



Revista Politécnica

ISSN: 1900-2351

ISSN: 2256-5353

rpolitecnica@elpoli.edu.co

Politécnico Colombiano Jaime Isaza Cadavid
Colombia

Imbachi-Gamba, Carlos Fernando; Villa Holguín, Aída Luz
INFLUENCE OF DESILICATION CONDITIONS ON THE SYNTHESIS OF HIERARCHICAL ZEOLITE Y
Revista Politécnica, vol. 15, no. 28, 2019, -June, pp. 85-96
Politécnico Colombiano Jaime Isaza Cadavid
Colombia

DOI: <https://doi.org/10.33571/rpolitec.v15n28a8>

Available in: <https://www.redalyc.org/articulo.oa?id=607866567009>

- How to cite
- Complete issue
- More information about this article
- Journal's webpage in [redalyc.org](https://www.redalyc.org)

redalyc.org

Scientific Information System Redalyc
Network of Scientific Journals from Latin America and the Caribbean, Spain and
Portugal

Project academic non-profit, developed under the open access initiative

INFLUENCE OF DESILICATION CONDITIONS ON THE SYNTHESIS OF HIERARCHICAL ZEOLITE Y

Carlos Fernando Imbachi-Gamba¹, Aída Luz Villa Holguín^{2*}

¹Chemical Engineer. Chemical Science Master Student. Environmental Catalysis Research Group. Medellín-Colombia. carlos.imbachi@udea.edu.co

²Biological Sciences, PhD. Universidad de Antioquia Professor. Environmental Catalysis Research Group. Medellín-Colombia. aida.villa@udea.edu.co

ABSTRACT

Hierarchical zeolites were synthesized by two methodologies, following desilication procedures of commercial zeolites. Starting from USY zeolite (Zeolyst CBV720, Si/Al=15), the effect of the amount of CTAB in the desilication media and the hydrothermal treatment time on the synthesized materials were analyzed. The results showed that the surfactant amount has a higher influence on relative crystallinity (%RC) and textural properties of the materials than synthesis time. All the samples showed a lower BET surface area compared with the starting zeolite, although mesopore surface area increased from 210.33 to 467.30 m²/g in the case of Z720-75 sample. In the case of USY zeolite with Si/Al=2.6 (Zeolyst CBV500), a previous dealumination with H₄EDTA and an acid washing with Na₂H₂EDTA steps were included. It was found that the micropore and the mesopore surface areas increased 13.96% and 11.23%, respectively, compared with the parent zeolite; furthermore, the %RC was 99% after treatment procedures.

Key words: Desilication, CTAB, NH₄OH, Hydrothermal treatment, Hierarchical zeolite.

Recibido: 03 de Marzo de 2019. Aceptado: 17 de Mayo de 2019

Received: March 03, 2019. Accepted: May 17, 2019

INFLUENCIA DE LAS CONDICIONES DE DESILICACIÓN EN LA SÍNTESIS DE LA ZEOLITA JERÁRQUICA Y

ABSTRACT

Se sintetizaron zeolitas jerárquicas por dos metodologías, siguiendo procedimientos de desilicación de zeolitas comerciales. Partiendo de la zeolita USY (Zeolyst CBV720 con Si/Al = 15), el efecto de la cantidad de CTAB en el medio de desilicación y el tiempo del tratamiento hidrotérmico fueron analizados. Los resultados mostraron que la influencia de la cantidad de surfactante en la cristalinidad relativa (%RC) y las propiedades texturales de los materiales fue mayor que el efecto del tiempo. Todas las muestras mostraron una menor área superficial BET comparada con el material de partida, pero el área superficial mesoporosa tuvo un incremento de 210.33 a 467.30 m²/g en el caso de la muestra Z720-75. Para la desilicación de la zeolita USY con Si/Al = 2.6 (Zeolyst CBV500), se incluyó una etapa previa de desaluminación con H₄EDTA y un lavado ácido posterior con Na₂H₂EDTA. Se encontró que el área superficial microporosa y el área superficial mesoporosa aumentaron 13.96% y 11.23%, respectivamente, comparado con el material comercial; además, el %RC se conservó en un 99% después de los tratamientos.

Palabras clave: Desilicación, CTAB, NH₄OH, Tratamiento hidrotérmico, Zeolita jerárquica.

Cómo citar este artículo: C. Imbachi, A. Villa, "Influence of desilication conditions on the synthesis of hierarchical zeolite Y", Revista Politécnica, vol. 15, no.28 pp.8596, 2019. DOI: <https://doi.org/10.33571/rpolitec.v15n28a8>

1. INTRODUCTION

Zeolites are widely used in catalytic processes due to their acidity, stability and microporous channels [1] [2]. One of their main applications is in the fluid catalytic cracking process [3] in the petroleum refining industry in which the heavy hydrocarbons (chains with more than 20 carbon atoms) are reduced to lighter compounds, in the range of gasoline and diesel [4] [5]. However, heavy hydrocarbons have diffusional transport restrictions into the porous of zeolites, since the molecular size of the majority of these hydrocarbons is higher than the zeolite channels size [6]. The low diffusion of the molecules into the catalyst is responsible of the production of undesired compounds like coke, a carbonaceous macromolecule that deactivates the catalyst [7] [8] [9].

One of the solutions to this problem is the generation of mesoporous channels in the zeolite [1] [10], using post-synthesis treatments as dealumination (using acid treatments [11] or steaming [12]) and desilication [13] [14] (using alkaline treatments), treatments in which atoms of aluminum or silicon are leached from the framework, respectively [15]. In the case of the dealumination process, some acids as nitric [16], citric [17] and oxalic acid [11] have been tested. While mineral acids are stronger and dissociate the zeolites, the best crystalline, textural and catalytic properties have been obtained with lactic [18] and citric [19] acids, due to their bifunctional nature: leaching and chelating nature with Al [20].

The desilication process is mainly carried out with sodium [13] [21] or ammonia hydroxide [22], at atmospheric pressure or under hydrothermal conditions at autogenous pressure, with or without the presence of directing agents (SDA) [23] that protect the structure and avoid the collapse of the framework during the treatments [24] [25]. Then, among the parameters that can affect the synthesis are the amount of SDA, temperature and the hydrothermal treatment time [4] [26].

Sodium hydroxide is stronger than ammonia hydroxide; furthermore, NaOH dissociates immediately in the aqueous media, while NH_4OH forms an equilibrium and its dissociation occurs slowly, giving a controlled desilication of zeolite [27]. Furthermore, if NaOH is used for the treatments, an ion exchange step is necessary later to reactivate the

catalyst [28]. Then, the use of ammonia hydroxide in the production of hierarchical zeolites using desilication process, is preferred instead of NaOH.

