming, or dealumination of acid zeolites dislocates aluminium from the lattice into extraframework aluminium. [12]

The basic properties of zeolites are much less studied than their acidic properties, due to the fact that industrial heterogeneous catalytic processes using basic catalysts are noticeably less developed than acid catalysed processes. [11]

To analyse the basicity of zeolites, one must determine the number and strength of those basic centres. The most widely used approach is the use of acid probe molecules that would react with the basic sites, and characterizing them by IR spectroscopy.

Sanderson postulated a principle for equalization of electronegativities for framework atoms in zeolites, calculating the mean electronegativity of the zeolite framework by the geometric average of the electronegativities of all atoms contributing to the framework. Using Sanderson's principle, the charge on the framework atoms and cations in zeolites can be estimated. [6] The higher the framework aluminium content, the higher the basicity of the framework oxygen atoms, because comparing to silicon, aluminium has lower electronegativity. Given that, zeolites are usually used as basic catalysts in their alkali-exchanged or impregnated forms. [6]

Zeolite Y's pore system comprises spherical cages, most commonly called supercages, with 1,3 nm in diameter. These supercages are connected with four neighbouring cages, through pores with 0,74 nm in diameter, through windows formed by TO4-tetrahedra. Hence, it is said that Zeolite Y has a three-dimensional 12-membered ring pore system, as it can be seen in figure 2. [13]

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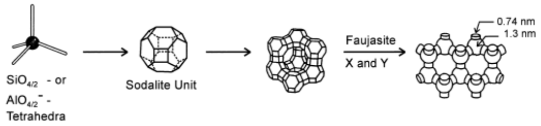

Figure 2 - Structure of zeolite Y [13]

Due to Zeolite Y's shape selectivity, the diffusion of compounds in its pores and the size of molecules that can be catalysed are somewhat limited. The strategy used to improve this situation was the creation of mesopores.

There are two main approaches: top-down techniques (that involve removal of Silica or Alumina) and bottom-up techniques that use soft or hard templates. Ultrastabilization of Ammonium-ion-exchanged zeolite Y in order to create USY is an example of a top-down process. [14]

The extra pore volume obtained with the creation of mesopores in the zeolite and surface area serve as a positive support for the catalyst particles that provide hydrogenation function of the bi-functional hydrocracking catalyst. [15] The creation of mesopores in zeolite Y gives rise to the concept of hierarchical zeolite structures. Hierarchical zeolite is a zeolite that contains two or more types of pores of different size, thus a mesoporous zeolite should be considered a hierarchical zeolite, since it has a secondary pore-structure system in the mesopores range (2-50nm). [15]

The Zeolite Y used in this work has a Si/Al ratio of 2,6 and was acquired from CROSFIELD.

2. Experimental

2.1. Modification Techniques

2.1.1. Ion Exchange

Zeolite NaY was ion exchanged with ammonium hydroxide and ammonium acetate, to replace Na+ ions by NH4+ ions. Since only about 73% of Na+ ions can be exchanged in a single ion exchange [16], several repetitions of the operation are necessary to exchange all sodium ions.

The procedure was carried out using a dissolution ratio of 1/10 (20g of zeolite mixed in 200mL of a solution of 0,1 M NH4NO3/NH4CH3COO). The mixture was stirred at 80 °C for 1 hour, centrifuged at 4250 rpm for 12 min to separate the solid product, which was then washed with H2O. The procedure was repeated 3 times to increase the degree of the exchange. Afterwards, the samples were dried overnight in an oven at 40°C.

Two samples were prepared: using NH4NO3 and NH4CH3COO (see Table 1).

Table 1 – Ion Exchanged samples

Zeolite	Solvent	Concentration	Sample name
NaY	NH_4NO_3	0,1 M	$NH_4Y(NO_3)$
	NH_4CH_3COO	0,1 M	$NH_4Y(OAc)$

2.1.2. Mesoporous Surfactant Templated Treatment

This approach is a destructive approach, which can sometimes lead to loss of crystallinity. It consists of hydrothermal treatment with a cationic surfactant, citric acid and a basic solution (NH4OH in this case). It has the advantaged of introducing mesoporosity without significantly compromising the Si/Al ratio or the pore distribution of the zeolite.

