The influence of swelling agents molecular dimensions on lamellar morphology of MWW-type zeolites active for fructose conversion

Anderson Joel Schwanke a,*, Sibele Pergher a, Urbano Díaz b, Avelino Corma b

Abstract

A new route to obtain pillared, disordered or desilicated MWW-type zeolites was developed assisted by quaternary ammonium surfactants with different hydrocarbon tail size acting as swelling agents (C12TA+ , C16TA+, C18TA+) and TPA+ both exchanged to their hydroxide forms instead of only one swelling agent (C4TA- or TPA-) in hydroxide form. Effect of surfactant concentration and swelling conditions were determinant to obtain MWW-type zeolites with different lamellar organization and spatial distribution of individual zeolitic layers. Specifically, soft swelling at 25 °C with C12TA+ preserved layer structure reaching a final disordered/pillared structure while pillared structures are obtained in the case of materials swollen with C18TA+ and C18TA+. Aggressive swelling processes at 80 °C favored desilication, damaging the layers structure in case of C12TA+ while pillared materials are obtained after swollen with C18TA+ and C18TA+ surfactants. It was proved that both swelling agents in hydroxide forms combining with swelling and pillaring procedure influenced on physico-chemical and morphological nature of MWW-type materials due to the particular conditions used. The obtained derivative MWW zeolites with different morphology, order and accessibility levels were firstly evaluated by catalytic dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) showing superior activity compared to beta zeolites reported in literature.

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1. Introduction

Zeolites are microporous crystalline aluminosilicates composed of tetrahedral units (Si or Al usually) coordinated by oxygen atoms. The different spatial organization between these tetrahedral units and their relationships generate different topologies of ordered porous structures with shape selectivity that play an important role in adsorption processes, ion exchange, separation, and catalysis [1–3]. However, the accessibility in the microporous range (usually, with pore sizes until 1 nm) imposes restriction for larger molecules that cannot access towards internal active sites, decreasing catalytic efficiency and imposing significant diffusional limitations [4,5].

In contrast, zeolites with a hierarchical pore system have received growing attention in recent times [4–8]. The strategy based on generating secondary mesoporosity regions in zeolites emerges as a way to facilitate molecular diffusion and increase the variety of reagents capable to achieve and react with internal active sites [6]. Among the strategies “bottom-up” to hierarchy zeolites, pillaring process is able to separate individual layers of two-dimensional (2D) zeolitic precursors. This procedure creates mesoporous regions by inserting organic or inorganic species as pillars, located in the interlayer space, together with intrinsic microporosity present in the zeolitic layers [9–11]. Considering the best examples in the state-of-art of successful hierarchical pillared zeolites, we found MCM-36 (MWW topology), ITQ-36 (FER topology) and recently, nanosheet pillared and self-pillared MFI-type zeolites [11–14].

The MWW topology until now, offers the major versatility in zeolite modifications [15]. Specifically, for MCM-36, pillaring procedure is carried out after the swelling of MWW precursors with long chain surfactants. Normally, swelling procedures in aggressive conditions (high temperatures, 90 °C) [16]. Another swelling procedure was carried by mild conditions (ambient temperature) followed by successive washing cycles with the intention to preserve the structure of individual layers. Indeed, this modification
facilitated the preparation of materials with less dissolved silica maintaining the integrity of the lamellar organization without the formation of undesirable mesoporous phase competitors [17]. However, for the catalytic point of view, pillared materials under aggressive swelling conditions still benefit for catalytic reactions once fragmented structure created by partial dissolution of crystals improves the reactant accessibility [18].

On the other hand, a recent study report that mild conditions could affect the swelling efficiency in MWW precursors with high Al content (Si/Al = −15) which depends of the type of cation-hydroxide used to generate high pH in swelling treatment [19]. According to Roth et al., [15] the swelling step is historically the most difficult and critical step for modifying precursors. Moreover, the effect of swelling with different swelling agents has being widespread to other zeolite precursors as ICP-1 based on germanosilicate and offer diversity to create more open zeolites structures showing that in swelling and pillaring, tiny details determine everything [20,21]. Recently, new strategies for direct synthesis of delaminated MWW-type monolayers using dual-template (with long chain lengths) have been reported [22,23]. However, the control of size galleries by surfactant size assisted method and pillaring process still need to be deeply explored [15].

Nowadays, great efforts has been made on effective routes for the synthesis of 5-HMF from C6-based carbohydrates. This demand comes from the necessity to obtain new sustainable fuels sources and chemicals through inexpensive and renewable materials with high added-value, proposing alternative efficient industry processes which could replace the limited fossil fuels [24,25]. Specifically, 5-HMF is a valuable biomass-derived platform intermediate, which is potentially used as fuel and additives in fine chemicals, pharmaceuticals and polymers [26–29].

The use of solid acid catalyst for dehydration carbohydrates has several advantages over liquid acid catalyst, such as easier separation, being recoverable and recyclable for successive reuses. Moreover, adjusting surface acidity of heterogeneous solid catalyst, selectivity to desired product can be achieved at shorter times, working with higher temperatures, voiding corrosion and safety problems [30,31]. Acidic H-Y, H-ZSM-5, H-mordenite, H-β, β-dealuminated, SO₄²⁻/ZrO₂ and SO₄²⁻/ZrO₂−Al₂O₃ has been used to produce 5-HMF from carbohydrates [32–36]. In addition, layered zeolites are one the most potential and promising materials to replace current used catalysts and advancement areas of study on porous and hierarchical materials [37]. In addition, has been demonstrated that the combined action between Brunsted and Lewis acidic sites were highly beneficial to 5-HMF production [38]. Thus, fructose dehydration would be a priori an ideal model substrate to evaluate the performance of pillared MWW catalytic materials for biomass conversion [39].

