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Optimization of ammonium fluoride route to hierarchical ZSM-5 zeolites

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Abstract

Preparation of hierarchical zeolites via a chemical etching is a hot topic as it strongly improves microporous material's diffusive properties and thus their catalytic activity. However, an issue that is often neglected is the softening the post-treatment condition. Herein we we report the optimization of NH_4F etching, using less concentrated solutions and milder treatment conditions. Following characterization by ICP-AES, XRD, ^{27}Al MAS NMR, TEM, and N_2 physisorption, it has been shown that it is possible to soften the post-treatment conditions by playing with three synthesis parameters: (1) Decreasing the $\text{NH}_4\text{F}/\text{ZSM-5}$ wt/wt ratio allows the generation of mesopores of different diameter (from 27 to 55 nm); (2) Decreasing the etching time provides precise control over the textural properties of the hierarchical ZSM-5; (3) Decreasing the initial NH_4F weight concentration also allows to tune the pore diameter from large (55 nm) to a small mesopore (5 nm).

Introduction

Zeolites are crystalline aluminosilicates presenting microporous networks (0.25 - 1 nm). These materials are extensively used in refining and petrochemical processes as catalysts but also to perform adsorption/separation [1–3]. Their high activity and selectivity are mostly associated with the strong acidity and the topology of microporous network, respectively [3]. If microporosity is one of the major advantages of zeolites, it's also a drawback as it causes diffusion limitation. Indeed, extensive diffusion path length favor secondary reactions leading to the deactivation of the catalyst and thus to the reduction of its lifetime. To overcome this problem, hierarchical zeolites, that is to say, zeolites presenting a secondary porosity (i.e., meso- and/or macro-porosity), have been synthesized by using two main strategies [4–6]. The first one, called *bottom-up* or *constructive approach*, allows to generate mesoporosity during the synthesis of the zeolite by adding mesoporegen agents. The mesoporegens could be hard template like carbon black, carbon nanotube, silica nanosphere, resins, polymers or soft template like surfactants. Mesopores are also formed by the self-assembly of nanosized zeolites with or without using supramolecular templates. Unfortunately, the bottom-up methods are not easily scalable to the industrial level, notably because of the use of costly templates, whereas post-synthetic treatment (i.e., *top-down* methods) can be easily transfer at an industrial scale [7,8].

The second strategy, called *top-down* or *destructive*, involves post-synthetic etching, such as selective dealumination and desilication. Up to now, most of the hierarchical MFI zeolites, prepared by the top-down approach, have been obtained via the desilication process, which was first reported in 1967 for mordenite [9]. According to the literature, the introduction of mesopores in MFI is optimal in the Si/Al window of 25 - 50 [8,10,11]. In these conditions, hierarchical zeolites present interconnected mesopores accessible from the external surface [5,11] while preserving the long-range order of the zeolite framework [10–12]. In addition, such treatments greatly enhance the molecular diffusion of branch alkane [13,14] and xylene [14] but also the accessibility to bulky molecules [15]. However, desilication treatment decreases the Si/Al ratio, which is known to be directly related to the Brønsted acid strength and, thus, to the catalytic activity and selectivity [10,11,15]. For Si/Al lower than 25, alkaline treatment induces the deposition of Al-rich debris that increases the number of Lewis acid sites and reduces the accessibility to the micropores and Brønsted acid sites [15,16]. However, a second post-treatment, with diluted HCl aqueous solution, allows removing a substantial part of Al-

rich debris from the mesopores and the accessibility to the micropores and the Brønsted acidity [16,17]. For MFI samples with Si/Al ratios higher than 50, the formation of mesopores is hampered due to the unselective dissolution of the zeolite framework [10,16].

More recently, an alternative way has been developed to prepare hierarchical ZSM-5 and pure silica MFI with either macro or mesopores using fluoride medium etching [18–22]. In the specific case of silica MFI, it has been shown that diluted HF in water or in acetone can be used to create holes and voids of approximately 0.1 to 1 μm in coffin shaped MFI crystal of about 200 μm length [22]. Diluted HF solutions were also used to preferentially etch latent track formed during ^{238}U ion beam irradiation allowing the preparation of parallel macropores [18]. The methodology was further extended to using NH_4F -HF solution [19] to add macropores and/or large mesopores to ZSM-5. If diluted HF solution is selective to Al, HF solution buffered with NH_4F removes Al and Si unbiasedly from the zeolite framework. Recently, it has been demonstrated that a pure NH_4F solution enables the preparation of hierarchical ZSM-5 in a more controllable manner [20,23]. Indeed, this treatment results in the unbiased extraction of Al and Si from MFI-type material by preferentially dissolving lattice defects and thus zeolites with whatever framework composition. It finally results in the generation of rectangular mesoporous voids of 10 to 40 nm while preserving the zeolite's crystallinity and micropore volume [20]. It can be under

According to the results from Qin et al. [20,21], the superiority of the NH_4F etching in comparison to desilication is its capability to create mesoporous voids while preserving the Si/Al ratio, the crystallinity, the microporosity and the concentration of acid sites of the ZSM-5. It has been also shown that this method can be applied to Silicalite and ZSM-5 with Si/Al ratio from 16 to 55 [20,21] but also to a large variety of zeolite structures (MOR [20], CHA [24], LTL [25]). Finally, this method has also the advantage to directly convert NH_4 -ZSM-5 into hierarchical NH_4 -ZSM-5, thus no need of performing several $\text{Na}^+/\text{NH}_4^+$ exchange as in the case of the desilication method. However, the treatment reported by Qin et al. [20] is relatively harsh, using extensive amounts of NH_4F .

