Improved THETA-1 for light olefins oligomerization to diesel: influence of textural and acidic properties.

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Abstract.

The increase in diesel demand, especially in Europe, and the need for high fuel quality requirements, is forcing refiners to move into additional processes for production of high cetane diesel in order to meet the present market trends. Oligomerization of light olefins into middle distillate range products is a viable option. The fuel produced through this technology is environmentally friendly, free of sulfur and aromatics, and the adequate choice of the heterogeneous catalyst will direct the selectivity towards low branched oligomers, which will result in a high quality product. In this work we show the benefits of combining basic desilication treatments for generation of additional mesoporosity in mono-directional Theta-1 zeolite, with selective acid dealumination steps that restore not only the microporosity to values close to those of the parent samples, but also the total and strong Brønsted acidity. These modified Theta-1 zeolites present an outstanding catalytic behavior for oligomerization of propene, with a largely increased initial activity, a much higher resistance to deactivation with time on stream, and an improved selectivity to products in the diesel fraction, as compared to the original microporous Theta-1.

Keywords:

Oligomerization, diesel, Theta-1 zeolite, desilication, selective dealumination, catalyst deactivation.

1. Introduction

The increase of diesel demand, especially in Europe, and the need for higher fuel quality requirements [1-2], is forcing refiners to consider additional diesel production processes. Oligomerization of short alkenes, such as propene and butenes, is an implemented, large-scale industrial route for the production of environmentally friendly synthetic liquid fuels, free of sulfur and aromatics [3]. Processes based on silica-supported phosphoric acid (SSPA) have been described for the production of highly branched naphtha range oligomers [4-7], and are still being operated, despite the numerous drawbacks related to feed hydration level or corrosion, among others [8].

For the production of diesel, where branching of the hydrocarbons has to be limited, SSPA is, however, not suitable, and zeolite based catalysts have been proposed for gas phase [1, 9-12] and liquid phase operation [13-16]. When oligomerization of light olefins is carried out in the presence of heterogeneous acid catalysts, the reaction mechanism involves carbenium ions and the branching degree of product oligomers –isoolefins- is known to be proportional to the size of the catalysts pore. Thus, in non-microporous catalysts, such as the solid phosphoric acid, and due to the absence of steric constraints, a highly branched product is formed. In the case of microporous zeolites, the branching will depend on the diameter of the channels [17], and the use of medium pore 10R zeolites such as ZSM-5, with a pore diameter of 5.5-5.6 Å, results in a limited branching of the product [11], thanks to its shape selectivity. In fact, there are two commercial light olefin oligomerization processes based on zeolitic catalysts, the Mobil Olefins to Gasoline and Distillate (MOGD) [11, 18] and the Conversion of Olefins to Diesel (COD, developed by Lurgi) processes [1, 19]. Although the diesel range molecules obtained with ZSM-5 were described as primarily methyl-branched olefinic chains, with one methyl branch every five carbon atoms [11] the number of methyl-branches can be reduced when using selectivated monodirectional 10R structures ([9, 20-22]), which have been claimed in the open [14] and in the patent literature [20-24].

Two problems arise when considering mono-directional zeolites for this process. On one hand diffusion limitations through the tubular pores and slow transport to/from the active site may result in low catalyst utilization. On the other hand, blocking of the mono-directional channels will completely disable the micropore for further use in the catalytic process, and lead to fast catalyst deactivation [25]. Thus, the generation of secondary mesoporosity by post-synthesis treatments will improve diffusion of desired products, avoid further oligomerization to bulkier coke precursors, and improve the efficiency of the zeolite usage by increasing the accessibility to the active sites. However, when considering the oligomerization of light olefins to diesel range compounds, we must keep in mind that, depending on the starting olefin, the reaction should proceed through several consecutive oligomerization steps in order to produce large

molecules in the range of middle distillates. In the case of propene oligomerization, at least three steps are needed to obtain diesel range products (see Scheme 1).
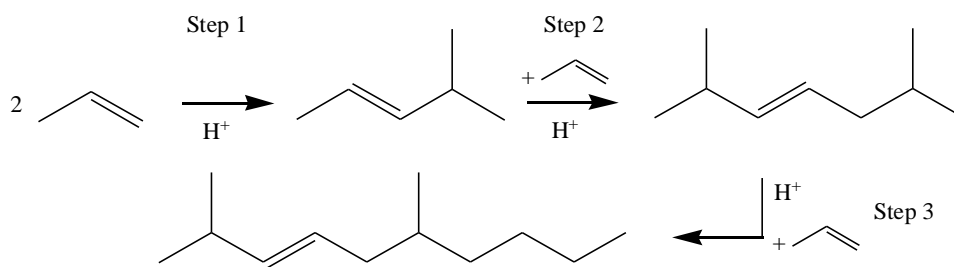
Scheme 1

One procedure for generation of mesopores in high silica zeolites is by controlled desilication in alkaline media [26-29]. In this case the mesopore formation results from preferential dissolution of Si from the zeolite framework and the Al content of the parent zeolite is known to affect the effectiveness of the treatment [28]. Moreover, variation of NaOH concentration, treatment time and temperature enables a certain tuning of the mesopore-size and volume. The formation of the mesopores, when performed in optimal conditions, does not necessary result in a loss of microporosity or structural integrity. However, in some cases a partial loss of micropore volume occurs which is related to the presence of amorphous extra-framework species located inside of the channels. When this occurs the micropore volume may be restored by washing with diluted acid solutions [28]. The loss of micropore volume will result in a lack of shape selectivity, which can lead to a loss of diesel yield and quality. Thus, the reduction of the micropore volume should be minimized in order to maintain shape selectivity to products with low branching degree, whereas the formation of the mesopores should be optimized to diffusion path lengths such that accessibility to the active sites and diffusion of the desired products is enhanced, but still favoring the formation of diesel range oligomers.

The desilication of TON zeolites to hierarchical micro-mesoporous structures has been addressed in two recent papers [25, 30], but the results were not completely satisfactory. Verboekend et al [30] described low desilication efficiency for ZSM-22 and severe pore blocking due to the presence of extraframework debris. Although mild HCl treatments were able to restore most of the micropore volume as compared to that of the parent zeolite, less than 40% of the initial Brønsted acid site density was restored. The group of Guisnet [25] has also described a permanent reduction of the total Brønsted acidity and, although an increase of the initial activity of ZSM-22 in 1-butene isomerization was observed, the additional mesoporosity did not improve the catalyst stability with TOS, contrary to what could be expected.

In a recent publication [12] we have shown that the combination of basic desilication treatments followed by selective dealumination with oxalic acid on ZSM-5 results in a largely improved activity and catalyst life for the oligomerization of light olefins. Here we show that this

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combination is even more effective for modification of monodirectional Theta-1 (TON) zeolites, and we present the positive effect of mesoporosity generation on catalyst life for this oligomerization reaction, as well as the need for fine-tuning the micro-mesoporous structure in order to achieve maximum diesel selectivity.