The Si extraction is efficient in zeolites with a Si/Al ratio higher than 25 [28]; otherwise, acid and alkaline treatments are necessary to obtain mesoporous in zeolites [29]. Verboekend et al. [30] synthesized hierarchical zeolites from a zeolite Y with a Si/Al ratio of 2.6. The authors included acid treatment with H_4EDTA , alkaline procedure with NaOH and washing with $\text{Na}_2\text{H}_2\text{EDTA}$ to clean the surface of the material from debris generated in the other steps and ion exchange step to remove sodium cations.

On the other hand, Javier García et al. [23] synthesized a hierarchical zeolite Y using NH_4OH and cetyltrimethylammonium bromide (CTAB) in a hydrothermal treatment for the desilication procedure, starting from a zeolite with Si/Al = 15 (0.84 g CTAB/g NH_4OH , 10 h of hydrothermal treatment, 150°C). High mesopore surface area was obtained and crystallinity of the material was maintained with this procedure. Although the mesoporous surface area increased, the effect of the treatment parameters on the crystalline and textural properties was not specified. In this research, the effect of the amount of CTAB and the hydrothermal treatment time on the desilication process of a zeolite with a Si/Al = 15 (CBV720, from Zeolyst), based on the synthesis reported by Javier García et al. [23] is analyzed.

In a complementary study, a zeolite with a Si/Al lower than 15 was dealuminated, desilicated and acid washed, and the obtained material was compared with the material reported by D. Verboekend, et al. [30]. The desilication process was carried out with the amount of CTAB and hydrothermal treatment time selected from results obtained with CBV720 material. H_4EDTA and $\text{Na}_2\text{H}_2\text{EDTA}$ were used for the dealumination and acid washing steps, respectively. The objective was to analyze the effect of this desilication step with NH_4OH assisted by CTAB in a zeolite with a Si/Al < 15 avoiding the use of NaOH.

2. METHODOLOGY

2.1. Reagents

The parent zeolites used in this research were zeolite Y with Si/Al = 2.6 (CBV500) and zeolite Y with a Si/Al

= 15 (CBV720), both purchased to Zeolyst International. Ammonia hydroxide solution (NH_4OH , 28-30%) and ethylenediaminetetraacetic acid (H_4EDTA , 99.8%) from Merck, ethylenediaminetetraacetic disodic acid ($\text{Na}_2\text{H}_2\text{EDTA}$, 99%) from Sigma-Aldrich, and cetyltrimethylammonium bromide (CTAB, >97%) from J.T. Baker. All the reagents were used as purchased.

2.2. Synthesis of materials

2.2.1. Effect of the amount of surfactant in the desilication process

For the analysis of the influence of the amount of surfactant on the desilication process, the synthesis proposed by Javier García et al. [23] was followed. Different amounts of surfactant were mixed with 64 mL of ammonia hydroxide solution 0.37 M in a mass ratio of 0 to 1.25 of CTAB/ NH_4OH , then 1 g of the parent zeolite Y (CBV720) was dispersed in the solution and mixed at room temperature for 20 minutes. Then, the dispersion was autoclaved for the hydrothermal treatment 10 h at 150°C. After the treatment, the samples were washed until achieving the pH of deionized water, filtered and dried at 80°C for 14 h. Finally, the calcination of samples was made at 550°C with a temperature rate of 5°C/min, 2 h under nitrogen atmosphere and then 2 h with dry air.

The samples were named Z720-X, where X corresponds to CTBA/ NH_4OH mass ratio (0, 25, 35, 75, 100 and 125) in the aqueous media used in the desilication step. The amounts of CTAB used in the procedure was higher than the critic micellar concentration ($\text{CMC} = 9.2 \times 10^{-4} \text{ M}$) of CTAB [31] [32], to guarantee the formation of micelles in the media.

2.2.2. Effect of the hydrothermal treatment time on the desilication process

To analyze the influence of the hydrothermal treatment time on the desilication process, the synthesis reported by Javier García et al. [23] was followed. A solution was prepared with 0.2075 g of CTAB and 64 mL of ammonia hydroxide solution 0.37 M, then 1 g of commercial zeolite Y (CBV720) was added and the mixing continued for 20 minutes at room temperature. Then, the dispersion was autoclaved for the hydrothermal treatment for 3, 5, 10 and 20 h at 150°C.

After the treatment, the samples were washed until pH of deionized water was achieved, filtered and dried at 80°C for 14 h. Finally, the calcination of the samples was made at 550°C with a temperature rate of 5°C/min, 2 h with nitrogen and then 2 h with dry air. The samples were named as Z720-YH, with Y the hydrothermal treatment time.

2.2.3. Effect of the desilication agent type on the hierarchical zeolite synthesis

For the modification of the zeolite Y with $\text{Si}/\text{Al} = 2.6$, the commercial zeolite CBV500 was dealuminated and acid washed following the procedure reported by D. Veboekend et al. [30] and desilicated according to Javier García et al. [23], with the amount of CTAB and hydrothermal treatment time found with the samples Z720-X and Z720-YH. First, 6.7 g of zeolite Y was added to H_4EDTA 0.15 M at 100°C for 6 h. The alkaline treatment was carried out using a ratio of 1 g zeolite to 64 mL of NH_4OH 0.37 M, CTAB was added in this step in a ratio of 0.25 g CTAB/g NH_4OH ; then, the suspension was stirred for 20 min at room temperature. After that, the suspension was autoclaved for hydrothermal treatment at 150°C for 10 h. The solid was filtered and washed until pH of deionized water. Finally, the acid washing of the zeolite was carried out at 100°C using $\text{Na}_2\text{H}_2\text{EDTA}$ 0.11 M for 6 h in a ratio of 6.7 g of zeolite to 100 mL of solution.

Between all the steps, the material was washed and dried at 65°C in the case of acid treatments and at 80°C for the alkaline treatment. The powder was calcined at 550°C for 5 h twice with a heating rate of 5°C/min under static air. The modified sample was named as Z500-VG.