This aim of this study, which follows on from the work of Qin et al. [20,23], is to show how this simple method can be used to create secondary porosity of controlled size. Thus, in this contribution, we will study the influence of the post-treatment conditions (i.e., initial NH_4F concentration, $\text{NH}_4\text{F}/\text{ZSM-5}$ wt/wt ratio, and etching duration) on the evolution of the porous structure, but also on the crystallinity and chemical composition. The ultimate materials and

their intermediates were subjected to textural analysis by N₂ adsorption and by TEM. The structural changes have been followed by XRD and ²⁷Al NMR spectroscopy, and the chemical composition by ICP-OES.

1 Experimental

1.1 Materials preparation

A commercial H-ZSM-5 sample (Grace Davison; Si/Al = 17) was used as a parent material to prepare hierarchical materials. Prior to treatment, the parent zeolite was brought into the ammonium form by three successive ion exchanges at 333 K for 6 h with 1 M NH₄Cl aqueous solution (20g of solution/g of zeolite).

In the *first set of experiments*, the concentration of NH₄F solution was kept constant, and the amount of NH₄-ZSM-5 was varied. In contrast, in the *second set of experiments* the concentration of the NH₄F solution was varied, keeping the concentration of zeolite constant. Thus, not only the NH₄F concentration but also the solid:liquid (zeolite:solution) ratio was varied.

The *first set of experiments* has been performed as follows: 8 g of NH₄F (98%, Sigma-Aldrich) has been dissolved in 12 g of distilled water under mechanical stirring (400 rpm) at 323 K. Then, between 1 and 4 g of NH₄-ZSM-5 was introduced into the solution and let under mechanical stirring (400 rpm) for 2 h at 323 K (Table 1). Intermediate samples have been taken out after 0.5, 1.0, and 1.5 h of reaction. Finally, the resulting materials have been thoroughly washed with distilled water and dry at 373 K overnight.

In the *second set of experiments*, between 8 and 0.25 g of NH₄F (98%, Sigma-Aldrich) was dissolved in 12 g of distilled water under mechanical stirring (400 rpm) at 323 K. Then, 1 g of NH₄-ZSM-5 was introduced into the solution and let under mechanical stirring (400 rpm) for 2 h at 323 K (Table 1). Intermediate samples were taken out after 0.5, 1.0, and 1.5 h of reaction. The resulting materials have been thoroughly washed with distilled water and dried at 373 K overnight.

Table 1: Amount of ZSM-5, NH₄F, water, and concentration of NH₄F used for each preparation.

	First set of experiments			Second set of experiments						
m(NH ₄ -ZSM-5) (g)	1	2	4	1						
m(NH ₄ F) (g)	8			8	6	4	2	1	0.5	0.25
m(water) (g)	12			12						
NH ₄ F content (wt%)	40			40.0	33.3	25.0	14.3	7.7	4.0	2.0

The samples were denoted NH₄F(X)-ZSM-5(Y)-Z, where X and Y respectively stand for the weight of NH₄F and NH₄-ZSM-5 in gram per 12 g of water, and Z is the reaction time in hours.

The maximum yield of modified zeolite (%Y_{max}) has been calculated from the total amount of material collected as follow:

$$\%Y_{\max} = \frac{\sum m_t}{m_{\text{ini}}} \times 100$$

where m_t is the weight of zeolite taken for different treatment times and m_{ini} is the initial weight of zeolite.

1.2 Catalyst characterization

Elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) using an OPTIMA 4300 DV (Perkin-Elmer) instrument.

X-ray diffractograms (XRD) were recorded at the ambient atmosphere on a PANalytical X'Pert Pro diffractometer using the Copper K_α radiation ($\lambda = 154.18$ pm). XRD measurements were performed from 5 to 50° (2 θ) in steps of 0.0167° with a count time of 150 s for each point.

²⁷Al MAS NMR spectra were recorded at 11.7 T on a Bruker Avance III HD 500 MHz spectrometer. NMR experiments were performed at ambient atmosphere on a 4 mm MAS probe

head using a spinning speed of 14 kHz and a recycling delay of 1s. The $\pi/12$ pulse length (selective pulse) was 2.5 μ s. Thanks to the $\pi/12$ pulse, the signal intensities are proportional to the amount of the different species [26]. Finally, it has been verified that the pulse length does not lead to any signal loss. Chemical shifts were referenced to a 0.1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution. In order to able the comparison, all spectra were normalized to 50 mg of dry zeolite.

Nitrogen adsorption isotherms were measured at 77 K on a TriFlex apparatus (Micromeretics). Prior to the analysis, all samples were outgassed at 573 K for 5 hours to a pressure < 0.2 Pa. The surface areas were determined from nitrogen adsorption values for seven relative pressures (P/P^0) ranging from 0.11 to 0.25 using the BET method. The microporous volumes and external surface area (S_{ext}) were determined with the t-plot method, where the thickness of the nitrogen layer was calculated from the Harkins and Jura equation and the total pore volumes (V_{tot}) were calculated from the amount of N_2 adsorbed at $P/P^0 = 0.99$. Finally, the mesoporous volume was estimated by calculating the difference between the two previous values ($V_{\text{meso}} = V_{\text{tot}} - V_{\text{micro}}$). The mesoporous size distribution was obtained by the BJH model applied to the desorption branch of the isotherm. As for t-plot analysis, the thickness of the nitrogen layer used to evaluate the pore diameter, was calculated from the Harkins and Jura equation.