The optimum conditions for generation of hierarchical Theta-1 zeolites are found to be considerably different depending on the physico-chemical properties of the starting sample, but in all cases the combination of an optimized basic treatment with an external surface selectivation has resulted in an important increase in catalyst life and substantial increases in selectivity to the diesel fraction.

2. Experimental

Catalyst preparation

Two Theta-1 zeolites with different aluminum content have been supplied by BP PNA in their ammonic form. Desilication treatment was performed by contacting the calcined (acid) zeolites with a basic solution of NaOH heated at the desired treatment temperature, under vigorous stirring. The liquid to solid ratio used was 33 by weight. After the desired time, the solid was separated by filtration and washed with deionized water until lowering the pH to a value of 7.0. The Na-zeolite obtained after the basic desilication was ion exchanged with a 0.1 M NH_4NO_3 solution (L/S=20, T=80ºC, t=2 hour, refluxed under vigorous stirring), washed with deionized water and dried overnight at 100ºC. This ion exchange treatment was repeated three times, in order to reduce Na content below 0.1 wt% as Na_2O, before calcination in a muffle for 3 hours at 500ºC. The ammonium exchanged samples were labeled as *M-TR-T-t-A,* where *M* is the NaOH solution concentration in mol/l, *TR* is the parent Theta-1 zeolite with Si/Al ratio of R, e.g. T25 or T50, *T* is the treatment temperature in °C, *t* is the duration of the desilication in minutes, and A stands for the ammonium exchange. In some instances the ammonium exchange was not performed and the desilicated zeolite, in its Na-form, was washed with a 0.8 M oxalic acid solution for 2 h, at 70ºC, for selective dealumination of the external surface. The dealuminated zeolite was separated from the solution by filtration, washed and finally calcined at 375ºC for 3 hours. These sample variants were named as *M-TR-T-t-OX*, where *–OX* stands for the oxalic acid treatment. For comparison purposes, the Na-zeolite obtained after the basic desilication was treated with a 0.5 M HCl solution for 2 hours at 80ºC (samples *M-TR-T-t-H*).

Catalyst characterization

The chemical composition of the catalysts was determined in a Varian-715-ES Inductivity-Coupled Plasma Analyzer (ICP). Textural properties were obtained from nitrogen adsorption isotherms measured at 77 K (-196ºC) using an ASAP 2000 Micromeritics instrument. The

micropore volume for the catalysts was calculated by the t-plot method and the mesopore volume according to the BJH correlation. The acidity of the zeolites was determined by infrared spectroscopy combined with adsorption-desorption of pyridine at different temperatures. Infrared spectra were measured with a Nicolet 710 FT-IR spectrometer. Pyridine adsorption–desorption experiments were carried out on self-supported wafers (10 mg·cm^{-2}) of original samples previously activated at 400ºC and 10^{-2} Pa for 2 h. After wafer activation, the base spectrum was recorded and pyridine vapor (6.5×10^2 Pa) was admitted into the vacuum IR cell and adsorbed onto the zeolite. Desorption of pyridine was performed in vacuum over three consecutive 1 h periods of heating at 150, 250, and 350ºC, each followed by an IR measurement at room temperature. All the spectra were scaled according to the sample weight. Brønsted and Lewis acidity was derived from the intensity of the IR bands at about 1450 and 1550 cm^{-1}, respectively, using the extinction coefficients given by Emeis [31].

Scanning electron microscopy (SEM) was performed using a Jeol JSM 6399 microscope (20 kV) equipped with a secondary electron images detector using gold-coated powder specimens. Transmission Electron Microscopy (TEM) characterization was carried out in a Philips CM10 (100 kV) microscope. Before TEM observation, the samples were prepared by suspending the solid in isopropanol, ultrasonicating for 1 min and placing one drop on a carbon coated copper grid (300 mesh).

X-ray photoemission spectra (XPS) were recorded in a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic Al X-ray source operating at 200 W. The samples were pressed into a small disc and evacuated in the pre-chamber of the spectrometer at $1 \cdot 10^{-7}$ Pa. Quantitative data were calculated from the Al2p and Si2p peak intensities after nonlinear Shirley-type background subtraction and corrected by the transmission function of the spectrometer. The CasaXPS software was used for spectra processing.

Catalytic tests

The catalytic experiments were performed in a 10 mm internal diameter down-flow stainless steel fixed bed reactor. The catalyst (0.25 mm and 0.42 mm particle size) was diluted in all cases with SiC (0.64 mm-0.25 mm) to obtain a bed volume of 4.0 cm^3 with the aim of minimizing thermal effects due to exothermicity of the reaction, and ensuring homogeneous temperature along the whole bed, both, in axial and radial directions. Dimensions of the catalyst particle and of the catalytic bed do fulfill the conditions of plug flow pattern given in [32]. The temperature in the catalyst bed was controlled by means of two independent heating zones with the corresponding thermocouples properly placed inside the catalytic bed. Before reaction, the catalysts were activated in-situ by increasing temperature up to 520ºC in N$_2$ flow (200 ml/min) at a rate of 2.0 º/min and calcination in air flow (200 ml/min) at 520ºC for 5 h. Then the reactor

was cooled down to the reaction temperature in a flow of N_2 (200 ml/min). Propene was co-fed (in the liquid phase) with propane in a 60:40 propene:propane molar mixture. The mixture was fed to the reactor as a liquid by means of a Gilson piston pump and the pressure was controlled during the reaction electronically through a Badger pneumatic valve. The liquid C_{5+} products were condensed in a cold trap at the exit of the reactor, whereas the non-condensable vapors entered an on-line chromatograph. The on-line analyses of the unconverted reactants and of the lightest reaction products (not condensed in the cold trap) were performed every 30-40 minutes on a Varian 3400 chromatograph equipped with a 30 m Plot/Al_2O_3 column and an FID detector. The liquids collected in the trap were analyzed by simulated distillation (SIMDIS) on a Varian 3800 equipped with a 10 m, 0.53 mm ID MXT-2887 metal column supplied by Restek Corp. using the software STAR SD from Varian following the ASTM D-2887 standard. In order to close the mass balance the mass flow of propene and rest of non-condensable vapors analyzed on-line were determined by using propane (with a known mass flow) as internal standard.

Only experiments with mass balances (MB) of 95% or higher were considered for discussion.

Experiments were performed to confirm the absence of interphase (external) and intraphase (internal) gradients [32] under the whole range of experimental conditions used herein.