2.3. Characterization of samples

X-Ray diffraction (XRD) analysis was carried out using a Panalytical Empyrean X-Ray diffractometer with a $\text{Co K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) generated at 40 kV and 40 mA. The 2θ was scanned from 5 to 55°. The relative crystallinity (%RC) was calculated for all the samples following the ASTM D3906-03 [33], using Equation (1) and the PANalytical X'Pert Highscore Plus software. The peaks selected for the analysis were at $2\theta = 22^\circ$, 24° , 28° and 32° that correspond to the crystallographic planes of (544), (440), (533) and (642), respectively.

$$\%RC = (100) \frac{(\text{sum of area under the curve of the peaks})_{\text{sample}}}{(\text{sum of area under the curve of the peaks})_{\text{parent}}} \quad (1)$$

With the N_2 adsorption/desorption isotherms the textural properties of the samples were obtained, using a Micromeritics ASAP 2020 Plus equipment. With the t-plot method the micropore surface area and volume were calculated; the mesopore surface area and volume were obtained with the BJH correlation and the surface area with the BET method, using the adsorption branch of the isotherms. With this information, the hierarchical factor (HF) was calculated; the HF brings information about the relation between the destruction of microporous and the generation of mesoporous. Zheng et al. [34] proposed a way to calculate that factor including textural properties obtained from the nitrogen physisorption analysis, Equation (2).

$$HF = \frac{V_{\text{micro}} S_{\text{meso}}}{V_{\text{meso}} S_{\text{BET}}} \quad (2)$$

Where micropore volume (V_{micro}), specific surface area of the mesopores (S_{meso}), mesopore volume (V_{meso}) and the BET surface area (S_{BET}) are related. Transmission electron microscopy (TEM) was carried out in a Tecnai F20 Super Twin TMP equipment using an accelerating voltage of 200 kV. The samples were added to a mixture of water and ethanol and dispersed for 10 minutes using an ultrasonic equipment; a drop of the suspension was placed in the Cu grill.

3. RESULTS AND ANALYSIS

3.1. Effect of the amount of SDA on the desilication process

In this step, different amounts of CTAB were added to the alkaline solution, previous to the desilication of the zeolite Y CBV720. Fig 1 shows XRD pattern of Z720-X samples. When a surfactant was not used in the synthesis (Z720-0), the crystalline phase of the zeolite was completely lost. However, when the surfactant was used in the desilication process (samples Z720-25 to Z720-125), the typical peaks of zeolite Y were obtained; the lower intensity of the peaks of the desilicated samples compared with the parent zeolite (CBV720), it is related with the desilication of the sample, which partly destroys the crystalline phase of the samples.

Fig 2 shows that there is an inverse relation between the CTAB/ NH_4OH mass ratio and the %RC; an increase in the amount of CTAB reduces the %RC of

the zeolite. This could be owing to the increase of the amount of micelles formed in the aqueous media. Consequently, an interaction of CTAB exists with the framework of the zeolite that is partially dissolved at an alkaline media [17] [23].

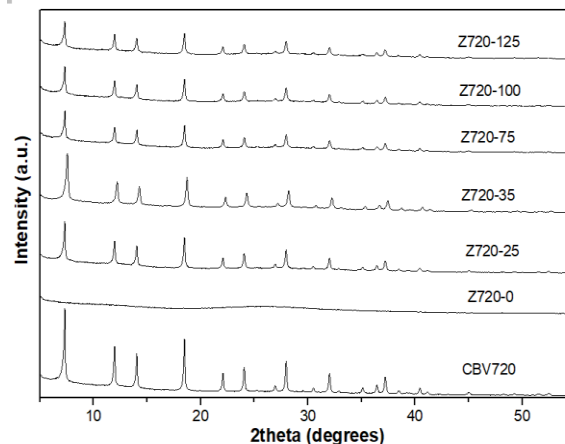


Fig 1. XRD of Z720-X samples and the parent zeolite (CBV720).

The interaction between the micelles and the framework is good with low amount of surfactant, but when it increases, the recrystallization of the framework is altered and the correct rearrangement of the atoms is disturbed, generating amorphicity in the material. When the CTAB/ NH_4OH mass ratio increases from 0.25 to 1.25, a decrease of 20% is observed in the %RC.

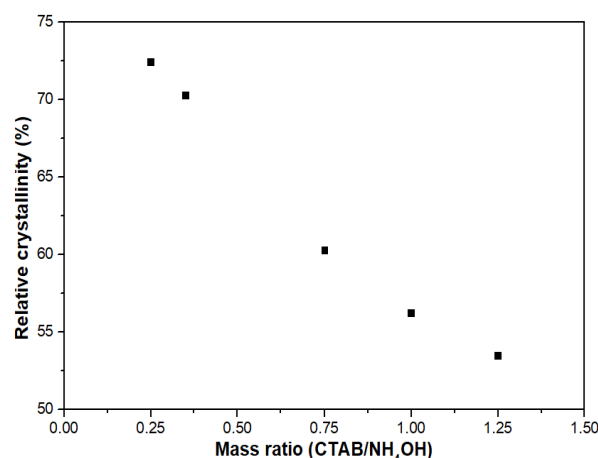


Fig 2. Effect of CTBA/ NH_4OH mass ratio on relative crystallinity.

Table 1. Textural properties of the samples (Z720-X) and the commercial (CBV720).

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_p (nm)	HF (-)
CBV720	770.44	560.11	210.33	0.494	0.232	0.262	2.56	0.24
Z720-25	621.38	353.09	268.29	0.446	0.148	0.298	2.87	0.22
Z720-35	663.21	299.98	363.22	0.455	0.127	0.328	2.74	0.21
Z720-75	730.28	262.98	467.30	0.504	0.112	0.391	2.76	0.18
Z720-100	715.55	266.88	448.68	0.498	0.114	0.384	2.78	0.19
Z720-125	698.51	257.79	440.72	0.479	0.110	0.369	2.75	0.19