Transmission electron microscopy (TEM) images were recorded with a JEOL TEM 100 CXII electron microscope operating at an acceleration voltage of 100 kV and equipped with a Keenview Camera. For TEM observations, the sample powders were deposited on 2.3 mm copper grid coated with an amorphous carbon film. The samples were prepared by dispersing in pure alcohol using ultrasonic cleaner and putting a drop of this suspension on carbon films on copper grids and purified with plasma cleaner.

2 Results and discussion

2.1 Study of the influence of the weight concentration of zeolite

In the first part of the study, from 1 to 4 g of zeolite was treated in 20 g of a 40 wt% NH_4F solution (see Table 1 for more details).

2.1.1 Structure of the etched samples

The impact of the treatment on zeolite crystallinity has been followed by XRD. Figure 1(a) shows the X-Ray Diffraction pattern of parent NH_4 -ZSM-5 and fluoride etched samples after

2h of treatment. Whatever the initial amount of NH₄-ZSM-5 used, XRD patterns present intense and narrow peaks characteristics of highly crystalline MFI structure. A careful analysis of the XRD patterns does not evidence amorphization of the structure, which could be detected via an increase in the intensity of the baseline and a decrease in the intensity of the peak characteristics of the MFI compared to those of the parent one. In addition, XRD patterns do not show additional peaks and notably those of (NH₄)₃AlF₆ ($2\theta = 17.2^\circ$ (111); 19.9° (200) and 40.5° (400) [27]) and (NH₄)₂SiF₆ ($2\theta = 18.3^\circ$ (111); 21.2° (200); 37.1° (222) and 43.1° (400) [28]). This indicates that a careful washing of the treated zeolite avoids the presence of fluoride compounds originating from the dissolution of the parent zeolite. It can also be noted that samples obtained after etching times of 0.5, 1.0, and 1.5 h are equally well crystallized and free of secondary phases (see Figure S1) independently of the initial solid:liquid ratio.

The study of the structure of the modified zeolites has been completed by ²⁷Al MAS NMR analysis, which provided local information on the Al environment. Figure 1(b) presents the normalized ²⁷Al MAS NMR spectra of the pristine and etched zeolites after 2 h of treatment. The parent NH₄-ZSM-5 exhibits a major peak at 55 ppm and a very small one at 0 ppm attributed to Al in tetrahedral coordination in the ZSM-5 framework and Al in the octahedral environment due to extra-framework species, respectively [17]. According to the respective area of these two peaks, the octahedral Al is no more than 1% of the total amount of aluminum atoms. ²⁷Al MAS NMR spectra of the etched samples also present the two peaks at 55 and 0 ppm. However, in the case of NH₄F(8)-ZSM-5(1)-2, where only 1 g of zeolite has been treated in a solution containing 8 g of NH₄F, the NMR spectrum evidences a third peak at -20 ppm attributed to AlF₃ [29]. This specie, which counts about 20 % of Al, has been solely observed in this sample. For the other samples treated for 2h (Figure 1.b) or less (Figure S2), the percentage of tetrahedral Al is always in the 99-97 % range and the remaining 2-3% aluminum is in octahedral environment. Thus, the peak at -20 ppm observed in the specific case of NH₄F(8)-ZSM-5(1)-2 has been attributed to a problem of washing. Indeed, during the etching step, the zeolite is partially dissolved into Si and Al fluoride species (such as AlF₃, (NH₄)₃AlF₆, (NH₄)₂SiF₆) that can precipitate or deposit at the external or internal surface of the zeolite. This point highlights the importance of the mandatory washing step to remove all fluoride species from the sample. This step is even more crucial when a large excess of ammonium fluoride treats a “small” amount of zeolite as it results in an extensive dissolution of the zeolite. The normalized ²⁷Al MAS NMR spectra to the same weight of dry NH₄-ZSM-5 does not show the

depletion of the Al_{tetra} peak during the etching independently of the treatment conditions (i.e., initial zeolite weight and etching time), which further evidences the preservation of tetrahedral Al.