This work aims to evaluate the influence of long chain surfactants used as swelling agents, which exhibit different molecular dimensions, on pillared MWW-type zeolites through soft and aggressive swelling conditions. The obtained MWW-type zeolites were firstly evaluated by catalytic dehydration of fructose to 5-HMF.

2. Experimental

2.1. MCM-22 precursor synthesis

Synthesis of precursor (P) was done similarly to literature [40]. Thus, 0.37 g of NaOH (Sigma Aldrich) and 0.37 g of NaAlO₂ (Riedel-de-Haën), were dissolved in 81.18 g of distilled water. In a next step, 4.98 g of hexamethylenimine (HMI, Sigma Aldrich) and 6 g of fumed silica (Aerosil 200, Degussa) were added to the mixture. The resulting slurry with Si/Al ratio = −25 was stirred for 2 h and hydrothermally treated in PTFE-lined stainless-steel autoclave with rotation (60 rpm) at 135 °C for 7 days. After the aging period, the autoclave was quenched and the MCM-22 precursor filtered, washed with distilled water and dried overnight at 60 °C. After calcination (580 °C for 12 h), resulting 3D-MCM-22 zeolite denoted (C).

2.2. Swelling precursor

Typically, 9.0 g of aqueous slurry of MCM-22(P) (20 wt% solids) was mixed with 35.0 g of an aqueous solution of 29 wt% C₁₈TA⁺Br⁻/OH⁻, C₆TA⁺Br/OH⁻ or C₁₂TA⁺Br/OH⁻ (50, 51 and 53% ionic exchange, respectively) and 11.0 g of an aqueous solution of 40 wt% TPA⁺Br/OH⁻ (45% ionic exchange). The resultant slurry was treated at 80 °C (aggressive swelling) or 25 °C (soft swelling) for 18 h. In Fig. A1 it is shown the previous experiments that succeeded the choice of this surfactant mixture. Swollen materials were washed with distilled water by successive centrifugation cycles (12000 rpm) up to ten times and dried at 60 °C for overnight.

2.3. Pillaring

Swollen materials were added in tetraethyl orthosilicate (TEOS, 98%, Aldrich), 1:5 wt/wt, at 80 °C for 24 in vigorous stirring under nitrogen atmosphere [17]. The materials were hydrolyzed with water (pH = 9, controlled with NaOH) at 40 °C for 12 h and dried at 60 °C for overnight. Calcination was done in tubular Pyrex reactor up to 550 °C with heating rate of 3 °C min⁻¹ under nitrogen flow, followed by 8 h under oxygen flow. All materials were converted to acidic form through three consecutive ion exchanges of 1 g of zeolite in 50 ml of 0.1 mol L⁻¹ NH₄NO₃ (Aldrich) solution at ambient temperature for 3 h, and subsequent calcination at 500 °C (heating rate of 5 °C min⁻¹) for 2 h under air atmosphere.

The modified materials were named by surfactant chain length used in swelling procedure (18, 16, 12) followed by type of swelling (aggressive or soft treatments were denoted “A” or “S”, respectively) followed by number of washing cycles. For the pillared materials, a “P” was added at the end of nomenclature. For example, when C₁₂TA⁺ was used with aggressive swelling, washed ten times and followed by pillaring process, nomenclature of the sample is 12-A-10-P.

2.4. Catalytic tests

Conversion of fructose to 5-hydroxymethylfurfural (5-HMF).

218 mg of fructose and 18 mg of zeolite catalyst were added into a 10 mL Pyrex reactor, containing 8.0 g of dimethyl sulfoxide (DMSO). The formed mixture was stirred in an oil bath at 120 °C for 3 h. The products, after fructose dehydration, were sampled at intervals and analyzed using HPLC. Fructose conversion (1), yield (2) and selectivity (3) of 5-HMF were calculated following the next equations:

\[
\text{Conversion : } \frac{C_{\text{fructose}}}{C_{\text{fructose}}} \times 100\% \\
\text{Yield : } \frac{C_{\text{5-HMF}}}{{C_{\text{fructose}}} \times 100\%} \\
\text{Selectivity : } \frac{C_{\text{5-HMF}}}{C_{\text{fructose}}} \times 100\%
\]
2.5. Characterization

Powder X-ray diffraction (XRD) patterns were collected on PANalytical Cubix fast diffractometer, using CuKα1 radiation and an X'Celerator detector in Bragg-Brentano geometry.

Nitrogen adsorption isotherms at –196 °C were measured with a Micromeretics ASAP 2010 manometric adsorption analyzer. Before the measurements, the samples were outgassed for 12 h at 300 °C. The specific surface area (SBET) was calculated by the BET method [41] from the nitrogen adsorption data in the relative pressure range from 0.06 to 0.11. The total pore volume (VTP) [42] was obtained from the absorbed amount of N2 at a relative pressure of about 0.99. The external surface area (SAex) and micropore volume (Vmicro) were estimated using the αS-plot method (with LiChrophor Si–1000 macroporous silica gel [43] as reference adsorbent) in the p/p0 range from 0.05 to 0.11. The pore size distribution (PSD) was obtained using the modified Barrett–Joyner–Halenda (BJH) method [44] with nitrogen adsorption branch data.

Elemental analysis was determined by ICP Varian 715-ES ICP-optical emission spectrometer, after dissolution of the solids in a HNO3/HF solution.