The selectivity results within the condensed liquid fraction (C_{5+}) are referred to the naphtha, diesel and heavy product fractions and given as the distribution (in wt%) of these fractions within the liquids collected. Thus, the values given are directly those determined by SIMDIS according to the following cut points:

Naphtha: C_5-173.9ºC

Diesel: 173.9-391.1ºC

Heavy fraction: 391.1-1000ºC

3.   Results and discussion

3.1 Catalyst characterization

Theta-1 is a zeolite with TON topology, isostructural with ZSM-22, Nu-10, KZ-2 and ISI-1. It comprises a monodirectional structure of 10-member ring (10R) elliptical channels (see figure 1) and grows in rod-like crystals. Two Theta-1 zeolites with Si/Al ratios of 25 (T1-25) and 50 (T1-50) were supplied by BP-PNA in their ammonic form and their chemical and structural properties have been modified by means of basic desilication, either alone or in combination with additional treatments. The samples prepared and their characterization will be presented in the following two sections.

The first sample studied, T1-50, has a Si/Al of 50, which is in the upper limit of the optimum chemical composition for effective desilication [27], which was described to range from Si/Al=25 to 50. The calcined acid form was treated with NaOH solutions of different concentrations, and under different experimental conditions as will be shown below. The modification of a second sample, T1-25, with a Si/Al ratio of 25, will be covered in a second section. Since the composition of this T1-25 sample is in the lower limit of the range considered as optimum for effective mesopore generation by NaOH treatments, the calcined (acid) zeolite has been directly desilicated or desilicated after a pre-dealumination step.

3.1.1 Modified T1-50 samples obtained by NaOH treatments

Calcined (acid) T1-50 has been desilicated under different experimental conditions, varying NaOH concentration, temperature and duration of the treatment, (base concentration ranging from 0.2 to 1.0 M, treatment temperatures between 65 and 95ºC, and treatment times between 30 and 90 min), with the aim of modifying the textural properties of the parent microporous zeolite. As will be shown below, besides generating additional mesoporosity, these controlled basic treatments can also result in deagglomeration of crystallite aggregates and/or decrease of the original zeolite's crystal size. The final step for obtaining the acid sample, by exchange of the Na^+ in charge-compensating positions, has also been varied. Thus, the Na-form of the desilicated zeolite a) has been treated with NH_4NO_3 followed by calcination, b) has been directly exchanged with an HCl solution, and c) has been directly treated with oxalic acid. The physico-chemical and acidic properties of the parent (T1-50), the calcined (HT1-50) and the modified (e.g. 0.2-HT1-50-65-30-A) samples are given in tables 1 and 2, respectively.

The basic desilication steps produce samples that are enriched in Al and the Si/Al ratio decreases when increasing the treatment severity, as compared to the starting T1-50. The influence of the desilication temperature on the mesopore volume in the range studied of 65 to 95ºC, is significant and the value is almost doubled when increasing temperature from 85 to 95ºC. When the treatment time was increased from 30 to 90 min or the NaOH concentration was increased from 0.2 to 1.0M and the treatment temperature was held constant at 85 °C, the mesopore volume increased as well, although to a lower extent than with the highest temperature treatment, and the Si/Al ratio was further decreased to around 30.

In any case, when the severity of the treatment increases, the yield of recovered zeolite, determined by means of equation 1 [33] is reduced and can drop as low as 25 % when using the highest NaOH concentration of 1.0 M.:

Yield (%) = g of desilicated sample recovered x 100/g of parent sample   *(1)*

Acid treatment of the desilicated samples, either with mineral HCl (sample 0.2- HT1-50-85-30-H) or with organic oxalic acid (0.2- HT1-50-85-30-OX), results in an increase in the Si/Al ratio from 35, obtained for sample 0.2- HT1-50-85-30-A, to a value around 50, and the removal of Na is complete, even when using the bulkier oxalic acid. It is important to note that the desilicated samples preserve most of their micropore volume even when using the ammonium exchange followed by calcination procedure in order to obtain the acid zeolite after the NaOH treatment. Table 1 shows a clear correlation between the micropore volume of the desilicated-ammonium exchanged and calcined samples, and their treatment yield, and it can be seen that high solid yields result in samples with high micropore volume preservation. As detailed in the Introduction, most of the micropore volume loss is usually related to the presence of extraframework debris within the channel system. If there is no significant sample dissolution and solid loss there will be no extraframework species blocking the mesopores. A possible explanation for this is that in these cases the mesopore increase is mainly due to a deaggregation or fragmentation of the rod-like TON crystals.

When using a non-selective HCl dealumination, the micropore volume is decreased to 0.069 cm^3/g, probably due to a partial destruction of the zeolite structure by the inorganic acid treatment. In fact, framework Al-O bonds are susceptible to hydrolysis in acid media, and when an inorganic acid, such as HCl is used, the whole crystals can suffer acid dealumination, and this can lead to a partial destruction of the structure, as confirmed by the results enclosed in table 1. However, the use of bulky organic acids, such as oxalic acid, is known to limit the acid attack to the external surface of the zeolite crystals [12, 34-35]. Thus, besides removing the possible extraframework species present, oxalic acid will selectively remove the most external – accessible- framework Al from the crystals without destroying the structure. The results enclosed in table 1 show that the samples treated with oxalic acid recover more than 90% of the initial microposity, and the selective reduction of the external Al concentration has been confirmed in our Theta-1 based samples by means of XPS measurements. Table 1 shows the surface compositions of the parent T1-50 and the desilicated 0.2-HT1-50-85-30 converted into the acid form by ammonium ion exchange or by treatment with oxalic acid, determined by XPS. The results clearly show that with oxalic acid treatment a selective dealumination of the external surface takes place, as can be deduced from the significantly higher Si/Al (XPS) obtained for sample 0.2-HT1-50-85-30-OX compared to that for sample 0.2-HT1-50-85-30-A.

The desilicated samples have been studied by Transmission Electron Microscopy (TEM) to evaluate their morphology and to confirm the mesoporosity generated by the basic treatments. The effect of the duration of the desilication treatment on the final mesoporosity is shown in figure 2. In general terms, it can be seen that the rod like crystallites of zeolite T1-50 (figure 2-

a) are more deagglomerate and fragmented along the c-axis after the desilication treatment (fig. 2-b to 2-f). According to the images, when the desilication duration is increased from 30 (figure 2-b) to 90 minutes (figure 2-c), the mesopores seem to grow and the fragmentation along the c axis seems to be lost. Moreover, the crystallites are more dispersed and isolated as can be seen in figure 2-d. The final step of converting the Na- desilicated Theta-1 zeolites into their acid form (NH_4^+ ion exchange followed by calcination vs. direct oxalic acid treatment) does not seem to affect the final topology, as can be seen when comparing figures 2-b and 2-e, corresponding to sample 0.2-HT1-50-85-30 ion exchanged with NH_4NO_3 (A) or treated with oxalic acid (OX), respectively. The last sample compared in this figure is HT1-50 treated with a 1.0M NaOH solution at 85ºC for 30 minutes (figure 2-f). Although difficult to quantify by TEM, the degree of mesoporosity generation for this sample is clearly larger. This is in agreement with its higher mesopore volume as determined from the N_2 adsorption isotherm.