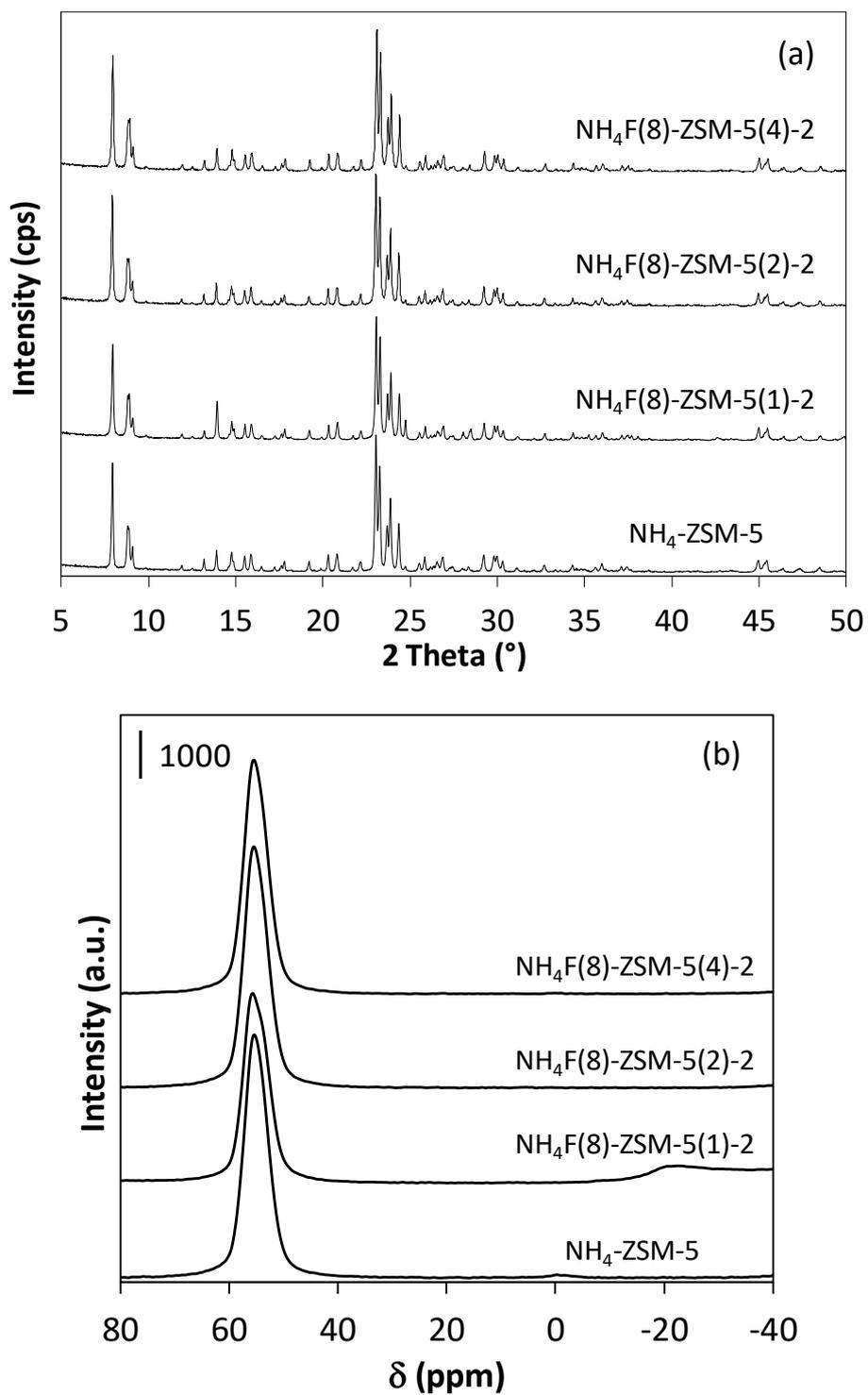


Figure 1: Impact of solid:liquid ratio on the zeolite structure characteristics: (a) XRD patterns and (b) ^{27}Al MAS NMR spectra of the parent $\text{NH}_4\text{-ZSM-5}$ and samples etched 2 h in a 40 wt% NH_4F solution.

Briefly, whatever the solid:liquid ratio and etching time, the crystallinity of the zeolite as well as the local environment of the aluminium have been maintained. These results are in agreement with those obtained with ZSM-5 samples with Si/Al ratio between 16 to 46 etched with a 40wt% solution of NH_4F in an ultrasonic bath [20] but also on $\text{NH}_4\text{-ZSM-5}$ (Si/Al = 19) treated by HF or HF- NH_4F solutions [19]. Therefore, in agreement with previous studies the etching in fluoride medium preserves the intrinsic composition of zeolite, which is not always the case of other etching approaches. For instance, Verboekend et al. [16] have shown that a typical desilication treatment (0.2 M NaOH at 338 K during 30 mn) resulted in a crystallinity loss from 20 to 40 % depending of the Si/Al ratio. In our specific case (i.e. ZSM-5 with Si/Al = 17), a loss of crystallinity of 20 % can be expected. In addition, after such treatment, a significant amount of EFAL is present, which has to be removed by acid washing.

2.1.2 Composition of the etched samples and yield

As mentioned previously, the procedure described by Qin et al. [20] is relatively harsh. Indeed, as shown in Table 2, the initial F/(Al+Si) atomic ratio is equal to 12.4 when 1 g of $\text{NH}_4\text{-ZSM-5}$ is treated in a solution containing 8g of NH_4F , which is 2.1 times more than necessary to dissolve the zeolite into AlF_6^{3-} and SiF_6^{2-} ions. Increasing the zeolite content in the etching solution allows to reduce this ratio significantly. However, the quantity of NH_4F used is still sufficient to mineralize 100 and 50% of 2 and 4 g of pristine zeolite. Fortunately, in all cases, the treatment time is insufficient to dissolve the solid phase completely. Indeed, according to Table 2, even in the harsher condition, the yield of etched zeolite is 10 %. Furthermore, this value increases to 60% when the zeolite amount increases. Thus, improving the yield in hierarchical zeolite by simply increasing solid:liquid ratio is easy.

Table 2: Initial F/(Al+Si) atomic ratio of the NH₄F/ZSM-5/water suspension, maximum yield of etched zeolite (% Y_{max}) and Si/Al atomic ratio, and porosity characteristics of the parent and NH₄F treated ZSM-5.

Samples	F/(Al+Si) _{ini} ^a	% Y _{max}	Si/Al ^b	S _{BET} m ² g ⁻¹	S _{Ext} ^c m ² g ⁻¹	V _{micro} ^c cm ³ g ⁻¹	V _{meso} ^d cm ³ g ⁻¹
NH ₄ -ZSM-5	-	-	17	325	14	0.16	0.03
NH ₄ F(8)-ZSM-5(1)-2	12.4	10	13	299	40	0.14	0.23
NH ₄ F(8)-ZSM-5(2)-2	6.2	25	15	355	37	0.15	0.28
NH ₄ F(8)-ZSM-5(4)-2	3.1	60	14	360	31	0.16	0.18

(a) Initial atomic ratio in the NH₄F/ZSM-5/H₂O suspension; (b) ICP-OES analysis; (c) t-plot analysis; (d) V_{meso} = V_{tot} - V_{micro}

As previously reported [20,30], chemical analysis of the samples (Table 2) confirms that NH₄F etching has no significant effect on the composition of zeolite. Indeed, the Si/Al atomic ratio is close to the parent zeolite and in the range of the uncertainty of Si/Al ratio determination. This conclusion is confirmed by the Si/Al ratio of samples after different treatment duration (Table S1), which shows the erratic variation of this value (from 13 to 18).