Thermogravimetric analysis (TGA) measurements were done in a Mettler-Toledo TGA/SDTA851E analyzer in air with a heating rate of 10 °C min⁻¹.

Field-emission scanning electron microscopy (FESEM) micrographs were recorded on a ZEISS Ultra 55 microscope operating at 2 kV.

Transmission Electronic Microscopy analysis (TEM) were recorded on a JEOL JEM 2100F operating at 200 kV. The samples were ultrasonically dispersed in dichloromethane and dropped to carbon copper grids.

Infrared (IR) with adsorption of pyridine were performed in a Nicolet 710 FTIR spectrometer using vacuum cells. The measurements were performed in self-supported wafers of 10 mg cm⁻² that were degassed overnight under vacuum (10⁻⁴ to 10⁻⁵ Pa) at 400 °C. The spectra were recorded and pyridine was introduced and, after equilibration, the samples were outgassed for 1 h at increasing temperatures (150/250/350 °C). After each desorption step, the spectrum was recorded at room temperature and the background subtracted in the pyridine case and absorption coefficients calculated by Emeis [45] were used.

HPLC analysis was performed on a Waters 1525 equipped with RID detector at 35 °C and ion exclusion column Coregel 87H3 (7.8 × 300 mm) at 60 °C with flow rate of 0.7 mL min⁻¹ and H2SO4 0.005 mol L⁻¹ as mobile phase. Amount of fructose and 5-HMF were determined using external calibration.

3. Results and discussion

3.1. XRD of swollen materials

Fig. 1 shows the XRD patterns of precursor and calcined MCM-22 samples, as well as the diffractograms of the MWW materials obtained after soft and aggressive swellings treatments and applying different washing cycles. For MWW precursor (P), diffraction 2θ bands located at 3.3° and 6.6° range corresponding to (001) and (002) reflections, relative to MWW zeolitic layer stacking with thickness of each individual layer of 2.5 nm, are observed [46]. These layers are connected by hydrogen bonds between silanol groups with the presence of HMI template molecules located between layers [47]. In addition, inlayer diffraction bands located at 2θ = 7.1° corresponding to (100) diffraction and reflections at higher 2θ angles, 25.1° and 26.2° assigned to (220) and (310) planes, are also detected. After calcination silanol groups were condensed together with the elimination of interlayer organic template, conventional zeolite 3D-MCM-22 (C) being obtained.

The soft swelling treatment using C12TA⁺ resulted in the overlapping of the (101) and (102) diffraction bands, yielding only a broad peak located between 8° and 10° 2θ range. This fact indicated partial order of vertical alignment order in the stacking direction, i.e., along axis c. The molecular dimensions of the swelling agents which are placed in the interlayer space, between individual MWW layers, are shown in Fig. 1 and A2. The XRD pattern obtained for the sample 16-S-3 showed basal spacing of 4.8 nm estimated from (001) reflection band. The difference of 0.3 nm may related with excess of swelling agent intercalated once after ten washing cycles the basal spacing was decreased to 4.5 nm, being (002) diffraction band also observed. The presence of TPA− and its dimension (0.88 nm, see Fig. A2) used with long-alkyl swelling surfactants for swelling may not be excluded of basal spacing value once that is also interacting with the long-alkyl surfactants. However, XRD pattern of swelling MWW with only TPA− agent did not show increase of basal spacing consistent with its molecular dimension (see Fig. A1).

In terms of MWW structural conservation, XRD patterns show that soft swelling treatment preserved the crystal structure, indicating that room temperature, although working with high basic pH (13.57), minimized fragmentation and dissolution of the silica from zeolitic layers. The intense diffraction bands detected in (100), (220), (310) intralayer peaks and the excellent ordering degree of swelling materials, as it is evidenced by emergence of (002) and (003) basal peaks confirmed that soft swelling conditions better kept MWW structure of the layers, without losing the order along axis c.

On the other hand, aggressive swelling 16-A-10 favored a separation between MWW layers with 4.5 nm with a broad (001) diffraction band (compared to 16-S-10) which indicated a vertical accommodation of surfactant in the interlayer space. Furthermore, aggressive treatment implied lower intensities in the (100), (220) and (310) diffraction bands of swollen materials, showing that partial structural damage of zeolitic structure was occurring. These hypotheses are confirmed both by the absence of repetitive (001) basal reflections, (002) and (003), indication lower ordering in the separation of the individual layers, and by the presence of broad region in the XRD pattern, between 15 and 30° 2θ, usually assigned to amorphous silica due to the partial dissolution of MWW layers [18].

![Fig. 1. XRD of swelling with C12TA⁺, C6TA⁺, C8TA⁺ materials with soft and aggressive procedure.](image-url)
The washing cycles carried out after swelling treatments were also evaluated. This step is useful to remove the excess of surfactant which could favor the formation of competitor mesophases, during the consecutive pillaring process. In addition, with this methodology, the pH present in the pillaring synthesis medium could be controlled, avoiding high pHs in the slurry that promotes the rapid polymerization of silica (TEOS) around of the MWW swollen nanocrystals and not only in the interlayer region. Fig. 2 shows that increasing washing cycles’ number, more effective was the surfactant removing. As consequence, a slight shift of (001) diffraction band was even observed, evidencing the convenience to eliminate the excess of swelling agents through consecutive washing cycles. However, after tenth washing cycle, (002) basal diffraction band was even observed, evidencing the convenience to eliminate the excess of swelling agents through consecutive washing cycles.