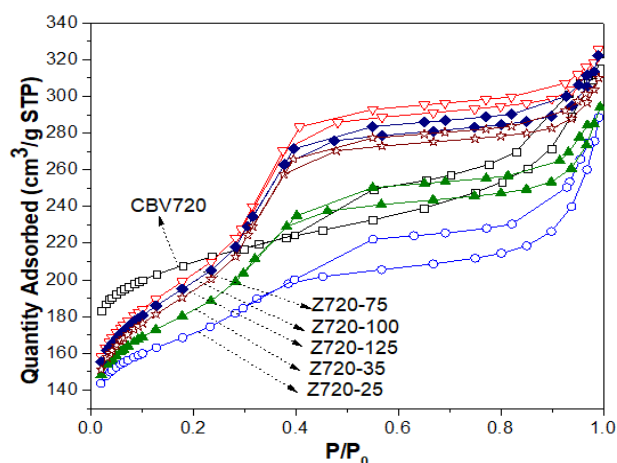


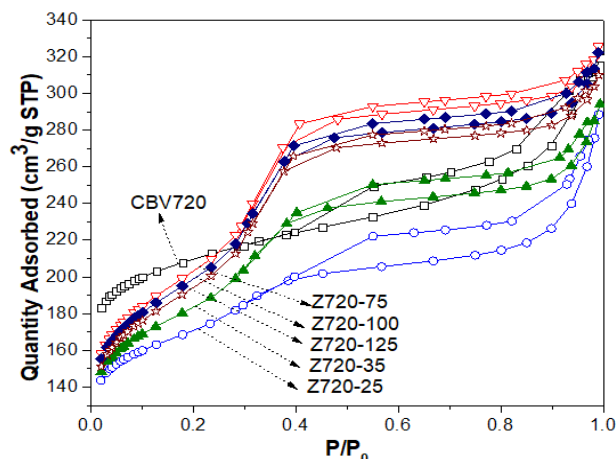
Fig 3 shows that the modified samples have a type IV isotherm, which means that the material, including the parent zeolite, have mesoporous channels in their structures. The value of P/P_0 in which the hysteresis loops starts suggests that the modified samples have a higher average pore diameter than the CBV720 sample.

In the same way, the hysteresis loops have a type II hysteresis, which is related with interconnected channels, an important characteristic of the materials for a good diffusion of molecules through the channels [35].

Table 1 shows the textural properties of the modified (Z720-X) and parent zeolite (CBV720). Specific surface micropore area decreases when the amount of CTAB increases in the desilication step; the HF values have a slight variations. J. van Alest et al. [27] obtained similar results, they reported a high $V_{\text{meso}}/V_{\text{micro}}$ values without change in the HF value. Therefore, the HF does not give a representative information about all textural properties variation after the procedures used for obtaining hierarchical zeolites.

The maximum values of BET area and specific surface mesopore area were obtained with Z720-75 sample. The increment can be explained due to the amount of micelles in the media, related with the amount of CTAB added in the desilication step. The hydrolysis of the Si-O-Si bonds in the zeolite drives to the rearrangement of its atoms [17] [23].

Increasing the amount of micelles formed in the aqueous media, the structure rearrangement could increase the amount of mesoporous channels in the zeolite, but exists a point of inflexion for the CTAB amount, where the micelles disturb the framework rearrangement instead of protect it, evidenced in the high variation in the %CR and the textural properties with the increment of the amount of CTAB [36]. The decrease in the microporous surface area is in accordance with the decrease of the %RC of the materials. For the generation of mesopores, many microporous channels are destroyed or collapsed. [37]


Fig 3. Nitrogen adsorption/desorption isotherms of Z720-X samples and the zeolite CBV720.

The average pore diameter (D_p) of the modified samples increased after the treatment respect to the parent zeolite, suggesting that the procedure was successful. Pore size distribution in Fig 4 is in accordance with the results in Table 1, all the modified samples have a similar D_p , which is higher than the D_p of parent zeolite, but the sample Z720-75 has the highest amount of pores in the range of 10 and 30 Å. The narrow pore distribution is related with the use of the surfactant, which acts as pore directing agent. Results of this research allowed to decrease the CTAB/ NH_4OH mass ratio to 0.75 respect the value used in the procedure reported by Javier Garcia et al. [23] that was 0.84.

3.2. Effect of the hydrothermal treatment time on the desilication process

In this case, in the desilication step a constant amount of CTAB was used, while the hydrothermal treatment time changed between 3 and 20 h.

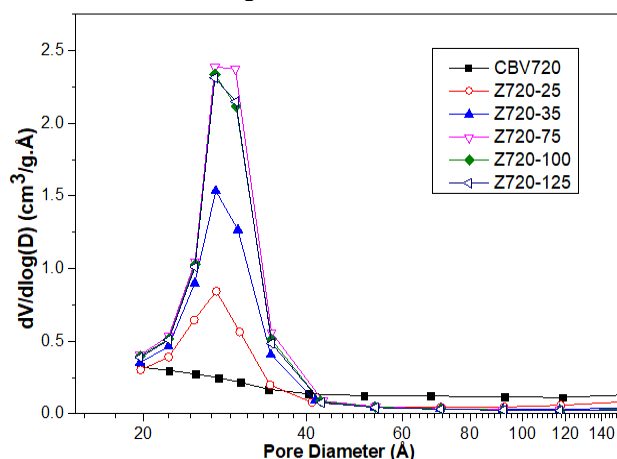


Fig 4. Pore size distribution of modified samples (Z720-X) and parent zeolite (CBV720).

Fig 5 shows that all Z720-YH samples conserved the crystalline phase of the zeolite Y. The samples have isotherms type IV that means that they have mesoporous channels, Fig 6, with hysteresis loops associated with capillary condensation of nitrogen and interconnected channels as the modified samples Z720-X. The value of P/P_0 in which the hysteresis loop starts show that all the materials have a higher average pore diameter respect the commercial sample, but the difference is low between the samples.

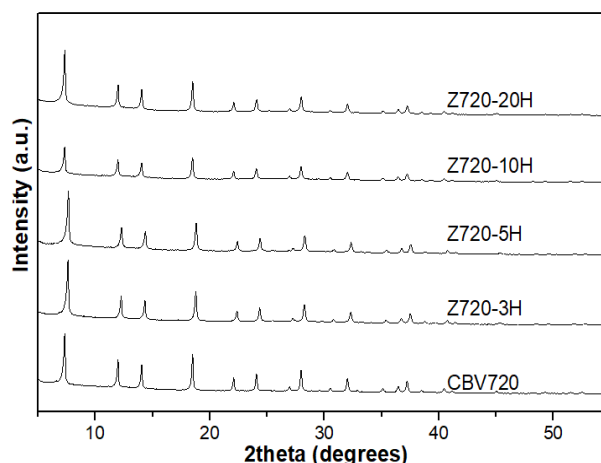


Fig 5. XRD of Z720-YH samples and the parent zeolite (CBV720).

Fig 7 shows the relation between the %RC and the hydrothermal treatment time. In the first three hours the %RC is ca 90%, probably because ammonia hydroxide is a weak alkaline solution and its dissociation in the aqueous media is slow; at three hours the hydrolysis of the Si in the framework is not complete. After 5 h of treatment and until 20 h, the %RC remains approximately constant at ca. 75%. This is probably because at this time, the hydrolysis is finished and until the autoclave is opened, the framework is in a constant rearrangement due to the alkaline pH in the media and the presence of the micelles of CTAB [38].