2.1.3 Influence of the etching condition on the generation of a mesoporosity

Figure 2 presents the nitrogen adsorption isotherm (a) and the BJH pore size distribution (b) of the parent and the etched NH₄-ZSM-5. According to Figure 2(a), the pristine NH₄-ZSM-5 exhibits a type I N₂ adsorption isotherm characteristic of a purely microporous material. Figure 2(a) also evidences that no matter of etching conditions employed, all N₂ isotherms present a hysteresis loop in the 0.9-1 range of P/P^o indicative of the creation of “large” mesopores.

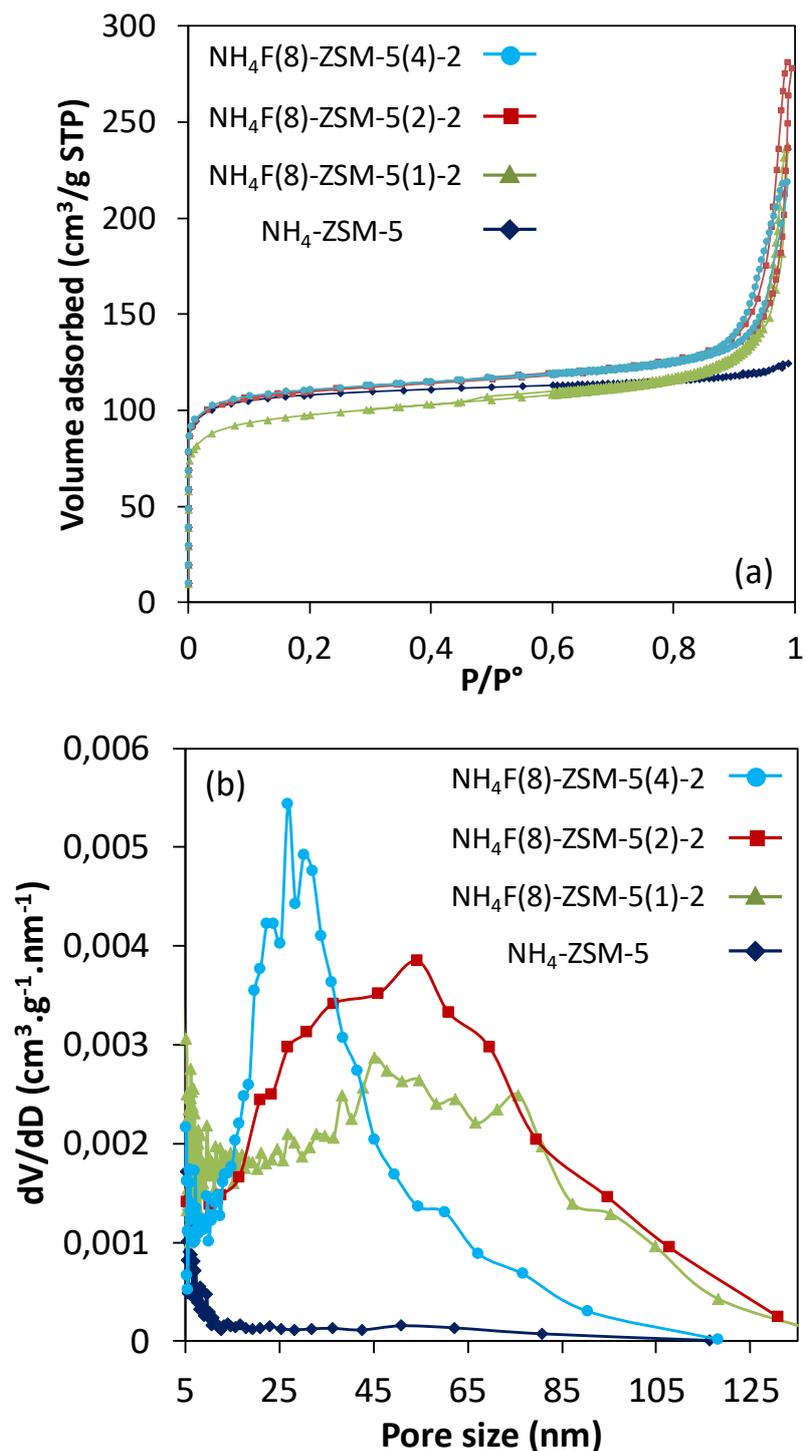


Figure 2: (a) N_2 adsorption isotherms and (b) BJH pore size distributions of the parent NH_4 -ZSM-5 and of samples etched 2 h in a 40 wt% NH_4F solution.

Noteworthy, the desorption branch is shifted to the lower P/P° values when increasing the ZSM-5/ NH_4F w/w ratio from 1/8 to 1/2. Then, playing with this parameter can adjust the mesopores diameter of etched zeolite. Indeed, Figure 2(b) shows a decrease in mean pore

diameter from 55 to 27 nm and a sharper pore size distribution when increasing the solid:liquid ratio.

Quantitative analysis of the different isotherms (Table 2) shows that NH_4F etching induces a slight increase in the BET surface area and the external surface area. Also a rise in the mesoporous volume (from 0.15 to 0.25 $\text{cm}^3 \text{g}^{-1}$) without significant modification of the microporous volume was observed. These values are fully in line with those reported by Qin et al. [20] for similar treatment.