For soft swelling treatment, using C_{12}TA^+ as intercalation agent, a modest coalescence of (101) and (102) reflection bands was detected, indicating that non-regular MWW layers separation occurred in vertical alignment, perpendicularly to axis c. This fact was confirmed by emergence of broad (002) reflection with (001) diffraction band with basal spacing of 3.0 nm, probably due to the insufficient amount of swelling agent in lateral accommodation between MWW layers. In contrast, aggressive swelling in presence of C_{18}TA^+ molecules caused the overlapping of (101) and (102) reflection bands, indicating poor vertical ordering of c-stacking crystals. The (001) diffraction band with a broad region is observed with basal spacing of 3.5 nm which suggests a lateral conformation of swelling agent.

In the case of MWW samples swollen with C_{18}TA^+ long chain surfactant (18-S-10 and 18-A-10 samples), some differences were observed comparing its low angle XRD patterns. The 18-S-10 sample showed an intense (001) diffraction band with basal spacing of 5.1 nm. Considering the theoretical estimation of molecular dimensions of C_{18}TA^+ with 2.3 nm (Fig. S2), the basal spacing value is consistent with the approximately molecular dimension of surfactant in vertical accommodation between individual MWW layers. In addition, (003) diffraction band is observed which indicate a swelling materials with high ordering. Moreover, on the right side of (001) diffraction band, a shoulder is founded with basal spacing of 3.9 nm. This value may indicate that a portion of surfactant with different accommodation between MWW layers due to excess of surfactant removed by washing cycles or even associated with flexibility and coiling effect that could occurs when a straights-chain hydrophobic groups of surfactant exceeds 16 carbon atoms [45].

Moreover, the high angle XRD pattern indicate a considerable decrease of (100), (220) and (310) diffraction bands which is not only attributed to partial damage of MWW structure treatment with C_{18}TA^+ in aggressive swelling but also the increase amount of organic intercalated (C_{18}TA^+ > C_{16}TA^+ > C_{12}TA^+) which corroborates with total loss mass observed by TGA of Fig. 3 and Table A4 when aggressive swelling. For 18-S-10 sample, the (001) basal spacing with 4.3 nm is lower than expected based on theoretical estimation dimensions of C_{18}TA^+. When compared the low angle XRD of both samples (18-S-10 and 18-A-10) the basal spacing value is close to value of the shoulder present in low angle XRD pattern of 18-A-10 sample, which also suggests a different accommodation which may related to surfactant removing by washing cycles or by the flexibility and coiling effect of C_{18}TA^+ surfactant. Regarding swelling ordering and MWW layer zeolitic preservation, soft swelling with C_{18}TA^+ maintain the (002) and (003) reflections which indicates a well ordering degree. In addition, the integrity of MWW layers is preserved by the (001), (220) and (310) diffraction bands that are not drastically affected after swelling.

![Fig. 2. TGA and DTG of swelling with C_{12}TA^+, C_{16}TA^+ and C_{18}TA^+ materials with soft and aggressive procedure.](image-url)

![Fig. 3. XRD of pillared materials swollen with C_{12}TA^+, C_{16}TA^+, C_{18}TA^+ with soft and aggressive procedure.](image-url)
3.2. TGA/DTG of swollen materials

From TGA and DTG of the derivative MWW samples (Fig. 2 and Table A4), different mass losses of swollen materials are observed. In general, increasing washing cycles, the amount of final incorporated surfactant decreased when soft treatments were carried out during the swelling process. Normally, the first loss mass observed at 110 °C, assigned to water adsorbed on surface of materials, was not detected for 16-S-3 sample due to marked hydrophobic character of the solid associated to high amount of swelling agent molecules located in the interlayer space.

The main mass loss of this last sample was observed between 180 and 340 °C, although HMI molecules could also be included into this temperature range come from structural directing agents used during the hydrothermal synthesis of MWW starting precursors. Furthermore, an additional weight loss was detected around 110–180 °C probably associated to some surfactant molecules located outside of interlayer region or weakly interacting with MWW crystals, being more pronounced when the number of washing cycles is higher. In Table A4, weight losses of MWW samples for the different temperature ranges are indicated. In the temperatures range oscillating between 180 °C and 340 °C, long chain amount of surfactants used as swelling agents remained located in the interlayer region, as well as HMI molecules placed in the MWW surface “cups” 12 MR were oxidized, this fact being even favored by the swelling conditions (temperature and pH). Between 340 and 480 °C, mass losses observed were similar for samples prepared through soft swelling treatments, being assigned to more stabilized HMI molecules located into the sinuoidal 10 MR microporous channel present in the inner of each individual MWW layer.

In addition, mass losses detected in the temperature range between 480 and 800 °C were due to residual long chain ammonium surfactants and HMI molecules which were not previously removed, as well as dihydroxylation water produced by condensation phenomenon of surface silanol groups. In the case of swollen 16-A-10 sample, a great amount of organic contribution is detected, even present in the temperature range oscillating between 110 and 180 °C. Probably, the aggressive swelling treatment favored the partial rupture of MWW layers, facilitating that confinement and interaction of swelling agents and HMI molecules with the zeolitic framework was weaker. As consequence, the weight loses from TGA curves were observed at lower temperatures than in the samples swollen through soft conditions, as previously confirmed by XRD and similarly described in literature [49].