A selection of samples was characterized for acidity by means of FT-IR spectroscopy combined with adsorption of pyridine and desorption at increasing temperatures. Before going into discussion of the relative acidity of the treated samples, figure 3-a shows the bands observed in the OH region for the T1-50 based samples after activation at 400ºC under vacuum (solid lines), and after adsorption of the pyridine (dotted lines). It can be seen that the band at 3740 cm^{-1}, assigned to non-acid external silanols is present of all the samples, before and after the adsorption of the basic probe. However, the band at 3600 cm^{-1}, assigned to the acid bridging hydroxyl disappears after exposure of the sample to the pyridine vapours. This indicates that all the Brønsted acid sites are interacting with pyridine, and are therefore accessible to the basic pyridine probe, even in the case of the parent HT1-50.

The acidity of the modified zeolites, determined as mmol of pyridine adsorbed per gram of zeolite at increasing desorption temperatures, is compared in table 2 to that of the parent T1-50 as well as to the calcined HT1-50 zeolites. The first thing to be noted is that calcination of the ammonic T1-50 sample results in a zeolite, HT1-50, with a reduced Brønsted acid site density. The spectra plotted in figure 3-a shows that all acid bridging hydroxyls are still accessible to the probe in the calcined HT1-50, so the acidity decrease is not due to partial blocking of the pores, but more likely to the presence of some extra-framework alumina (EFAL) species substituting the acid protons in charge compensation positions. The total Brønsted acidity of the calcined T1-50 treated with a 0.2M NaOH solution, sample 0.2-HT1-50-85-30-A, given in table 2 by the amount of pyridine retained at the lowest desorption temperature, 150ºC, is lower than that of the starting zeolite, T1-50 (NH_4^+), which was converted into its acid form by the "in-situ" activation performed at 400ºC and under vacuum in the IR cell. This lower amount of total and strong Brønsted acid sites (retaining pyridine at 350ºC), as well as the larger presence of Lewis sites in 0.2-HT1-50-85-30-A, can be due to some dealumination taking place during the

calcination performed after the ammonium exchanges. However, the FT-IR spectra in the -OH region (figure 3-a) shows again that the extra-framework species are not preventing access to the active sites, but more probably the extra-framework Al species are in ion-exchange positions.

When the NaOH treated sample is directly washed with a diluted HCl solution (sample 0.2-HT1-50-85-30-H) for removal of Na^+, the Lewis acid site density decreases, but the amount of total Brønsted acid sites remains similar to that of the ammonium exchanged sample (see table 2), despite its lower micropore volume. When treating the NaOH treated sample with oxalic acid, 0.2-HT1-50-85-30-OX, the amount of Lewis sites is also sensitively lower than for the ammonium ion exchanged and calcined mesoporous zeolite, 0.2-HT1-50-85-30-A, but both, the total Brønsted acidity and the number of stronger Brønsted acid sites are similar to that of the unmodified Theta-1.

The use of acid treatment with 0.1M HCl has been described as a route for successfully restoring the microporosity of alkaline treated ZSM-22 [30], since by means of this treatment amorphous extra-framework Al species are washed away. These species were described to be mainly located on the external surface of the crystals, blocking the uni-directional channels of the TON zeolite. However, whereas the micropore volume of the desilicated zeolites was recovered in a large extent with the HCl treatment, less than 40% of the Brønsted acidity was restored. The main difference between the referenced work and our approach is that Verboekend et al apply the acid treatment after performing NH_4^+ exchange and calcination of the alkaline treated zeolite, and herein we describe the direct washing of the NaOH treated mesoporous zeolite with the acid solution. In our case, besides reducing the number of preparation steps, the dealumination of the zeolite framework that takes place from ion-exchange followed by calcination is avoided. This was already proven to be critical for ZSM-5 based oligomerization catalysts [12] and will be shown to be even more important with Theta-1, especially for samples with a lower Si/Al ratio.

When increasing the concentration of the NaOH solution (sample 1.0-HT1-50-85-30-A) the total Brønsted acid site density is decreased to values close to those of the calcined parent zeolite (HT1-50), though the amount of the strongest Brønsted acid sites, which are able to adsorb pyridine at 350ºC, is maintained (see values enclosed in table 2).

At this point it is important to note that with the adequate combination of post-synthesis basic and acid treatments proposed in this work, it is possible to obtain mesoporous Theta-1 zeolites, with mesopore volumes up to 0.200 cm^3/g, in the range of those reported in the literature for samples obtained under similar desilication conditions [25, 30], but preserving more than 90% of their micropore volume. This was achieved by directly treating the alkaline treated zeolite in

its Na-form with an acid solution, either HCl or oxalic acid, which in a single step will remove the alkali cation and the amorphous extra-framework debris formed during the desilication. Moreover, the use of oxalic acid instead of HCl for directly removing Na^+ preserves the total Brønsted acid site density of the parent microporous zeolite and, additionally, this selective dealumination of the external surface of the crystals should have a positive effect on the quality of the diesel fuel produced, by decreasing the average branching degree of the oligomers, whose formation on the external surface will be reduced, according to previous results described in the literature [9, 25, 36].

3.1.2 Modified T1-25 samples obtained by NaOH treatments

Sample T1-25, with a starting Si/Al molar ratio of 25, has also been treated with NaOH solutions with the aim of generating mesoporosity. It must be taken into account that its aluminium content is higher and its crystal size is larger (see figure 4) than that of T1-50 and that this is expected to affect the effectiveness of the desilication treatment. As in the previous section, the study of the desilication conditions includes varying the NaOH concentration, desilication time and temperature. The effect of performing a dealumination of the sample prior to NaOH treatment has been also studied. The samples prepared, their physico-chemical and their acidic properties are given in tables 3 and 4, respectively. The acid –calcined- HT1-25 zeolite is included for comparison reasons.

Comparing the textural properties of HT1-25 and HT1-50 samples desilicated by the same preparation conditions, one can see that the treatment is less effective for the former. The mesopore volume of the final HT1-25 based samples (desilicated and converted into their acid form by any of the procedures proposed in this work) is lower than that of the samples obtained (by an equivalent procedure) when starting from HT1-50, and the loss of micropore volume is larger, unless the acid zeolite is obtained by direct acid treatment (-H and –OX samples). This can be due to the higher Al content of the parent sample, T1-25, which will limit the desilication degree, and thus the generation of mesoporosity, as well as to its larger crystal size (see figure 4). In any case, the results enclosed in table 3 clearly show that diffusion through the zeolite's structure is enhanced after desilication, as it is possible to obtain the N_2 adsorption isotherm on the treated samples, an analysis that was not possible for the parent HT1-25.