USY zeolite with Si/Al= 2,5 was the starting material for this experience. 5g of zeolite were dissolved in 50 mL of deionized water and stirred. Citric acid 10% (m/m) was added in 4 times, each one left to stir for 15 minutes. After the 4 additions, the sample was centrifuged, washed and left to dry in open air for 1 hour. Afterwards 50 mL of H2O were added to the sample, followed by 2,5 g of cationic surfactant (CTABr - Cetyltrimethylammonium bromide) and 10 mL of Ammonium Hydroxide (35%). After mixing well, the resulting mixture was left in an over at 80 °C for 24 hours.

The cationic surfactant is very important in this procedure, because it introduces mesoporosity and protects the zeolite's structure from citric acid, since it dissolves aluminium ions. Also, it allows for a much higher hierarchy factor and more efficient microporosity preservation. [14] The proportion of surfactant/zeolite should always be ½, which is half of the zeolite amount is the optimum amount of surfactant. This was verified by previous work at Lennard-Jones building at Keele University.

After the drying process, the sample is centrifuged and washed with H2O, followed by calcination. The calcination programme used is the following:

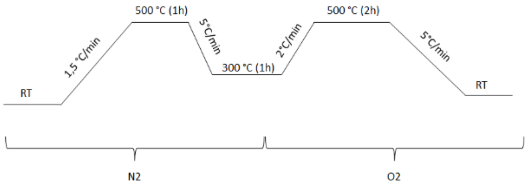

Figure 3 - Calcination programme used in zeolite samples

The maximum temperature for this type of zeolite is 500°C, instead of 550°C [17], otherwise the sample is partially destroyed. This was verified by previous work at Lennard-Jones building at Keele University. This procedure was done with different amounts of citric acid, in order do decide which one gave the best results. The amount of citric acid was calculated in milliequivalents, for 5 g of zeolite.

Table 2 - Samples prepared with different amounts of citric acid

Amount of zeolite (g)	Amount of citric acid (meq)	Amount of citric acid (g)	Sample name
5g	1,5 meq	4,80 g	1.5 USY
	3,0 meq	9,61 g	3.0 USY
	4,5 meq	14,4 g	4.5 USY
	6,0 meq	19,21 g	6.0 USY

2.1.3. Calcination

Calcination is a thermal treatment that affects the physico-chemical properties of heterogeneous catalysts and enhances its activity. [18] This treatment was only applied to one of the samples (NH4Y 6 IE calcined), because it was verified that it became amorphous due to this thermal treatment. The calcination programme used was the following:

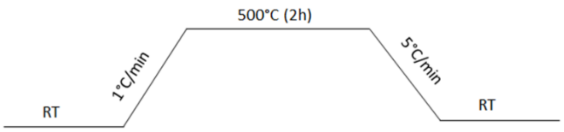

Figure 4 - Calcination programme used for sample "NH4Y 6IE calcined"

In this work, 6 samples were prepared, with different properties and different amounts of citric acid, in order to find out which one is the optimum preparation method. The original zeolites as made by the respective companies were also characterized for comparison and as a way to validate the results obtained.

Two different routes were in study: Route 1 and Route 2. Route 1 consists of ion exchanging NaY to NH4Y first, and then treat it with citric acid, while Route 2 is treating NaY with citric acid, and then ion exchange it to NH4Y. The samples were labelled as follows:

Table 3 - Summary of the samples prepared

Sample name	Sample nr	Description
NH4Y IE	1	Starting material: NaY from Zeolyst Sample was ion exchanged 4 times with NH_4NO_3 and NH_4CH_3COO. Two samples resulted but were treated as only one, since their properties were the same.
NH4Y 6	2	Starting material: NH4Y IE After the ion exchange, sample received mesoporous templated surfactant treatment with 6 meq citric acid
NH4Y 6 calcined	3	Starting material: NH4Y IE After the ion exchange, sample was calcined and then received mesoporous templated surfactant treatment with 6 meq citric acid
NH4Y 4.5	4	Starting material: NH4Y IE After the ion exchange, sample received mesoporous templated surfactant treatment with 4.5 meq citric acid
NaY 6	5	Starting material: NaY from Zeolyst Sample received mesoporous templated surfactant treatment with 6 meq citric acid and then was ion exchanged with NH_4CH_3COO.
NaY 4.5	6	Starting material: NaY from Zeolyst Sample received mesoporous templated surfactant treatment with 4.5 meq citric acid and then was ion exchanged with NH_4CH_3COO.
Original NaY		NaY from Zeolyst
Original NH4Y		NH4Y from CROSFIELD

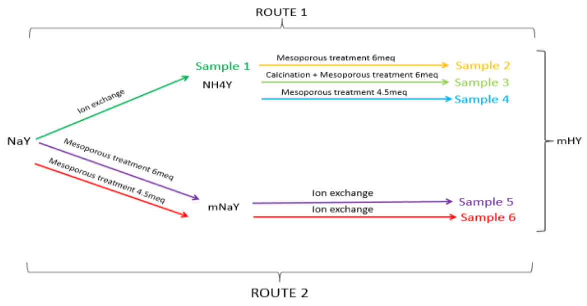

Figure 5 - Diagram showing the different routes and the different treatments received by the samples

2.2. Characterization Techniques

N_2 sorption experiments were made to evaluate the specific surface area of materials, the pore size, volume and distribution. The weighed sample (22-27 mg) is placed in the sample holder (a 12 mm bulb cell), which is loaded into the outgasser station. The outgassing is run overnight at 300°C for 300 min with a heating rate of 1 °C/min from RT and a cooling rate of 5 °C/min until 100 °C. After this, the sample is left to cool down naturally and then degassing. Afterwards, the sample is transferred to the sorption station and the sorption experiment begins.

The instrument used was a *Quantachrome Autosorb C1*, with N2 used as adsorptive gas. Data analysis was performed in the *Quantachrome ASiQwin 3.0*: *MultiPoint BET* was used to calculate surface area, *t-plot* method to estimate micropore volume and micropore and external surface areas, and DFT to determine pore size distribution and diameter.

X-ray powder diffraction (XRD) patterns were collected to analyse the crystallinity of the samples. The powdered sample is deposited and spread over a diffraction plate. Then it was loaded onto the sample holder of the XRD machine, after which the experimental parameters are set and the programme is started. Determination of the unit cell size was also made using a silicon internal standard, in order to calculate the $Si/Al_{framework}$.

The equipment used was a Bruker D8 Advance with nickel filtered CuKα radiation. The patterns were scanned in a 2θ range between 5–60°, with a coupled 2θ/θ scan type, at an angular rate of 0,3°/min and a 0.01° step.

Infrared Spectroscopy (IR) was used to quantify and characterize acid sites (using pyridine adsorption) and to test accessibility, using different probe molecules to distinguish between external and internal pores. Sample preparation and loading was the same for all probe molecules with the exception of CO. The samples were pressed at roughly 0,5 ton into a pellet holder and loaded into the IR cell. Regarding the CO probe, the CO was loaded in the gas flask before the sample and liquid nitrogen was introduced underneath the gas flask in order to freeze the residual CO2 existing inside, preventing it from going into the system. In all experiences using the CO probe, the amount used was approximately 7,5 torr. For the pyridine experiments, the activation programme was run overnight and the system was purged with N2 (roughly 2 hours before the data collection started). The background spectrum was collected, followed by the spectrum before injecting pyridine. An excess volume of 2 µL of pyridine was injected in the system, to guarantee that all sites were covered. After a few minutes, the excess and physisorbed species was removed by pressure gradient. Then, the desorption programme followed the scheme in figure 6.