On the opposite, C12TA+ did not exhibit similar mass losses compared with solids swollen with C16TA+ and C18TA+ surfactants. From DTG curves, it is observed that 12-S-10 sample contained only reduced amount of swelling agents intercalated in the interlayer region. In addition, its loss mass is 18% higher than precursor (P) which corroborates with a lateral conformation of surfactant, as previously confirmed by XRD. For this sample, the mass loss being of 17% in 110–340 °C temperature range. Aggressive swelling treatment for 12-A-10 sample showed a loss mass 27% higher than MWW precursor (P). Furthermore, the total loss mass in 12-A-10 sample is 14% higher than 12-S-10 and may suggests a lateral conformation of surfactant as previously showed in XRD results. In the case of 18-S-10 sample, TGA and corresponding DTG are similar to those obtained for 16-S-type materials. Specifically, main weight loss was detected in 180–340 °C temperature range, indicating that large amount of stabilized swelling agents was located in the interlayer region, providing a strong interaction between surface of MWW layers and surfactant molecules which favored well-ordered MWW materials, such as was confirmed from above discussed XRD results. For 18-A-10 sample, this main loss mass associated with the swelling agents was greater than those detected from soft swelling treatments (36%).

3.3. XRD of pillared materials

In Fig. 3, XRD patterns of the MWW derivative materials after pillaring process are shown. For 16-S-10-P material, the (001) (002) and (003) diffraction peaks indicate a stacking order of layers. In addition, the broad (001) reflection showed a pillared material with basal spacing centered at 4.2 nm. XRD diffractogram of pillared 16-A-10-P sample, obtained through aggressive swelling treatment, exhibited a broad (001) reflection with basal spacing centered at 4.1 nm. In addition, the (220) and (310) reflections are slight suppressed after pillaring which is attributed to amorphous silica deposited into material leading to increase the intensity of diffraction region between 15 and 30° 2θ and confirmed by the ICP analysis of Table 1.

XRD patterns of 18-S-10-P shown a broad (001) diffraction peak with basal spacing at 3.6 nm which is characterized by absence of basal (002) and (003) peaks that indicates inhomogeneity of stacking order of layers. For 18-A-10-P sample, a broad (001) diffraction band with basal spacing centered at 4.0 nm was observed. Furthermore, the increase of diffraction region between 15 and 30° 2θ indicate silica incorporation after pillaring which is confirmed by ICP, Table 1.

After pillaring process, XRD patterns of 12-S-10-P and 12-A-10-P samples did not show intense (001) basal peaks, as it early expected by TGA and XRD results of corresponding swollen samples, because negligible amount of C12TA+ surfactant was intercalated between MWW layers associated to lateral conformation, respectively. However, although with a small presence of surfactant molecules in the interlayer space, MWW materials showed partial disorganization level with small pillars, confirmed by broad (001) reflections and moderate coalescence observed between (101) and (102) diffraction peaks in the case of 12-S-10-P material.

3.4. Nitrogen adsorption isotherms of pillared samples

Nitrogen adsorption isotherms of MWW modified materials are shown in Fig. 4. 3D-MCM-22 (C) zeolite exhibited Type I isotherm with a high adsorbed amount of N2 at low relative pressures (p/p0 < 0.1) confirmed thus its microporous nature. In prominence, the MWW pillared materials and previously swollen with C16TA+ and C18TA+ swelling agents, showed isotherms with high quantity of N2 adsorption at low p/p0 (due to strong adsorbate-adsorbent interactions and/or filling micropores), and a step adsorption between 0.12 and 0.4 of p/p0 corresponding to the capillary condensation phenomena occurred in the mesoporous region created by pillaring. In the case of isotherms of the 12-A-10-P and 12-S-10-P samples, the N2 adsorption at low pressures is due mainly to the presence of micro pores these materials. In addition, the isotherm of the 12-A-10-P sample exhibit a progressive increase of the quantity of N2 adsorption at relative pressures higher than 0.35, which is associated to mesoporosity present in MWW structure caused by desilication phenomenon.

Pore size distribution (Fig. 4, right side), of the samples under study showed pore sizes (PS) ranging between supermicropores and small mesopores. In the case of 12-S-10-P sample PS between 1.5 and 2.2 nm were found, on the contrary, the 12-A-10-P sample did not show pores in the pillars sizes range. For the 18-S-10-P and 18-A-10-P samples PSD ranges between 1.6-2.5 nm and 2.1–4.0 nm were found, respectively. Instead, for 16-S-10-P and 16-A-10 pillared samples the PS ranges between 1.8-2.5 nm and 1.8–2.8 nm were found. In a general form, it was observed aggressive swelling
treatment and subsequent pillaring generate materials with broader pore size distributions.

Textural properties results are shown in Table 1 for the MWW-type samples obtained after pillaring procedure, being observed a significant increase in the specific surface area and pore volume of all pillared samples compared with standard 3D-MWW zeolite (C).

Similarly, for 18-S-10-P and 18-A-10-P pillared materials, the increase of the specific surface area of 840 and 850 m$^2$ g$^{-1}$, respectively, was observed compared to MCM-22 (C) with 520 m$^2$ g$^{-1}$. This fact clearly evidenced that pillaring process was successful after soft and aggressive swelling treatments. Respect to micropores, the sample obtained with aggressive swelling and pillaring with C$_{18}$TA$^+$ showed the absence of micropores and followed by C$_{16}$TA$^+$ which presents small quantity of micropores (0.01 cm$^3$ g$^{-1}$). This indicates aggressive treatment may obstruct the microporous structure of individual MWW layers due to silicon (deposit on MWW layers) from pillaring process may block the micropores. This effect is supported when 18-A-10-P is compared to aggressive swelling and pillaring sample 12-A-10-P which is desilicated (no silica was incorporated from pillaring) which maintains significant microporosity and increased the interparticle pore volume ($V_{\text{int}}$) compared with 3D-MWW zeolite (C). The possibility of formation of competing mesophases (type M41S, MCM-41) in swelling medium of 18-A-10 was also take into account. It well know that basic medium with surfactant, silicon and aluminum sources (which would be supplied from MWW layers) are the mean reactants to M41S formation. However, if a mesophase was formed, the presence of diffraction bands in low angle XRD pattern should be maintained after direct calcination of swollen 18-A-10 sample. The swollen 18-A-10 sample was calcined and no XRD diffraction bands characteristics of mesophases were found (see Fig. A5). Nevertheless, a complementation with textural analysis should be done since poorly crystalline with no XRD pattern but quite porous mesophases can also formed. Moreover, diffraction bands characteristic of MWW zeolite are present in 18-A-10-P and the catalytic activity showed that microporosity still existing.