Figure 4 shows the TEM pictures for some of the desilicated HT1-25 based samples compared to that of the non-modified Theta-1 zeolite. The lower effectiveness of the desilication treatment when directly treating zeolite HT1-25, as compared to desilicating samples HT1-50, is also evidenced by the TEM images given in figure 4. In fact, if we compare the images corresponding to samples 0.2-HT1-50-85-30-A (figure 2-b) and 0.2-HT1-25-85-30-A (see

figure 4-b) the fragmentation is much more evident for the former. However, employing more severe NaOH desilication conditions (1.0 M solution) performed after pre-dealuminating sample HT1-25 results in an important fragmentation of the crystals (see figure 4-c, corresponding to sample 1.0-HCl-HT1-25-85-30-A), and in the highest mesopore volume of the T1-25 based samples studied in this work.

It is very important to note the significant increase in the total Brønsted acidity for all the desilicated HT1-25 based samples, as determined by pyridine adsorption (see table 4). This is due to the fact that the probe molecule is now able to access all the bridging acid hydroxyls, as can be seen from the spectra included in figure 3-b, whereas in the case of the acid HT1-25 obtained by calcination in static air of the parent ammonic sample, more than 40% of the total acid sites were not accessible to pyridine (Figure 3-b). This confirms that with the basic treatments we obtain a more accessible pore structure, which presents considerably lower restrictions to the diffusion of pyridine.

3.2 Catalytic behavior of modified Theta-1 for light olefin oligomerization

3.2.1   T1-50 based samples.

Figure 5 shows the propene conversion and selectivity to C_{5+} products obtained with the different desilicated HT1-50 based zeolites working at a contact time of 0.17 h. This contact time is considerably lower than that required for industrial operation, usually higher than 0.5 h in order to obtain complete olefin conversion [11, 37]. However, working at this lower contact time of 0.17 h enabled the performance of a comparative study of the different catalysts, their initial activity and also their deactivation rate, by means of reactions of 6-8 hours of time on stream.

The effect of the treatment temperature at a constant NaOH concentration of 0.2 M and a desilication time of 30 min is shown in figure 5a. The first thing to be noted is the increase in propene conversion obtained for all the desilicated zeolites, as compared to the parent T1-50. It can be seen that, when increasing the desilication treatment temperature, there seems to be a slight decrease in the initial olefin conversion, but the deactivation rate of the catalyst is considerably reduced, and the selectivity to diesel improves.

Figure 5-a shows that the decrease in catalyst deactivation rate for the desilicated mesoporous zeolites is very large in all cases and the stability with TOS seems to increase with the treatment temperature, presumably due to the increase in the mesopore volume (see table 1). However, a maximum in the selectivity to diesel is observed for the sample treated at 85ºC, and higher temperature desilication results in an observed decrease in the diesel fraction.

Figure 5-b shows the influence of the desilication time and of the NaOH concentration on propene oligomerization activity. The sample obtained by longer NaOH treatment (90 min)

deactivates slightly faster, at least during the first few hours. However, the main effect of increasing the treatment time is a lower selectivity to the desired diesel fraction. As in the case of the highest NaOH desilication temperature (sample 0.2-HT1-50-95-30) the mesopore volume of this sample is higher and the low diesel selectivity can be related to an excessive reduction of the diffusion path lengths of the primary products (gasoline range oligomers), that will exit the microporous structure before getting involved in secondary reactions leading to heavier diesel range oligomers.

Finally, the concentration of the basic solution has been varied from 0.2 M to 1.0 M, while maintaining the temperature at 85ºC, and the duration at 30 min. The results, presented also in figure 5-b, show that using the higher base concentration is beneficial for the catalyst life, as deactivation rate seems to decrease for sample 1.0-HBP2-85-30-A. However, the more severe treatment results, again, in a decrease in diesel selectivity.

The catalytic results obtained up to now show that when the severity of the desilication treatment is increased the deactivation rate is reduced and catalyst lifetime is improved, presumably due to increasing the mesoporosity generated and shortening diffusion path lengths. However, the selectivity to diesel reaches a maximum value for intermediate mesopore volumes and it starts to decrease if the mesoporosity is further increased. So it can be concluded that the optimum mesoporosity is the one that enables a compromise between catalyst life and selectivity to the desired product fraction. At this point it is important to remark that the formation of products in the diesel range (C_{10}-C_{24}) when oligomerizing propene implies at least four consecutive propene additions to take place, and if the formation of mesopores goes beyond a certain extent (mesopore volumes around 0.1 cm^3/g), the diffusion of the primary products (belonging to the naphtha fraction) will be favoured, before being consumed in consecutive oligomerization steps to heavier diesel range products. Similar results were obtained in a previous study based on modified (mesoporous) ZSM-5 catalysts for olefin oligomerization [12].

Alternative procedures for obtaining the acid form of desilicated T1-50.

The last step in our final catalyst preparation comprised a conventional ion exchange procedure with NH_4NO_3, in order to remove the Na^+ present in exchange positions and to recover Brønsted acidity. However, if this ion exchange is followed by calcination in static air at 500ºC, extra-framework aluminium species may be formed. An interesting alternative is treating the Na-zeolite directly with an acid solution. In addition to Na^+ removal, this treatment would most likely also eliminate extra-framework debris [28] and, depending on the experimental conditions, some framework dealumination could occur as well. Moreover, if the acid treatment is performed with a bulky reagent, such as oxalic acid, this can be selective for preferentially

removing the aluminium located close to the external surface, as was shown in the previous section. In this section we compare the catalytic behaviour of the T1-50 based samples obtained by means of the standard ion exchange procedure of the Na^+ sample obtained with NaOH 0.2 M, at 85ºC for 30 min with those prepared by direct acid treatment of the desilicated Na-zeolite. In a first approach, oxalic acid has been used (sample 0.2-HT1-50-85-30-OX). In a previous work, this direct selectivation proved to be beneficial in the case of desilicated ZSM-5 based catalysts when used for oligomerization of light olefins [12] as the catalyst obtained in this way showed improved activity and selectivity to diesel coupled with lower deactivation rate. Here, a non-selective acid washing with a 0.5 M HCl solution is also included for comparison purposes (0.2-HT1-50-85-30-H).

Figure 6 shows that the activity of the desilicated sample selectively dealuminated with oxalic acid is above 92% propene conversion for more than 9 hours TOS. This is a substantial improvement as compared to the non-selectivated sample (0.2-HT1-50-85-30-A). The selectivity to diesel is reduced, although it is still considerably larger than that of the parent T1-50 zeolite, and its quality is expected to improve due to the removal of external acid sites [9, 36]. The non-selective HCl treatment, although not as efficient as the oxalic acid one, also results in a better stability towards deactivation than the ammonium exchanged catalyst, but with a lower selectivity to diesel.