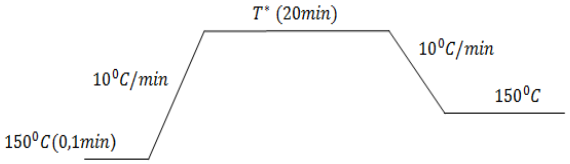

Figure 6 - Pyridine desorption programme used in the IR experiments (T*= 200,250,300,350,400,450 °C)

For the different probe molecules used to test the accessibility, the heating was turned off after the activation programme was complete and the sample was left to cool down to room temperature.

The FTIR instrument used is presented in figure 27. It is a Thermo Scientific Nicolet iS10 spectrometer with a DTGS detector with KBr windows, a KBr beamsplitter and an optical velocity of 0.4747 cm/s. All spectra were collected in transmission mode, with a resolution of 4 cm-1 and 64 scans/spectrum, except the CO gas phase spectra, which were collected with a resolution of 1 cm-1. Background spectra were collected before each main spectra collection.

SEM/EDS were performed to assess the morphology and elemental composition of the samples. A small amount of powdered sample is pressed at 2 ton and placed on an aluminium stub, which was previously covered with a small amount of conductive carbon dag. Afterwards, the stub with the sample impregnated in the glue is left on a hot plate for 1 hour to dry. The sample needs to be carbon coated before being ready for analysis. When the sample is ready, the stub is attached to the sample holder on the SEM instrument. The analysis is started after the chamber is evacuated. The SEM used for this analysis was a *Hitachi TM3000* with a *Quantax 70 EDS* incorporated.

The Zeolite Y used in this work has a global Si/Al ratio of 2,6 and was acquired from CROSFIELD. This material did not have any mesopores.

3. Results and Discussion

Sorption analysis showed the existence of mesopores in samples 3, 4, 5 and 6. Sample 3 was disregarded because it was completely amorphous. Sample 5 was the one with more mesopores, but its crystallinity was near 50%, which is not very good.

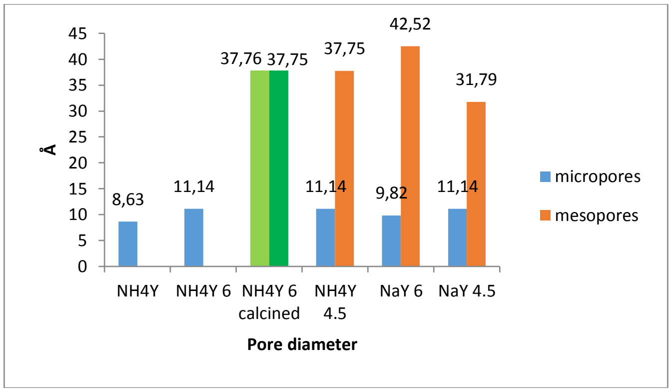

Figure 7 - DTF pore diameter of micro and mesopores for all samples

Using the XRD patterns obtained, it was possible to calculate the relative crystallinity. All the crystallinity percentages were repeated using the XRD patterns with the silicon standard, since using an internal standard is a more efficient way to ensure the results are accurate, because they all have the same "baseline". After comparing both crystallinity results it was decided to use the results obtained with the internal standard in all further calculations and reasoning.

Table 4 – % crystallinity of all samples

Sample name	Sample nr	%XRD	%XRD with silicon standard
NH4Y IE	1	98,1%	100,4%
NH4Y 6	2	56,6%	35,2%
NH4Y 6 calcined	3	0,19	0,1%
NH4Y 4.5	4	19,9%	18,8%
NaY 6	5	50,8%	49,8%
NaY 4.5	6	71,8%	70,95%
Original NaY		94,3%	100%
Original NH4Y		100%	100%

The crystallinity percentages were calculated using the original NH4Y from CROSFIELD as 100%.