### 3.5. ICP analysis of swollen and pillared materials

In Table 1, Si/Al molar ratios of materials after swelling (in parenthesis) and pilliration post-synthesis treatments is shown. The starting zeolitic precursor MCM-22(P) presented Si/Al molar ration of 22, decreasing after swelling process which indicated that partial dissolution of some silica units from individual MWW layers.

This decrease was more marked for aggressive than for soft swelling treatments. After pillaring process, Si/Al molar ration increased due to intercalation in the interlayer space of silica pillars, being more pronounced when C$_{16}$TA$^+$ and C$_{18}$TA$^+$ surfactants showed a certain increase in the specific surface area and partial disruption along c-stacking direction compared with 3D-MWW (C) zeolite and a modest pillaring for 12-S-10-P sample. For pillared MWW materials previously swollen with C$_{16}$TA$^+$ molecules through soft or aggressive swelling treatments marked an increase in the specific surface area of approximately 54% compared with 3D-MCM-22 (C) zeolite.

Similarly, for 18-S-10-P and 18-A-10-P pillared materials, the increase of the specific surface area of 840 and 850 m$^2$ g$^{-1}$, respectively, was observed compared to MCM-22 (C) with 520 m$^2$ g$^{-1}$. This fact clearly evidenced that pillaring process was successful after soft and aggressive swelling treatments. Respect to micropores, the sample obtained with aggressive swelling and pillaring with C$_{18}$TA$^+$ showed the absence of micropores and followed by C$_{16}$TA$^+$ which presents small quantity of micropores (0.01 cm$^3$ g$^{-1}$). This indicates aggressive treatment may obstruct the microporous structure of individual MWW layers due to silicon (deposit on MWW layers) from pillaring process may block the micropores. This effect is supported when 18-A-10-P is compared to aggressive swelling and pillaring sample 12-A-10-P which is desilicated (no silica was incorporated from pillaring) which maintains significant microporosity and increased the interparticle pore volume ($V_{\text{int}}$) compared with 3D-MWW zeolite (C). The possibility of formation of competing mesophases (type M41S, MCM-41) in swelling medium of 18-A-10 was also take into account. It well know that basic medium with surfactant, silicon and aluminum sources (which would be supplied from MWW layers) are the mean reactants to M41S formation. However, if a mesophase was formed, the presence of diffraction bands in low angle XRD pattern should be maintained after direct calcination of swollen 18-A-10 sample. The swollen 18-A-10 sample was calcined and no XRD diffraction bands characteristics of mesophases were found (see Fig. A5). Nevertheless, a complementation with textural analysis should be done since poorly crystalline with no XRD pattern but quite porous mesophases can also formed. Moreover, diffraction bands characteristic of MWW zeolite are present in 18-A-10-P and the catalytic activity showed that microporosity still existing.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Si/Al (ICP)</th>
<th>$S_{\text{ext}}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{tot}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{TP}}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{int}}$ (cm$^3$ g$^{-1}$)</th>
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<td>(8) 9</td>
<td>710</td>
<td>460</td>
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<td>670</td>
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<td>0.33</td>
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<tr>
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<td>(10) 39</td>
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<td>760</td>
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<tr>
<td>18-A-10-P</td>
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<td>850</td>
<td>850</td>
<td>0.65</td>
<td>–</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Values in parenthesis correspond to the swollen materials.

a) The interparticle pore volume ($V_{\text{int}}$) was obtained from the difference between $V_{\text{TP}}$ (obtained at 0.99 of $p/p^0$) and the pore volume obtained at 0.6 of $p/p^0$. This value correspond to pore volume of sizes from 4 to 100 nm.
silica pillars. The fact by swelling with C$_{12}$TA$^+$ not be as effective with other swelling agents as C$_{18}$TA$^+$ and C$_{16}$TA$^+$ may due to the particular conditions used (C$_{12}$TA$^+$ and TPA$^+$ in hydroxide forms with aggressive treatment) and can be associated to desilication phenomenon occurred in 12-A-10-P sample.

3.6. Microscopic analysis of pillared materials

In Fig. 5, morphology of 2D zeolitic precursor of MCM-22 (P) (image a) and 3D calcined MCM-22 (C) (image b) are shown from SEM microscopy. In both cases, hexagonal disk-shaped crystals of average sizes of ~1.4 $\mu$m were observed by successive vertical stacking growth of MWW layers. Comparing images 5a and 5b, flat plates were observed after calcination process due to surface silanol condensation phenomenon. For 12-S-10-P (image 5c) material, the morphology is maintained while a partial amorphization is observable in 12-A-10-P sample (image 5d).