The results presented up to now show that the stability towards deactivation with TOS of monodimensional Theta-1 based catalyst can be largely improved when a secondary mesopore system is generated under controlled conditions, followed by selective dealumination of the sample using the appropriate procedure. The slight decrease in the selectivity to diesel should not be relevant when working under more realistic conditions, e.g., at higher contact times. We have to remark here that the contact time used for these comparative experiments is rather low, 0.17 h, in order to see differences among the different catalysts during 6-8 h TOS tests, and that at higher contact times (0.5-10 h), more representative of industrial operation the formation of heavier oligomers, belonging to the diesel fraction, will be favoured [11].

3.2.2   T1-25 based samples.

As in the case of T1-50, the different desilication process variables have been studied individually for T1-25. When varying the basic treatment temperature, figure 7-a shows that both, the initial activity and the selectivity to diesel achieve their maximum values when the treatment is performed at 85ºC. When the desilication is carried out at low temperatures, e.g. 45ºC, there is no effect on the catalytic behaviour as compared to the parent sample, whereas the improvement obtained when desilicating at 85ºC is very noticeable. The sample desilicated at

the highest temperature studied, 95ºC, has slightly lower initial activity and selectivity to diesel than sample 0.2-HT1-25-85-30-A, but a lower deactivation rate.

When the duration of the desilication treatment was increased from 30 to 90 minutes the sample obtained presents a lower initial activity and a lower selectivity to diesel (see figure 7-b). As in the case of T1-50, it is likely that both activity and diesel selectivity will reach a maximum for an optimized desilication treatment. If the severity, and therefore also the mesopore volume, is further increased, the benefits due to better diffusion will be lost due to a lack of shape selectivity.

Desilication of dealuminated T1-25.

In order to improve the efficiency of the desilication treatment, sample T1-25 was dealuminated with a concentrated HCl solution in a first step, followed by desilication performed at 85ºC for 30 minutes using two different NaOH concentrations, 0.2 and 1.0 M. Results in figure 8 show that the acid pre-dealumination step produces catalysts more stable towards deactivation. This can be related to higher mesopore volume of these samples compared to those obtained by direct desilication of HT1-25, as can be seen in table 3. However, we can see that when mesoporosity is increased beyond a certain point (see sample 1.0-HCl-HT1-25-85-30-A), selectivity to diesel starts to decrease. In any case, the improvement in propene oligomerization activity obtained with the three desilicated samples as compared to the parent T1-25 is significantly large (see figure 8).

Selective dealumination of desilicated T1-25.

Figure 9 shows that, as in the case of T1-50, the selective dealumination with oxalic acid of desilicated HT1-25 based samples results in a catalyst with an improved catalyst life, with a lower deactivation rate than the corresponding ammonium exchanged zeolites. This occurs independently of the conditions employed for the previous desilication procedure. Moreover, in the case of the HT1-25 based samples, there is no penalty in the selectivity to diesel when the conventional ammonium exchange is substituted by the oxalic acid treatment. The basic treatment at 95ºC results in a larger increase in the mesopore volume than at 85ºC and this difference is maintained after the treatment with oxalic acid. This may be the reason for a slightly lower selectivity to diesel, but also for the lower deactivation rate of the catalysts, especially after selectivation. Thus, the best catalytic results for this series of catalysts are those corresponding to sample 0.2-HT1-25-95-30-OX, which was obtained by selective dealumination with oxalic acid of HT1-25 desilicated by means of a 0.2 M NaOH solution for 30 minutes at 95ºC. Again we would like to note that, although the study presented here is performed at a contact time of 0.17 h, performing the oligomerization reaction at higher contact

times, closer to industrial operation, will improve the process in terms of olefin conversion and also selectivity to the desired diesel fraction [11].

CONCLUSIONS.

Modification of mono-directional medium pore Theta-1 (TON) zeolites by means of an optimized combination of basic desilication and selective oxalic acid treatments has led to enhanced mesoporous zeolites with reduced diffusion path length and improved accessibility to the active sites. This has been achieved with almost complete preservation of Brønsted acid site density and micropore volume, thus maintaining the shape selective properties of the 10R, 1D structure, which are necessary for producing a high quality diesel fuel mainly formed by linear or mono-methyl-branched oligomers. It has been shown that the optimum combination of post-synthesis treatment conditions has to be adapted according to the physico-chemical properties of the parent zeolite.

Increasing the mesoporosity of Theta-1 zeolites by desilication results in all cases (independent of the desilication degree) in an important increase in initial activity and especially in the catalyst lifetime, as the deactivation rate is drastically reduced. However, the selectivity to diesel goes through a maximum with respect to the mesopore volume generated. Up to a certain mesopore volume, the effect is beneficial and diesel selectivity increases with the mesoporosity. If desilication is pushed too far, the diffusion path lengths will be too short, and the products formed in the first oligomerization stage (dimers, trimers) will diffuse out of the zeolite structure before getting involved in further reactions that would led to the production of larger diesel range olefins.

The catalysts prepared by direct removal of Na^+ cations after desilication by acid treatments have shown to be more active and more stable towards deactivation than those prepared by ammonium exchange followed by calcination. Among the acid treatments, the bulkier oxalic acid treatment gives the best results, presumably due to a larger preservation of micropore volume and Brønsted acid site density.

When starting from Theta-1 with lower Si/Al ratios, performing an acid dealumination step before the basic desilication results in catalysts with improved stability towards deactivation with TOS.

Acknowledgments

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Table 1: Desilicated T150 samples. Physico-chemical properties.

Sample	Si/Al (ICP)	Si/Al (XPS)	BET (m^2/g)	S_{Micro} (m^2/g)	S_{Meso} (m^2/g)	V_{Micro} (cm^3/g)	V_{Meso} (cm^3/g)	Y(%)[b]
T1-50 (NH$_4^+$)	50	34	228	199	40	0.095	0.084	---
H-T1-50	51	n.d.[a]	225	192	41	0.100	0.089	---
0.2- HT1-50-65-30-A	38	n.d.	238	189	37	0.093	0.058	92
0.2- HT1-50-85-30-A	35	16	253	180	66	0.089	0.107	93
0.2- HT1-50-95-30-A	36	n.d.	246	179	72	0.087	0.200	79
0.2- HT1-50-85-90-A	32	n.d.	258	183	64	0.090	0.127	76
1.0- HT1-50-85-30-A	29	n.d.	275	210	34	0.101	0.159	25
0.2- HT1-50-85-30-H	51	n.d.	212	147	71	0.069	0.111	96
0.2- HT1-50-85-30-OX	49	69	264	93	72	0.092	0.117	93

[a] *n.d.: not determined*

[b] *Yield (%) = g desilicated sample obtained x 100/g parent sample treated.*

Table 2: Desilicated T1-50 based samples. Acidity as determined by FT-IR combined with pyridine adsorption.