Sample 3 is obviously destroyed, since its crystallinity is nearly 0. Comparing the two different routes in study, route 2 is more effective. Na+ is more stable than NH4+, and that reflects on the crystallinity results: the two samples on route 2 are more crystalline than the samples on route 1. Between those two (sample 5 and 6), sample 5 appears to have more mesopores, but since its crystallinity is around 50%, some of that may be amorphous material. Hence, sample 6 can be considered the best sample, since it had little crystallinity loss and a reasonable amount of mesopores. Ergo, the optimum amount of citric acid is concluded to be 4,5 meq.

Unit cell size was calculated according to [19] and [20]. As expected, the samples that suffered the surfactant-templated mesoporous treatment have smaller unit cell size than the original zeolites. Increasing mesoporosity causes decreasing the unit cell size due to a slight dealumination by the citric acid.

SEM images give information on the shape and size of the particles, whereas EDS measurements have information on the elemental composition of the zeolite samples. From the EDS measurements it was possible to estimate the Si/Al ratio and the %Na in the samples.

Table 5 – Composition of all samples

	Si/Al	Na/Al	%Na
NH4Y IE	2,5	0,168	1,47%
NH4Y 6	2,77		
NH4Y 6 calcined	7,79	0,095	0,22%
NH4Y 4.5	4,03	0,244	1,48%
NaY 6	3,84	0,210	0,76%
NaY 4.5	3,39	0,184	0,73%
original NaY	2,51	0,989	7,82%
original NH4Y	2,37	0,204	0,88%

The Si/Al obtained in sample 2 is an indication that the mesoporous treatment did not work as expected, since the Si/Al ratio is approximately the same as the original samples. Sample 3, as it is destroyed, presents the higher Si/Al ratio, which is already known that is due to the loss of crystallinity. In mesoporous samples, the Si/Al ratio is expected to increase to about 3-5. [16] This is the case of samples 4,5 and 6.

Regarding the sodium percentages, original NaY has naturally a much higher percentage than all other samples. Sample 4 has a sodium percentage far too high, since it is bigger than the original NH4Y sample, which is not possible. Samples 5 and 6, as expected, have a slightly higher %Na, as they were made by route 2. There was always a residual amount of sodium in all samples: it is very difficult to remove it completely because it gets trapped in the sodalite small cages.

The Si/Al ratios obtained were compared with the $Si/Al_{framework}$ obtained by XRD experiments:

Table 6 - Si/Al (global and framework) ratios for all samples

	Si/Al (SEM)	Si/Al framework (XRD)
NH4Y IE	2,5	2,30
NH4Y 6	2,77	3,92
NH4Y 6 calcined	7,79	-
NH4Y 4.5	4	4,16
NaY 6	3,84	3,25
NaY 4.5	3,39	3,04
original NaY	2,51	2,54
original NH4Y	2,37	2,28

In theory, the $(Si/Al)_{framework}$ should be higher than the global Si/Al ratio, considering that some of the aluminum atoms are outside the framework. In the samples prepared by route 1 (samples 2 and 4) this result is verified. Yet, in samples 5 and 6 (route 2) the (Si/Al) framework is lower than the global Si/Al ratio. This can indicate a slight desilication by the acid treatment, existing some extra-framework Si in the form of amorphous silica.

The IR experiments were divided into two parts: pyridine adsorption to quantify the acid sites in zeolite Y and using various probe molecules to distinguish between external and internal pores.

Pyridine adsorption showed that the samples created by route 2 present more BAS than the ones prepared by route 1 and low frequency OH groups are almost not accessible to pyridine, while high frequency OH groups and silanols are all accessible.

Based on the peak heights of the spectra of pyridine desorption at different temperatures, the amount of Lewis and Brønsted acid sites in the samples was calculated.