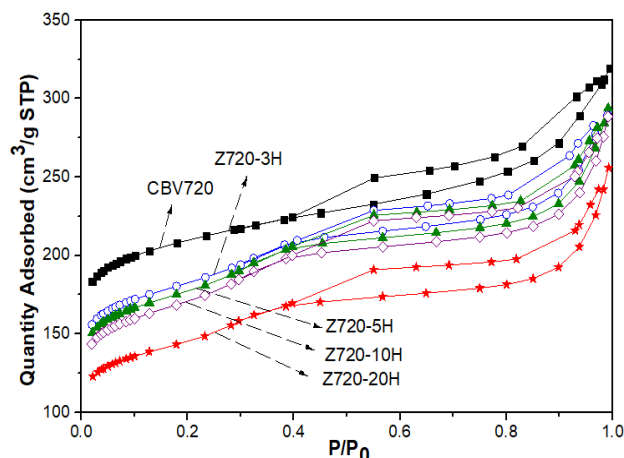


Fig 6. Nitrogen adsorption/desorption isotherms of Z720-YH samples and the parent zeolite (CBV720).

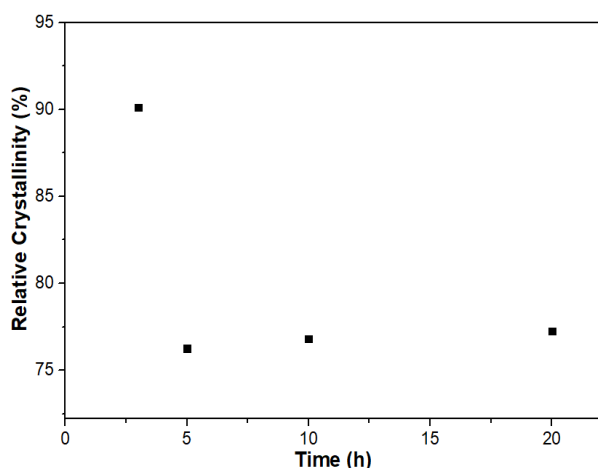


Fig 7. Effect of hydrothermal treatment time on relative crystallinity.

Table 2. Textural properties of the samples (Z720-YH) and the parent zeolite (CBV720).

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D_p (nm)	HF (-)
CBV720	770.44	560.11	210.33	0.494	0.232	0.262	2.56	0.24
Z720-3H	665.96	418.53	247.43	0.448	0.175	0.273	2.69	0.24
Z720-5H	646.27	386.96	259.31	0.454	0.162	0.292	2.81	0.22
Z720-10H	621.38	353.09	268.29	0.446	0.148	0.298	2.87	0.22
Z720-20H	527.26	288.01	239.25	0.396	0.122	0.274	3.00	0.20

Table 2 shows that the hierarchical factor of the samples is approximately constant as happened with the Z720-X samples, except for the sample Z720-20H (HF = 0.20). In general all the textural properties of the Z720-20H samples are lower than the others. Probably at 20 h the structure of the material starts to collapse by itself in irreversible way.

The effect of the hydrothermal treatment time is lower than the effect of the amount of CTAB in the media, i.e., a minimum change in the amount of surfactant in the media brings significantly variations in the crystalline and textural properties of the materials, while increasing to double the hydrothermal treatment time does not give significantly changes in the textural properties after 5 hours. In general, all the modified samples have a higher average pore diameter than parent zeolite CBV720.

The time that gives the maximum value for the mesopore generation in the framework is 10 h (sample Z720-10H). However, the BET and the micropore surface area decreased with the increase of treatment time. With 5 h of treatment under autogenous pressure, is possible to obtain almost the same crystalline and textural properties that at 10 h. We suggest that only 5 h are necessary to obtain mesopore channels in the zeolites. This analysis allows to reduce the hydrothermal time from 10 to 5 h, decreasing costs and energy consumption.

After 10 h of treatment, the generation of mesopores decreased with a conservation of the crystalline phase. The %RC with 10 and 20 h of treatment remains constant. Then, after 10 h the Y zeolite framework reaches its most stable form, and the rearrangement continues only in the amorphous part of the material guiding the pores to collapse or get

blocked, the final consequence is the reduction of the S_{meso} of the sample.

Table 2, shows that all the modified samples have a higher average pore diameter than the parent zeolite, and the average pore diameter increases with hydrothermal treatment time. Furthermore, in Fig 8 is observed that when the time increases until 10 h, the amount of pores ($10 < D_p < 30 \text{ \AA}$) enhanced.

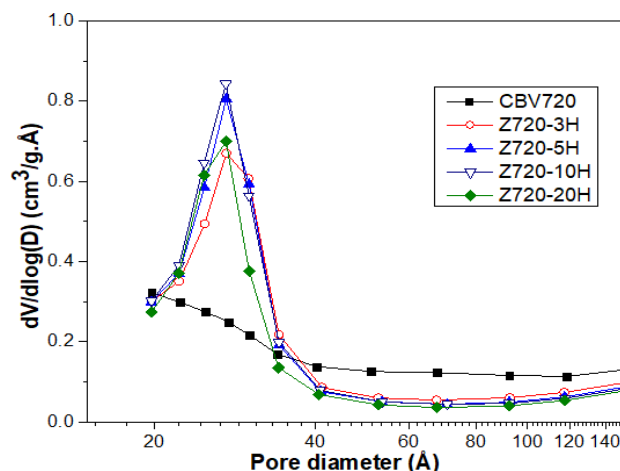


Fig 8. Pore size distribution of modified samples (Z720-YH) and parent zeolite (CBV720).

3.3. Effect of the desilication agent

In this analysis, the desilication step with ammonia hydroxide was tested over a Y zeolite with $\text{Si}/\text{Al} = 2.6$ in a full dealumination-desilication strategy. Fig 9 shows that the XRD of Z500-VG and the parent zeolite (CBV500) is the same. Fig 10 shows that the parent zeolite (CBV500) and the modified Z500-VG sample have isotherms type IV, and that the modified sample has best textural properties than the parent zeolite.