This study has been completed by TEM analysis. The image of the pristine ZSM-5 shows uniform, well-defined crystals with average lengths and widths of about 400 and 200 nm, respectively, and the typical hexagonal morphology (Figure 3 (a)). After 2 h of etching and whatever the amount of zeolite used, TEM images evidenced the fragmentation of the ZSM-5 crystal (Figure 3 (b, c, d)) and/or the formation of mesopores channels (Figure 3 (c, d, h)). TEM images also reveal the presence of rectangular mesopores in most of the zeolite fragments, as clearly evidenced by Figure 3 (e and g). A closer inspection of those “rectangular” voids shows that even after high segmentation and deep etching, the ZSM-5 is still highly crystalline (Figure 3 (f)). It can be noted that all those results are in perfect agreement with those obtained by Qin et al. [20] with a ZSM-5/ NH_4F w/w ratio of 1/8, a reaction time and temperature of 1h and 323 K and the ultrasonication of the solution. Thus, our results evidenced that similar hierarchical materials can be obtained by using soft etching conditions (i.e., by increasing the solid:liquid ratio and avoiding ultrasonication).

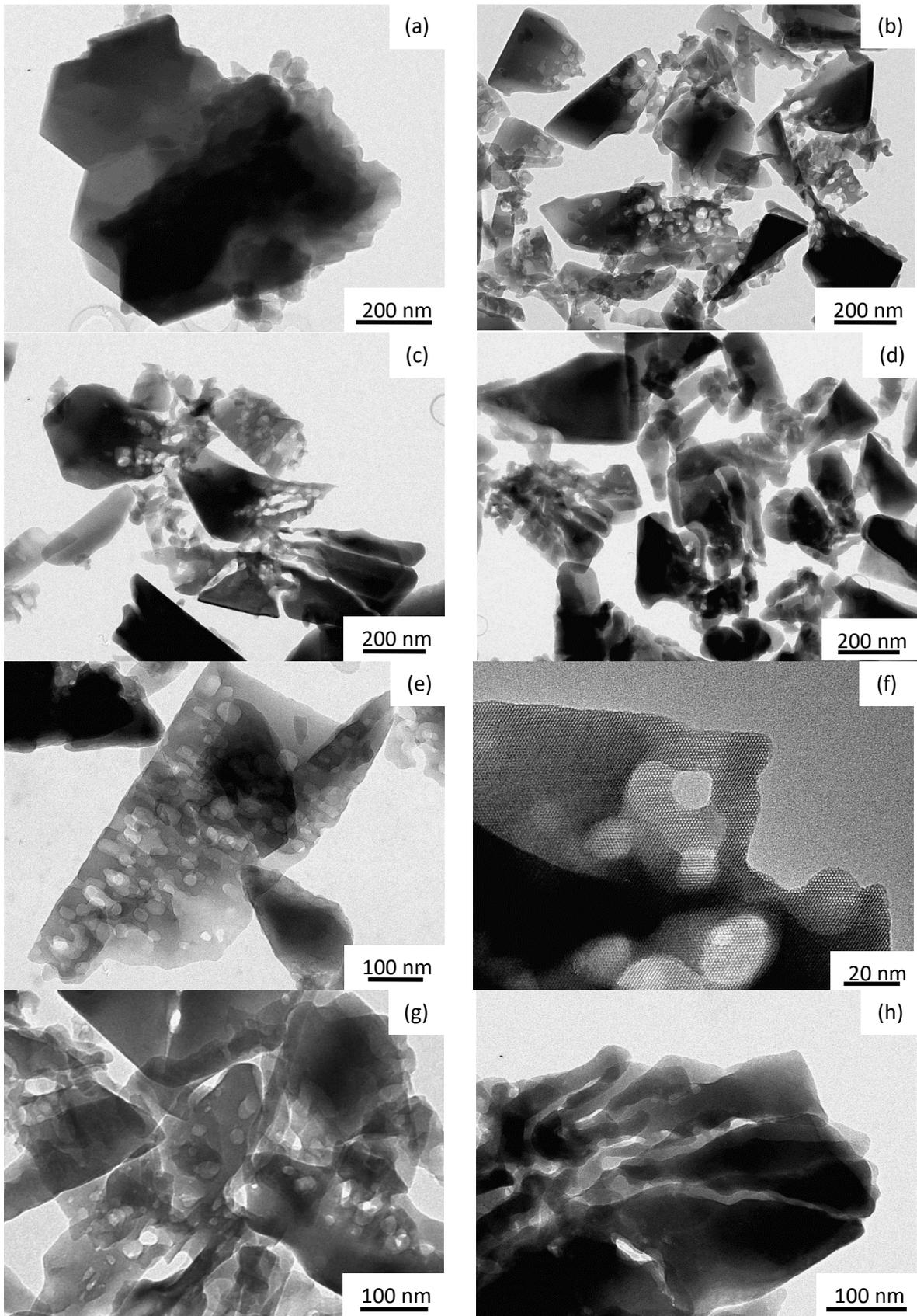


Figure 3: TEM monitoring of the dissolution of MFI as function of the amount of zeolite treated in 20 g of 40 wt% of NH_4F solution for 2h – (a) $\text{NH}_4\text{-ZSM-5}$; (b, e, f) $\text{NH}_4\text{F(8)-ZSM-5(1)-2}$; (c, g) $\text{NH}_4\text{F(8)-ZSM-5(2)-2}$; (d, h) $\text{NH}_4\text{F(8)-ZSM-5(4)-2}$

In conclusion, it is thus clear that after two hours of etching and by varying the ZSM-5/NH₄F w/w ratio, it is possible to create mesopores of different diameters without affecting the structural characteristics of the parent zeolite, and mostly by preserving the microporous volume. However, our study has evidence that for the lowest w/w ratio, the evolution of the mesopores diameter and volume stagnate or slightly decreases. This result suggests that the etching time is too long, resulting in zeolite dissolution without improving the porous characteristics.