Table 7 - Amount of Brønsted and Lewis acid sites in all samples

	Py-BAS (mmol/g)	Py-LAS (mmol/g)
Sample 1	1,054	0,142
Sample 2	0,664	1,156
Sample 3	0,068	0,407
Sample 4	0,228	0,748
Sample 5	0,796	0,623
Sample 6	0,656	0,177
Original NaY	0,002	2,540

The spectra of the pyridine desorptions showed that the samples prepared by route 2 have more Brønsted acid sites and the ones prepared by route 1 have more Lewis acid sites. The intensity of all OH groups (silanols and bridging OH groups in small and large cages) was higher in the samples prepared by route 2, an indication that route 2 is preferable. It was observed that low frequency (LF) OH groups were almost not accessible to pyridine, while high frequency (HF) OH groups and silanols were all accessible. Despite LF groups having very poor accessibility, they were more accessible in samples prepared by route 2. After the mesoporous treatment, the samples showed an increase in LAS and a decrease in BAS, comparing to sample 1 (NH4Y IE).

Regarding the accessibility tests, they were performed in zeolites BEA and ZSM-5 as well. However, ZSM-5 is currently being studied at the Birchall Centre, so it will not be mentioned in this article. The probe molecules were first injected individually, to see which ones were worth it to combine with other. This was experimented in zeolite Y. When the molecules to be used ere decided, they were experimented in zeolites BEA and ZSM-5.

Table 8 - Different probe molecules used with each sample

Sample	1st probe molecule	2nd probe molecule
NH4Y IE	C_9H_{20}	CD_3CN
	di-t-Bu-Py	-
	C_9H_{20}	-
	CD_3CN	-
	tri-isopropylbenzene	-
original NH4Y	tri-isopropylbenzene	-
BEA 12.5	C_9H_{20}	CO
ZSM-5 (40)	C_9H_{20}	
ZSM-5 (AK0654)	C_9H_{20}	CO
ZSM-5 (AK0658)	C_9H_{20}	CO

A substituted pyridine (di-t-Bu-Py) was used, and was expected not to enter the zeolite's pores (7,5 Å), due to its big dimensions (7 Å). In fact, by comparing its spectra with the one from pyridine injection, it should be possible to distinguish between acid sites in the external and internal surface. However, di-t-Bu-Py was able to enter the zeolite Y's micropores. Tri-isopropylbenzene, whose kinetic diameter is 9,3 Å, is too big to enter the zeolite's pores. So, comparing its spectra with the one from pyridine, it showed the existence of some LAS in the external surface (in the form of EFAL species). CD_3CN, as expected, since it is a small molecule (4 Å), it was able to access all OH groups. Nonane was also experimented and the result was as expected: it was able to interact with all OH groups. So, an experience combining the two probe molecules was made: nonane was injected first, and then CD3CN. It was not successful though, because the CD_3CN was displacing the existing nonane and entering the pores. Hence, CO was used as the second probe molecule.

Zeolite BEA showed a peak from the CO, when it was injected first, and when it was injected after nonane, which means that CO is interacting with the LAS. This result was not expected, given that CO is not strong enough to displace nonane, and so it was theorized that maybe all the LAS were in the external surface. However, that is very unlikely.

4. Conclusions

The main goal of this work was to create mesopores in zeolite Y, for further use in biodiesel catalysis. This work was part of an ongoing investigation on the subject, which also involves other researchers, and was developed in the Birchall Centre at Keele University.

The overall results have shown that the Surfactant Templated Treatment was more successful using route 2, given that it showed small crystallinity loss and reasonable amount of mesopores. The mesoporous samples had a decrease on the amount of Brønsted sites and an increase of the Lewis sites, as expected. It was also verified that the more mesoporous the sample is, the easier it is to access OH groups.

Sorption experiments showed higher degree of mesoporosity in sample 5 (NaY 6), but since it had some crystallinity loss, it can be attributed to amorphous material. Nonetheless, route 2 was considered a better way of creating mesopores.

SEM/EDS results showed an increase in the Si/Al in all treated samples. This was as expected, since the creation of mesopores causes dealumination.

Future work should now be done to further test the accessibility, by running the same experiments on zeolite Y and comparing the results. Also, other probe molecules can be used, such as other substituted pyridines (lutidine and collidine), to characterize hydroxyls.

5. References

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