SEM micrographs of pillared MWW material, previously swollen with C$_{16}$TA$^+$ and C$_{18}$TA$^+$ surfactant molecules, are shown in Fig. 6. In the case of samples obtained from soft swelling process, MWW layers integrity was maintained (images a and c). In addition, analyzing the c-stacking of disk-shaped crystals (see insets in Fig. 6), both samples showed more expanded particles than 3D-MCM-22 (Fig. 5b). Pillared 18-A-10-P sample obtained after

![Fig. 5. SEM analysis of precursor P(a) and MCM-22 zeolite C (b). Images (c) and (d) corresponding to 12-S-10-P and 12-A-10-P materials, respectively.](image)

![Fig. 6. SEM analysis of 16-S-10-P (a) and 16-A-10-P (b). Images (c) and (d) corresponding to 18-S-10-P and 18-A-10-P materials respectively.](image)
aggressive swelling process using C₁₈TA⁺ surfactant, exhibited aggregation phenomena of curved disk-shaped crystals with presence of non-zeolitic component in form of amorphous silica which is attributed to dissolution of MWW layers after aggressive swelling and residual silica which may not participate of the pillars between MWW layers. Micrographs showed in Fig. A6 conﬁrms this hypothesis. For the sample 12-A-10-P desilication phenomena were observed by TEM of Fig. A7 where mesoporous regions are opened in particle crystals.

Fig. 7 shows a general scheme summarizing the dimensions influence of swelling agents used during soft or aggressive conditions on the ﬁnal MWW pillared materials. It was observed that behavior surfactants between MWW layers directly depends of the length of surfactant alkyl-chain and the type of swelling treatment (soft or aggressive) which conducts to different surfactant accommodations. Soft swelling with C₁₂TA⁺ conducts to lateral accommodation conﬁrmed by XRD and TGA analysis. After pillaring it was observed a gently and almost negligible increase of basal spacing together with a moderate coalescence of (101) and (102) diffraction bands by partial loss of vertical alignment order in the stacking direction along axis c. This features added with moderate increase of silica after pillaring, the increase of speciﬁc surface maintaining its microporosity and pore size ranging close to small mesopores region conducts a disordered/pillaring material. Aggressive swelling C₁₂TA⁺ exhibited lateral conformation together with desilication phenomenon attributed to temperature of swelling (80 °C) and C₁₂TA⁺ as swelling agent. The decrease of Si/Al ratio = 9 of swollen maintaining similar value after pillaring indicates large mesopores created not by robust pillars between MWW layers but for removal some MWW units from particle crystals as observed by TEM and nitrogen adsorption isotherm analysis.

Swelling with C₁₆TA⁺ surfactant lead to vertical accommodation and both soft and aggressive swelling formed pillared materials. Soft swelling and pillaring material possesses more stacking ordering as observed by presence of (002) and (003) diffraction bands. Swelling with C₁₈TA⁺ lead to vertical accommodation with aggressive swelling with a portion of swollen different conformation between layers which may attributed to surfactant removing by washing cycles or the coiling and ﬂexibility effect of C₁₈TA⁺. The pillared form showed a broad (001) diffraction band associated with decrease of stacking order of layers along axis c. Moreover, the microporosity of MWW layers was drastically affected by aggressive swelling where no values of microporous surface and volume are presented. This effect may be related to considerable dissolution of MWW layers promoted by swelling agents (C₁₈TA⁺ + TPA⁺) both exchanged to their hydroxide forms.

3.7. Acidity of pillared materials by pyridine adsorption followed by FTIR

Alternatively, surface properties of pillared MWW materials were investigated by FTIR spectroscopy through adsorption-desorption of pyridine. Fig. 8 shows the FTIR spectra in the hydroxyl region of MWW pillared materials, being detectable vibration bands at ~3620 cm⁻¹ and 3670 cm⁻¹ which correspond to surface bridged hydroxyl groups associated to framework Al–OH–Si and extra-framework aluminum species generated upon
calcination process, respectively. Furthermore, the vibration bands centered at ~3730 and ~3748 cm\(^{-1}\) were assigned to internal and external silanol groups, respectively [50].

In detail, vibration band at ~3620 cm\(^{-1}\) (BAS) is clearly detectable in the spectra of calcined 3D-MCM-22 and pillared 16-S-10-P samples, confirming that bridged hydroxyl groups (Al-OH-Si) are preserved after soft swelling and consecutive pillaring processes [51]. At the meantime, vibration band intensity located at 3748 cm\(^{-1}\), assigned to the presence of external silanol groups, was notably increased for 16-S-10-P and 16-A-10-P samples due to intercalated silica pillars placed in the interlayer space. Moreover, vibration bands centered at ~3729 cm\(^{-1}\), associated to surface silanol groups, decreased after pillaring process, indicating that silica pillars interacted with external silanol groups present in the MWW layers.

All pillared MWW materials contained acidic sites with different strength which were detected using pyridine as adsorbed probed molecules (values in Table A8). Specifically, vibration bands at 1610 cm\(^{-1}\) (also 1453 cm\(^{-1}\)) and 1544 cm\(^{-1}\) (also and 1635 cm\(^{-1}\)) are characteristics of pyridine adsorbed on Lewis (LAS) and Brønsted (BAS) acidic sites, respectively. In addition, vibration band observed at 1447 cm\(^{-1}\) is assigned to hydrogen bonded species by interaction with hydroxyl groups on the zeolite surface [51].