2.1.4 Influence of etching time

To verify the above hypothesis, the duration of the etching time has been varied from 0.5 to 2h. As an example, Figure 4 presents the N₂ adsorption isotherms (a) and the pore size distributions (b) obtained for the highest ZSM-5/NH₄F w/w ratio (i.e., 1/2). Figure 4(a) clearly shows a shift of the position of the hysteresis loop to the lower P/P^o with decreasing the etching time, which is associated with a decrease in the pore diameter. This is confirmed by Figure 4(b), which evidenced a shift of the pore diameter from 27 to 11 nm, as well as a decrease in the width at half maximum. These textural modifications do not induce a significant change in the S_{BET}, S_{ext} and V_{micro} but a “strong” decrease of V_{meso} from 0.18 to 0.10 cm³ g⁻¹ (Table S1).

It should be noted that all these trends have been observed whatever the solid:liquid ratio was used. Indeed, when the amount of zeolite used was 1 or 2 g (i.e., ZSM-5/NH₄F w/w ratio = 1/8 or 1/4) the decreases in the etching time induces a shift of the pore size from 55 to 28 nm or from 54 to 16 nm (Figure S3). Also, a decrease of V_{meso} from 0.23 to 0.19 cm³ g⁻¹ or from 0.28 to 0.13 cm³ g⁻¹ (Table S1) and thus without modification of the microporous volume (Table S1).

The impact of the etching time is also observed by the TEM study. Indeed, after 1h of etching, images show highly fragmented zeolite for ZSM-5/NH₄F w/w ratio = 1/8 (Figure 5 (a)), whereas for higher ratio (i.e., 1/4 and 1/2), the TEM images indicate less and less advanced dissolution of crystal interfaces leading to the formation of mesoporous channels (Figure 5 (c and e)). With increasing etching time up to 2h, the highly fragmented zeolite leads to the formation of numerous mesoporous “rectangular” voids (Figure 5 (b)), whereas for a higher solid:liquid ratio, the dissolution conduce to the fragmentation of the zeolite crystals and the apparition of the first mesoporous voids (Figure 5 (d and f)).