Fig 8, in accordance with data in

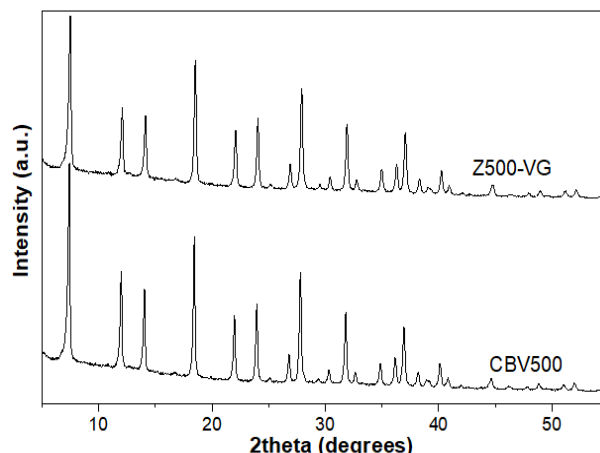


Fig 9. XRD pattern of Z500-VG sample and the parent zeolite (CBV500).

Mesoporous surface area was higher in sample reported by D. Verboekend et al [30] (Z500-Ver), but its %RC was lower (ca. 20%) to the properties found for Z500-VG, Table 3. This difference could be owing to the use of NaOH 0.1 M as desilicated agent that is a strong basic compound, and it dissociates completely in aqueous media; the desilication is fast and without control, generating a high amount of mesoporous, but without protection of the framework of the zeolite [21].

The use of a weaker basic solution as ammonia hydroxide brings more control of the desilication step, due to its dissociation equilibrium in water [27]. The assistance of the surfactant contributes to the decrease of the collapse of the structure [18] [23], and the acid washing in the last step helps to clean the channels of the solid from the debris generated in the dealumination and desilication steps [39]. Furthermore, the use of NH_4OH instead of NaOH avoided the additional ion exchange step in the synthesis, because there is not sodium deposition as happens when sodium hydroxide solution is used as desilication agent.

The sample Z500-VG has a higher micropore surface area than the parent zeolite, which means that a secondary micropore system was generated over the sample with the procedure employed. The H_4EDTA has a higher molecular size than the micropore channels of the zeolite guiding the dealumination only to the external part of the particles. Furthermore, ammonia hydroxide can get

into the micropore system, extracting Si atoms from the framework and generating the secondary pore system.

For the Z500-VG sample, the mesoporous surface area had a slightly increase from 58.47 m²/g to 65.04 m²/g while the microporous surface area increased from 706.32 m²/g to 804.94 m²/g, it means that the procedure was successful in the generation of pores, but needs improvement to generate pores with a higher pore diameter, an enhancement that could be reached by changing the dealuminating agent or the conditions of the treatment.

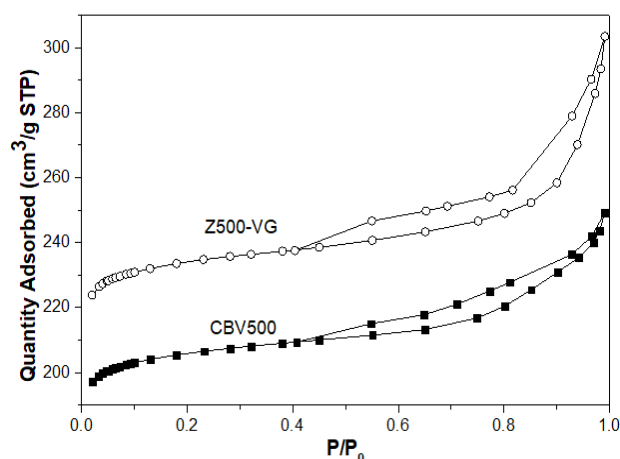


Fig 10. Nitrogen adsorption/desorption isotherms of Z500-VG sample and parent zeolite (CBV500).

Table 3. Textural properties of the sample Z500-VG, Z500-Ver (Ref. [30]) and the parent zeolite (CBV500).

Sample	%RC	S _{BET} (m ² /g)	S _{micro} (m ² /g)	S _{meso} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	Dp (nm)
CBV500	100	764.79	706.32	58.47	0.386	0.293	0.093	7.38
Z500-Ver	20	n.d.	n.d.	296.00	0.60	0.13	0.47	n.d.
Z500-VG	99	869.98	804.94	65.04	0.469	0.333	0.136	9.74

n.d. = No data reported.

The pore diameter increased from 7.38 nm to 9.74 nm. Probably using another organic acid for the dealumination of the sample that does not have diffusional problems with the zeolite would increase the amount of Al extracted from the framework turning the desilication process more efficient.

Fig 11 shows that the pore size distribution of modified sample Z500-VG has a maximum peak at ca. 120 Å, while the parent zeolite has its maximum value at 100 Å. Finally, there is a high dispersion of the pore sizes in the modified sample, related with the three steps mesopore formation in the material.

The mesoporous formation in Z500-VG sample was tested with TEM (Fig. 12A) and HR-TEM (Fig. 12B) analysis. Fig 12A shows the presence of mesopores with at least 20 nm of diameter and the interconnection between them. The crystals conserved their morphology and have a high amount of mesoporous channels. Fig 12B indicates that not only the material conserves its morphology, but also their lattice fringes, information that corroborates the presence of a crystalline phase in the particles.

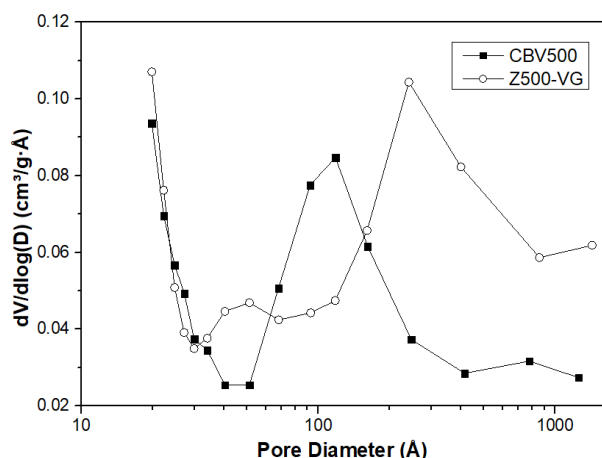


Fig 11. Pore size distribution for the modified sample Z500-VG and parent zeolite (CBV500).

Mesoporous channels, which open to external surface are also identified. From images, is concluded that the material Z500-VG conserves its morphology and crystallinity due to the mild treatment conditions, that allow generate mesopores in the zeolite, increasing its surface area and average pore diameter without a significant change in relative crystallinity and textural properties of the material.

4. CONCLUSIONS

The effect of the amount of surfactant CTAB on the desilication step and the hydrothermal treatment time on the crystalline and textural properties of the zeolite Y with Si/Al = 15 was analyzed. A higher effect of the amount of surfactant respect to the time was observed. An inverse relation between the %RC and the amount of surfactant was found. The hydrothermal treatment time had the same effect than the amount of surfactant on the crystalline and textural properties of the samples but softer. It was possible to improve the synthesis proposed by Javier Garcia et al. [23], reducing the amount of CTAB and the hydrothermal treatment time.