Catalyst	Acidity (mmol pyridine/g)					
	Brønsted sites			Lewis sites		
	T=150ºC	T=250ºC	T=350ºC	T=150ºC	T=250ºC	T=350ºC
T1-50 (NH4$^+$)	0.225	0.203	0.107	0.024	0.023	0.018
HT1-50-CM	0.174	0.159	0.062	0.017	0.016	0.007
0.2- HT1-50-85-30-A	0.220	0.169	0.102	0.031	0.026	0.023
0.2- HT1-50-85-30-OX	0.240	0.240	0.111	0.011	0.011	0.010
0.2- HT1-50-85-30-H	0.221	0.184	0.133	0.017	0.015	0.011
1.0- HT1-50-85-30-A	0.189	0.163	0.112	0.025	0.024	0.015

Table 3: Desilicated T1BP3 samples. Physico-chemical properties.

Sample	Si/Al	BET (m2/g)	S_{Micro} (m2/g)	S_{Meso} (m2/g)	V_{Micro} (cm3/g)	V_{Meso} (cm3/g)	Y (%)
T1-25	25	Diffusional problems					--
HT1-25	25	Diffusional problems					--
0.2-HT1-25-65-30-A	19	202	162	40	0.079	0.046	93.7
0.2-HT1-25-85-30-A	18	209	145	53	0.071	0.067	88.5
0.2-HT1-25-95-30-A	21	229	175	67	0.084	0.087	52.4
0.2-HT1-25-85-90-A	17	216	139	65	0.068	0.091	n.d. [a]
0.2-HT1-25-85-30-H	31	261	200	71.4	0.098	0.138	n.d.
0.2-HT1-25-85-30-OX	28	254	208	64	0.100	0.079	89.15
0.2-HT1-25-95-30-OX	29	255	200	72	0.096	0.096	44.7
0.2-HCl-HT1-25-85-30-A	20	231	176	68	0.084	0.092	83.9
1.0-HCl-HT1-25-85-30-A	15	249	186	44	0.089	0.145	72.6

[a] *n.d.: not determined*

[b] *Yield (%) = g desilicated sample obtained x 100/g parent sample treated.*

Table 4: Desilicated HT1-25samples. Acidity as determined by FT-IR combined with pyridine adsorption.

| Catalyst | Acidity (mmol pyridine/g) | | | | | |
| | Brønsted sites | | | Lewis sites | | |
	T=150ºC	T=250ºC	T=350ºC	T=150ºC	T=250ºC	T=350ºC
T1-25 (NH4$^+$)	0.160	0.158	0.064	0.022	0.021	0.015
HT1-25-CM	0.153	0.145	0.112	0.027	0.025	0.025
0.2- HT1-25-85-30-A	0.248	0.236	0.180	0.023	0.023	0.018
0.2- HT1-25-85-30-OX	0.2971	0.295	0.194	0.020	0.020	0.017
0.2- HT1-25-85-30-H	0.288	0.265	0.184	0.017	0.017	0.013
0.2- HT1-25-95-30-A	0.262	0.213	0.191	0.035	0.034	0.034
0.2- HT1-25-95-30-OX	0.296	0.281	0.236	0.022	0.020	0.020
0.2-HCl- HT1-25-85-30-A	0.260	0.257	0.152	0.038	0.022	0.015

Figure 1: TON framework type, viewed along [001]. Si and Al atoms in tetrahedral positions painted in yellow, bridging oxygens in red.

Figure 2: TEM pictures for parent HT1-50 (calcined) (a); 0.2-HT1-50-85-30-A (b); 0.2-HT1-50-85-90-A (c, d); 0.2-HT1-50-85-30-OX (e), 1.0-HT1-50-85-30-A (f). Scale bar in all pictures is 200 nm.

Figure 3: FT-IR spectra in the –OH region after activation at 400ºC under vacuum (solid lines) and after adsorption of pyridine and desorption at 250ºC (dotted lines) for parent, calcined and desilicated T1-50 based samples (a), and for parent, calcined and desilicated T1-25 based amples (b).

Figure 4: TEM pictures for parent T1-25 (a); 0.2-HT1-25-85-30-A (b); 1.0-HCl-HT1-25-85-30-A (c). Scale bar in all pictures is 500 nm.

Figure 5: Propene conversion vs. TOS and selectivity to the different fractions during the first 3 hours of reaction for the desilicated HT1-50samples compared with the parent T1-50. T=200ºC, P=40 bar, τ=0.17h. a) Effect of treatment temperature; b) Effect of treatment time and NaOH concentration.

Figure 6: Propene conversion vs. TOS and selectivity to the different fractions during the first 3 hours of reaction for the desilicated T1-50 samples compared with parent T1-50. Effect of selective dealumination with oxalic acid. T=200ºC, P=40 bar, τ=0.17h.

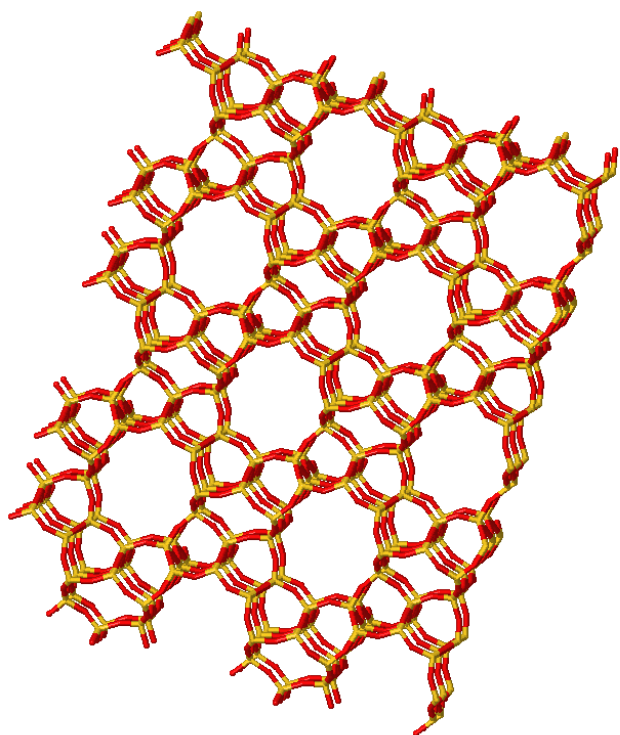Figure 7: Propene conversion vs. TOS and selectivity to the different fractions during the first 3 hours of reaction for the desilicated T1-25 samples compared with parent T1-25. T=200ºC, P=40 bar, τ=0.17h. a) Effect of desilication temperature; b) Effect of treatment time.

Figure 8: Propene conversion vs. TOS and selectivity to the different fractions during the first 3 hours of reaction for the desilicated HT1-25 samples compared with parent HT1-25. T=200ºC, P=40 bar, τ=0.17h. Effect of previous dealumination of the zeolite.