The IR spectra showed that the intensity band focused on 1544 cm\(^{-1}\) decreased after pillaring process which indicated that the number of BAS was “diluted” by insertion of silica pillars. This decreasing is pronounced in materials obtained through aggressive swelling treatment 16-A-10-P and more significantly to 18-A-10-P sample that possesses more disordered pillar and favored partial amorphization of the MWW layers which suggests considerable non-zeolitic component. On the other hand, LAS estimated by the vibration band intensity centered at 1454 cm\(^{-1}\) was higher for 16-A-10-P sample due to aluminum extra-framework present in the solid after aggressive swelling and consecutive pillarization post-synthesis treatments.

The characterization results showed that through the combined action of swelling conditions (soft or aggressive) and interlamellar agents, with different molecular dimensions, modulation of physico-chemical and morphological nature of derivative MWW-type materials is possible. Different accessibility level achieved together with preserved acidity in the obtained MWW pillared zeolites open the possibility to analyze and evaluate these materials from catalytic point of view.

3.8. Catalytic test

In fact, molecular size of fructose (0.85 nm) and 5-HMF (0.59 nm) limits their access and diffusion through internal two-dimensional 10 MR sinusoidal channels of MWW zeolite (0.40 × 0.55 nm), the reaction being presumably carried out in external active sites located in the surface of MWW individual layers. Fig. 9 shows fructose conversion and 5-HMF yield using MWW materials as heterogeneous catalysts. Blank test reaction (without solid catalyst) led 8% and 15% of yield for 5-HMF after 1 and 3 h, respectively, similarly to those reported in the bibliography for the same reaction conditions [52]. In our case, all MWW materials were active to fructose dehydration, reaching conversions close to 100% after 3 h.

Conventional 3D MCM-22 zeolite (C) showed 61% of yield for 5-HMF in 2 h, confirming that probably certain diffusional problems
limit the reaction process, being performed in the external surface of zeolite crystals. However, the obtained yield was higher compared with other microporous commercial β zeolite (51%) and similar to hollow mesoporous β zeolites (63%) [33,53]. After 3 h of reaction, 5-HMF yield progressively decreased up to 57% after 5 h (not shown). This tendency was due to cocking formation on active sites or secondary reactions which rehydrate final product, forming presumably insoluble humins (brown products were visible at final reaction), formic acid and levulinic acid. Indeed, levulinic acid was identified between 2 and 5 h of reaction process.

Specifically, disordered/pillared 12-S-10-P material showed a yield of 68% for 5-HMF within 3 h of reaction. The high activity achieved can be due to order absence of MWW layers perpendicularly aligned to axis c which partially opened external surface of 12 MR supercages, previously inaccessible in the 3D calcined MCM-22 (C). This effect increased external surface and accessibility of the pillared material, being preserved the starting MWW structure and the Si/Al molar ration (Si/Al = 28). However, levulinic acid was identified, as well as a decrease of 7% in the 5-HMF yield after 1 h and 3 h of reaction, respectively.

In the case of pillared 16-S-10-P, 16-A-10-P and 18-A-10-P materials, maximum conversion and yield were reached within 2 h of reaction because swelling, pillaring improved catalyst accessibility and reactant diffusion of reactant and products to active sites. In detail, higher conversion and yield was achieved for pillared 16-S-10-P sample and 18-A-10-P samples within 45 min of reaction. Indeed, turnover frequencies (TOF, Table 2) showed highest activities for both materials. Even, 16-S-10-P material which exhibited similar specific surface area, achieved higher performance (78% for fructose conversion and 51% for 5-HMF yield) than 16-A-10-P sample (46% and 30%, respectively). This difference may be related to higher MWW layer integrity obtained in the pillared materials swollen through soft conditions that avoided structure amorphization. Hence, soft swelling treatment favored the formation of more robust (without amorphous phases), accessible and active pillared MWW catalysts.

The pillared 18-A-10-P sample showed best performance within 1 h of reaction, reaching 85% and 65% for fructose conversion and 5-HMF yield, respectively. Even, although acidity decreased (Table S10), 18-A-10-P material showed higher catalytic activity. This shows that fragmented structure created by partial dissolution of layers together with a high distribution of mesopores created by pillaring (layers which increased the access to active sites located in the external supercages) were more effective than layer structure preservation of the 16-S-10-P sample for this reaction conditions used. As result, dehydration was favored, facilitating products diffusion and achieving higher 5-HMF yield (67%) than 16-S-10-P within 2 h of reaction and maximal yield within 3 h (69%). The DTG (see Fig. A10) for pillared MWW materials used as catalysts and recovered after 3 h of reaction showed total weight losses of 25, 20, 20 and 28% for 3D calcined MCM-22 (C), 12-S10-P, 16-S-10-P, 16-A-10P and 18-A-10 samples, respectively. These values confirmed that partial deactivation of the catalysts could occur, being associated to cocking formation and consequent coke deposition on active sites, this effect being more acute for pillared samples where active sites were more accessible.

### 4. Conclusions

We have demonstrated that surfactant molecular dimensions play a key role during the swelling of MWW precursors, generating a valid alternative route to obtain derivative MWW-type zeolites with controlled physico-chemical and morphological nature, being possible to establish both accessibility level and associated acidity through desilicication effect. Soft and aggressive treatments, using C12TA+ as swelling agent, produce partial disordered/pillared materials, and in the case of aggressive methodology, even desilication. Swelling with C16TA+ surfactant leads pillared materials with minimal structure damage by soft swelling. Aggressive swelling with C18TA+ and C25TA+ create pillared MWW with more mesoporosity range and structure damage. The MWW materials demonstrate potential use for fructose conversion, especially pillared MWW-type zeolites which exhibited higher 5-HMF yield in just 45 min of reaction.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.micromeso.2016.11.007.

### References