It was found that the use of ammonia hydroxide assisted by the cationic surfactant CTAB instead of sodium hydroxide in combination with the acid treatments with H₄EDTA and Na₂H₂EDTA allowed to generate microporous and mesoporous channels in the commercial zeolite Y with Si/Al = 2.6, with better textural properties and conserving the crystalline phase of the material. Further, the desilication step with ammonia hydroxide avoided the ion exchange

steps necessary in the synthesis of hierarchical materials using sodium hydroxide as desilication agent, reducing cost and time in the synthesis. Owing to properties of hierarchical synthesized materials, they could be a good option for cracking of probe molecules as 1,3,5-triisopropylbenzene.

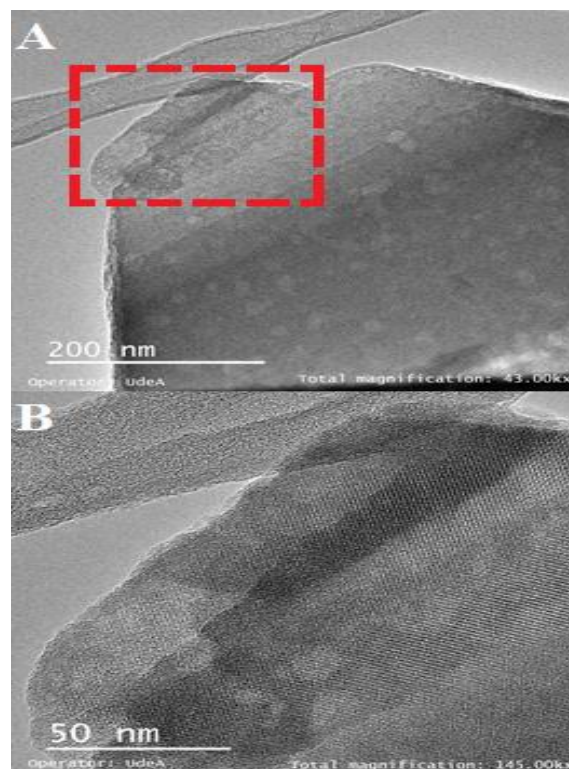


Fig 12. TEM (A) and HR-TEM (B) images of the sample Z500-VG. The zone shown in the rectangle in (A) corresponds to image in (B).

5. ACKNOWLEDGEMENTS

The authors acknowledge to Colciencias, Instituto Colombiano de Petróleo (ICP) and Universidad de Antioquia (UdeA) for financial support through Contract 039-2017.

6. REFERENCES

- [1] Holm, S., Taarning, Martin, E., Egeblad, K. & Christensen, Hviid, C. Catalysis with hierarchical zeolites, *Catalysis Today*, 3-16, 2011.
- [2] Zhang, K. & Ostraat, M. Innovations in hierarchical zeolite synthesis, *Catalysis Today*, 3-15, 2016.
- [3] Sadeghbeigi, R., *Fluid Catalytic Cracking Handbook*, United States of America, Elsevier, 2012.

- [4] Bartholomew, C. H. & Farrauto, R. J., *Fundamentals of industrial catalytic processes*, New Jersey, John Wiley & Sons, 2006.
- [5] Kulprathipanja, S., *Zeolites in industrial separation & catalysis*, Germany, Wiley-VCH Verlag GmbH & Co, 2010.
- [6] Cheng, W., Kim, G., Peters, A., Zhao, X., Rajagopalan, K., Ziebarth, M. & Pereira, J., *Environmental fluid catalytic cracking technology*, *Catalytic Reviews*, 39-79, 1998.
- [7] Bartholomew, C. Mechanism of catalyst deactivation, *Applied Catalysis A: General*, 212, 17-60, 2001.
- [8] Cerqueira, H., Caeiro, G., Costa, L. & Ribeiro, F. Deactivation of FCC catalysts, *Journal of Molecular Catalysis A: Chemical*, 292, 1-13, 2008.
- [9] Cuadros, J. F., Melo, D. C., Maciel, R. & Wolf Maciel, M. R., *Fluid Catalytic Cracking Environmental Impact: Factorial Design Coupled with Genetic Algorithms to Minimize Carbon Monoxide Pollution*, *Chemical Engineering Transactions*, 26, 243-249, 2012.
- [10] Vogt, E. T. C. & Weckhuysen, B. M., *Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis*, *Chemical Society Reviews*, 44, 7342-7370, 2015.
- [11] Müller, M., Harvey, G. & Prins, R., Comparison of the dealumination of zeolites beta, mordenite, ZSM-5 and ferrierite by thermal treatment, leaching with oxalic acid and treatment with SiCl₄ by ¹H, ²⁹Si and ²⁷Al MAS NMR, *Microporous and mesoporous materials*, 34, 135-147, 2000.
- [12] Agudelo, J. L., Hensen, E., Giraldo, S. A. & Hoyos, L. J., Influence of steam-calcination and acid leaching treatment on the VGO hydrocracking performance of faujasite zeolite, *Fuel Processing Technology*, 133, 89-96, 2015.
- [13] Martínez, C., Verboekend D. & Pérez-Ramírez, J., Stabilized hierarchical USY zeolite catalysts for simultaneous increase in diesel and LPG olefinicity during catalytic cracking, *Catalysis Science & Technology*, 3, 972-981, 2013.
- [14] Jong, K. P., Zecevic, J., Friedrich, H., Jongh, P. E., Bulut, M., van Donk, S., Kenmogne, R., Finiels, A., Hulea V. & Fajula, F., Zeolite Y crystals with trimodal porosity as ideal hydrocracking catalysts, *Angew. Chem. Int. Ed.*, 49, 10074-10078, 2010.
- [15] Li, K., Valla, J. & Garcia-Martinez, J., Realizing the commercial potential of hierarchical zeolites: New opportunities in catalytic cracking, *ChemCatChem*, 6, 46-66, 2014.
- [16] Giudici, R., Kouwenhoven, H. W. & Prins, R., Comparison of nitric and oxalic acid in the dealumination of mordenite, *Applied Catalysis A: General*, 203, 101-110, 2000.
- [17] Etim, U., Xu, B., Zhang, Z., Zhong, Z., Bai, P., Qiao, K. & Yan, Z., Improved catalytic cracking performance of USY in the presence of metal contaminants by post-synthesis modification, *Fuel*, 178, 243-252, 2016.
- [18] Ji, D., Liu, H., Wang, X., Liu, H., Gao, X., Xu, C. & Wei, S. Mesoporous Y zeolite from NaY with low Si/Al by one-step method based on bifunctional surfactant, *Materials Chemistry and Physics*, 196, 284-287, 2017.
- [19] Qiao, Ke, Li, Xuejin, He, Lifeng, Liu, Xinmei, Yan, Zifeng, Xing, Wei, Qin, Lihong, Dai, Baoqin & Zhang, Zhihua, An efficient modification of ultra-stable Y zeolite using citric acid and ammonium fluosilicate, *Applied Petrochemistry Research*, 4, 373-378, 2014.
- [20] Pu, X., Liu, N. W. & Shi, L., Acid properties and catalysis of USY zeolite with different extra-framework aluminum concentration, *Microporous and Mesoporous Materials*, 201, 17-23, 2015.
- [21] Gackowski, M., Tarach, K., Kuteranski, L., Podobinski, J., Jarczewski, S., Kustrowski, P. & Datka, J., Hierarchical zeolites Y obtained by desilication: Porosity, acidity and catalytic properties, *Microporous and Mesoporous Materials*, 263, 282-288, 2018.
- [22] Gackowski, M., Kuteranski, L., Podobinski, J., Sulikowski, B. & Datka, J., IR and NMR studies of hierarchical material obtained by the treatment of zeolite Y by ammonia solution, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 193, 440-446, 2018.
- [23] García-Martínez, J., Johnson, M., Valla, J., Li, K. & Ying, J. Y., Mesoporous zeolite Y - high hydrothermal stability and superior FCC catalytic performance, *Catalysis Science & Technology*, 2, 987-994, 2012.
- [24] Tao, Y., Kanoh, H. & Kaneko, K., ZSM-5 monolith of uniform mesoporous channels, *Journal of the American Chemical Society*, 6044-6045, 2003.
- [25] Jin, J., Peng, C., Wang, J., Liu, H., Gao, X., Liu, H. & Xu, C., Facile synthesis of mesoporous zeolite Y with improved catalytic performance for heavy oil fluid catalytic cracking, *Ind. Eng. Chem. Res.*, 53, 3406-3411, 2014.
- [26] Cejka, J., Van Bekkum, H., Corma, A. & Schueth, F., *Introduction to zeolite molecular sieves*, Amsterdam, Elsevier, 2007.
- [27] Van Aelst, J., Verboekend, D., Philippaerts, A., Nuttens, N., Kurttepli, M., Gobechiya, E., Haouas, M., Sree, S., Denayer, J., Martens, J., Kirschhock, C., Taulelle, F., Bals, S., Baron, G., Jacobs, P. &