Figure 9: Propene conversion vs. TOS and selectivity to the different fractions during the first 3 hours of reaction for the desilicated T1-25 samples compared with parent T1-25. Effect of selective dealumination with oxalic acid. T=200ºC, P=40 bar, τ=0.17h.
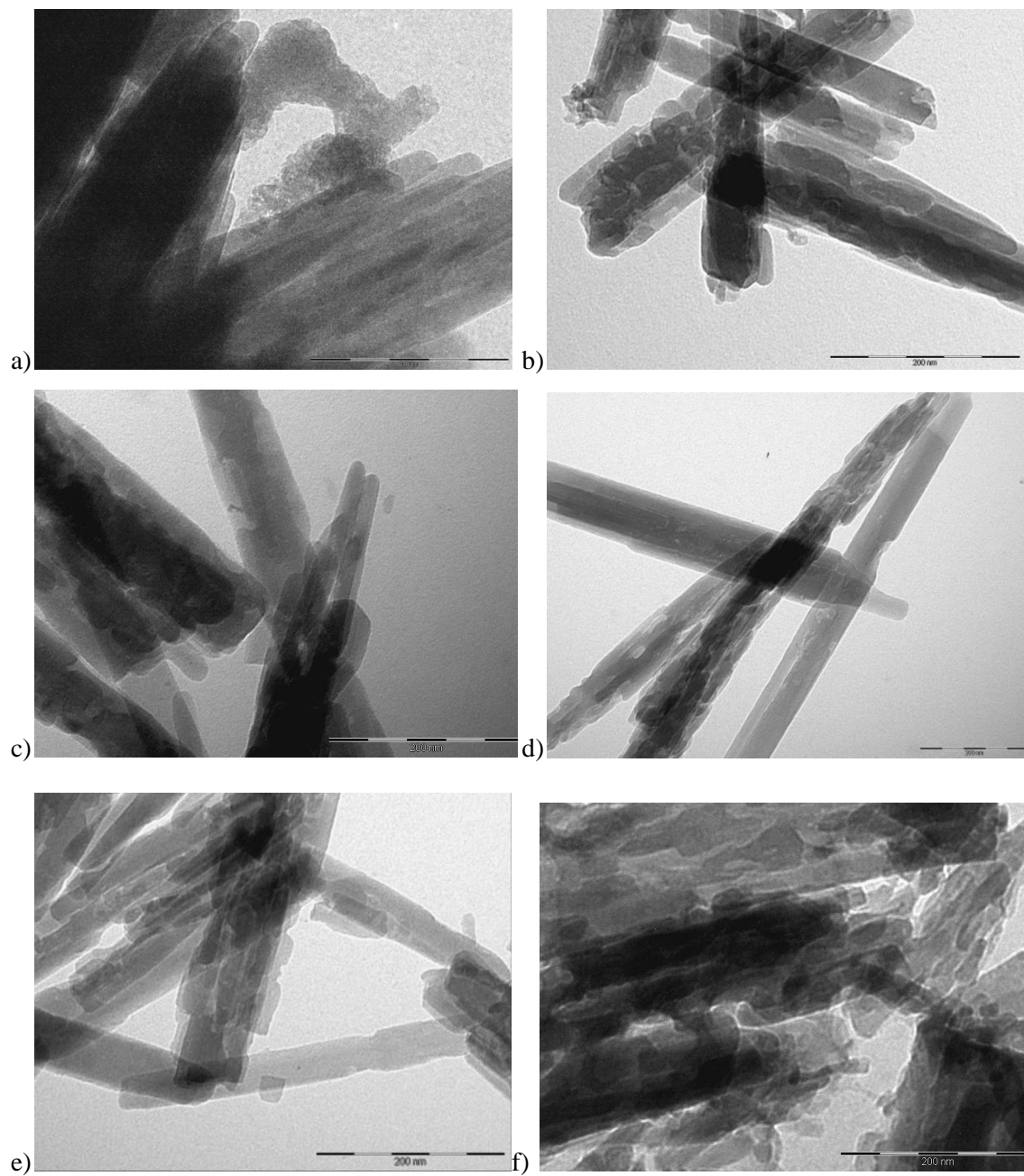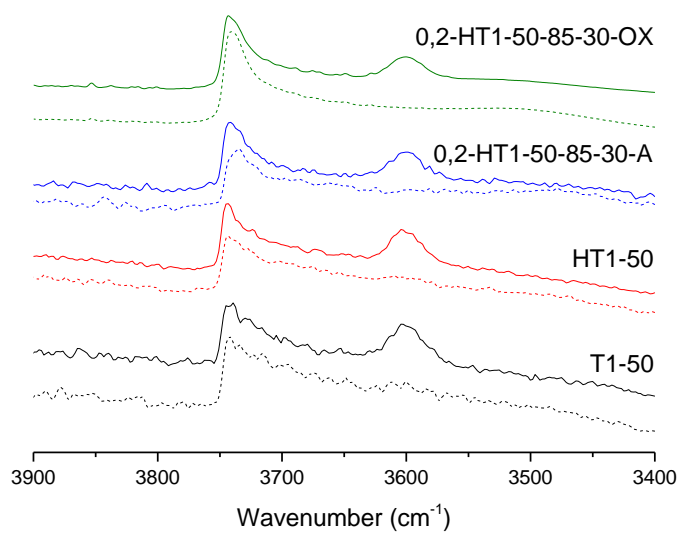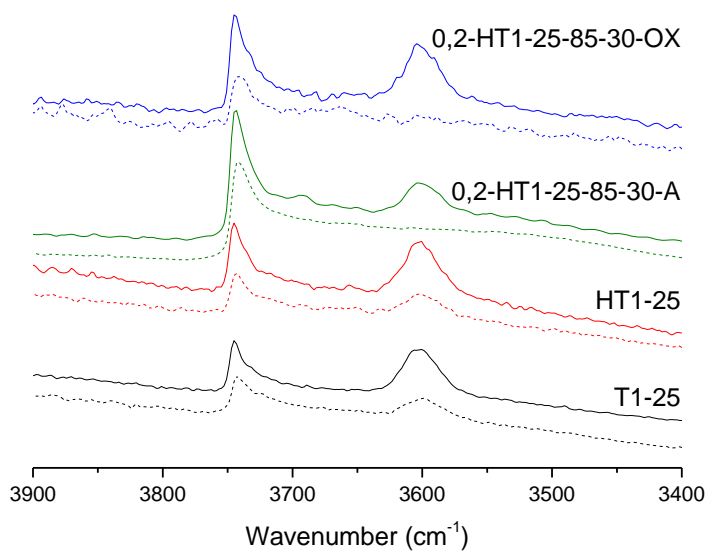
FIGURE 1

FIGURE 2

a)

b)

c)

d)

e)

f)

FIGURE 3

a)

b)

FIGURE 4

a)

b)

c)

FIGURE 5

a)

b)

FIGURE 6

FIGURE 7

a)

b)

FIGURE 8

FIGURE 9