Sels, B., Catalyst Design by NH₄OH Treatment of USY zeolite, *Advanced Functional Materials*, 25, 7130-7144, 2015.

[28] Li, W., Zheng, J., Luo, Y. & Da, Z., Effect of hierarchical porosity and phosphorus modification on the catalytic properties of zeolite Y, *Applied Surface Science*, 382, 302-308, 2016.

[29] Qin, Z., Shen, B., Yu, Z., Deng, F., Zhao, L., Zhou, S. & Yuan, D., A defect-based strategy for the preparation of mesoporous zeolite Y for high-performance catalytic cracking, *Journal of Catalysis*, 298, 102-111, 2013.

[30] Verboekend, D., Vilé, G. & Pérez Ramírez, J., Hierarchical Y and USY zeolites designed by post-synthetic strategies, *Advanced Functional Materials*, 22, 916-928, 2012.

[31] Kuperkar, K., Abezgauz, L., Prasad, K. & Bahadur, P., Formation and growth of micelles in dilute aqueous CTAB solutions in the presence of NaNO₃ and NaClO₃, *Journal of Surfactants and Detergents*, 13, 293-303, 2010.

[32] Modaressi, A., Sifaoui, H., Grzesiak, B., Solimando, R., Domańska, U. & Rogalski, M., CTAB aggregation in aqueous solutions of ammonium based ionic liquids; conductimetric studies, *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 296, 104-108, 2007.

[33] American Society for Testing and Materials, ASTM D3906-03: Standard Test Method for Determination of Relative X-ray diffraction intensities of faujasite Type Zeolite containing materials, United States of America, 2013.

[34] Zheng, J., Yi, Y., Wang, W., Guo, K., Ma, J. & Li, R., Synthesis of bi-phases composite zeolites MFZ and its hierarchical effects in isopropylbenzene catalytic cracking, *Microporous and Mesoporous Materials*, 171, 44-52, 2013.

[35] Zhu, Y., Murali, S., Stoller, M. D., Ganesh, K. J., Cai, W., Ferreira, P. J., Pirkle, A., Wallace, R. M., Cychosz, K. A., Thommes, M., Su, D., Stach, E. A. & Ruoff, R. S., Carbon-Based supercapacitors produced by activation of graphene, *Science*, 24, 1537-1541, 2011.

[36] Vartuli, J. C., Schmitt, K. D., Kresge, C. T., Roth, W. J., Leonowicz, M. E., McCullen, S. B., Hellring, S. D., Beck, J. S., Schlenker, J. L., Olson, D. H. & Sheppard, E. W., Effect of surfactant/Silica molar ratios on the formation of mesoporous molecular sieves: Inorganic mimicry of surfactant liquid-crystal phases and mechanistic implications, *Chemistry of Materials*, 6, 2317-2326, 1994.

[37] Li, Cheng, Guo, Linlin, Liu, Peng, Gong, Ke, Jin, Wenlong, Li, Lei, Zhu, Xiaochun, Liu, Xianchun & Shen, Baojian, Defects in AHFS-dealuminated Y

zeolite: A crucial factor for mesopores formation in the following base treatment procedure, *Microporous and Mesoporous Materials*, 255, 242-252, 2018.

[38] Guzmán-Castillo, M. L., Armendáriz-Herrera, H., Pérez-Romo, P., Hernández-Beltrán, F., Ibarra, S., Valente, J. S. & Fripiat, J. J., Y zeolite depolymerization-recrystallization: Simultaneous formation of hierarchical porosity and Na dislodging, *Microporous and Mesoporous Materials*, 143, 375-382, 2011.

[39] Li, W., Tu, C., Zheng, J., Luo, Y. & Da, Z., Influence of acid wash on the structural and catalytic properties of the hierarchical zeolite Y, *Chemistry select*, 5, 934-939, 2016.