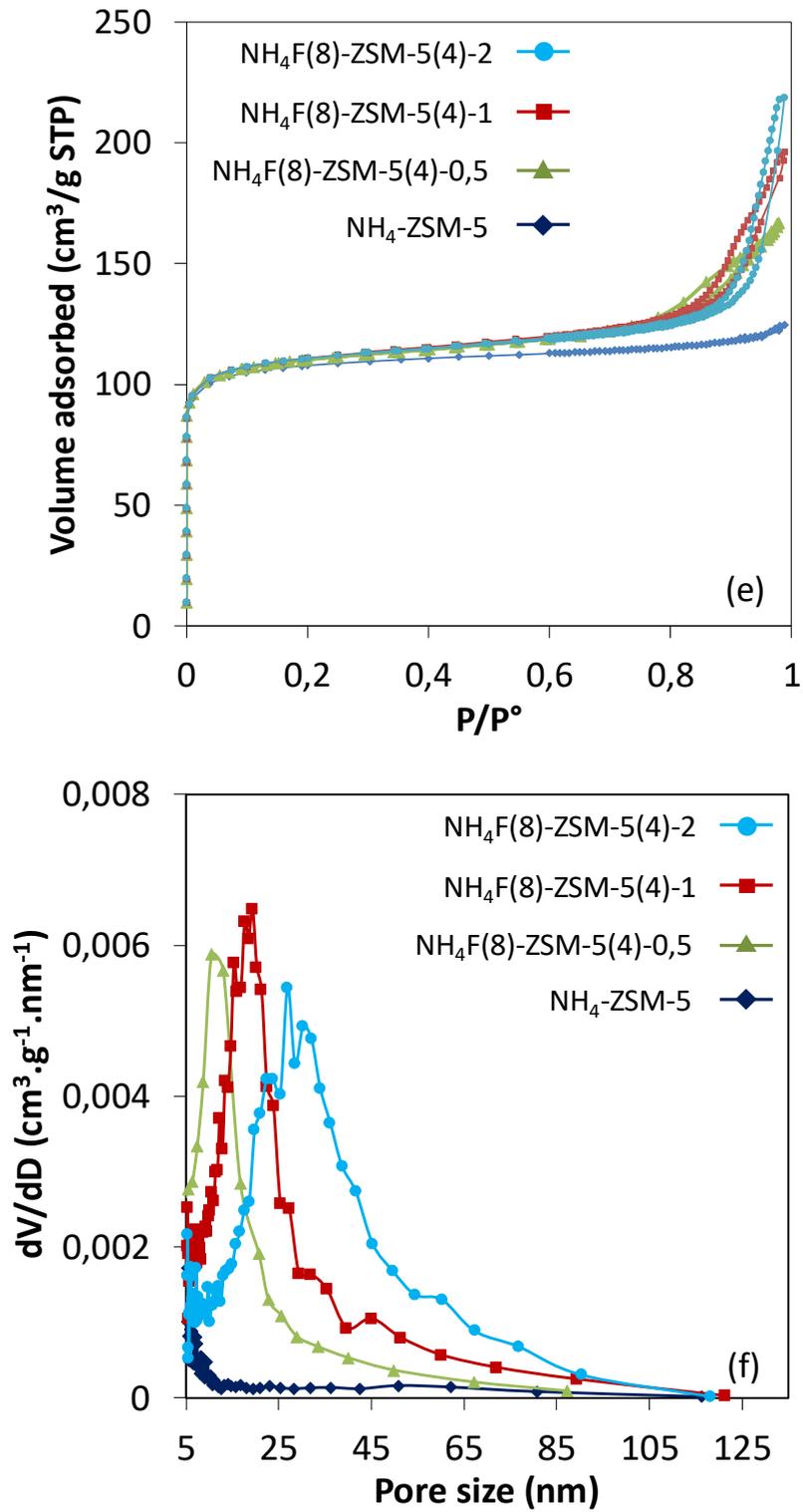


Figure 4: (a) N₂ adsorption isotherms and (b) BJH pore size distributions of the NH₄-ZSM-5 and of samples etched in 20 g of a 40 wt% NH₄F solution for 0.5; 1.0 and 2.0 h. Amount of zeolite used: 4 g.

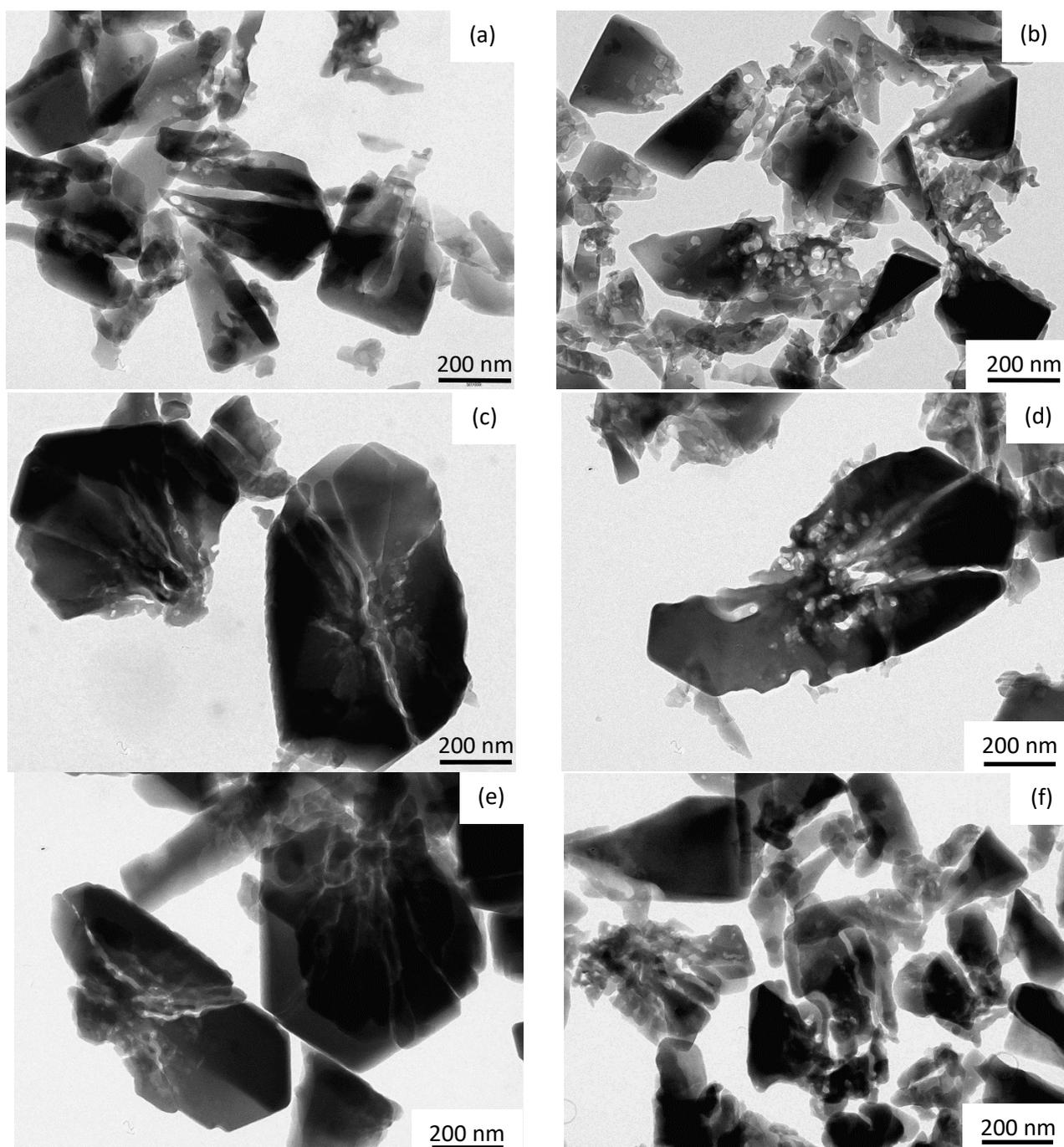


Figure 5 : TEM monitoring of the dissolution of 1 (a, b), 2 (c, d), and 4g $\text{NH}_4\text{-ZSM-5}$ (e, f) in 20 g of 40 wt% of NH_4F solution for 1h (a, c, e) and 2h (b, d and f)

To conclude, the nitrogen adsorption measurements have evidenced that the NH_4F etching of ZSM-5 under well-controlled conditions allows to adjust the mesopore diameter (from 55 to 11 nm) and the mesoporous volume (from 0.25 to 0.10 $\text{cm}^3 \text{g}^{-1}$) by simply varying the amount of treated zeolite (i.e., the solid:liquid ratio) or the etching time. Most importantly, these

modifications have been done by preserving the microporous volume as well as the structural integrity of the pristine zeolite.

The evolution of the porosity as a function of the treatment time is in line with the data presented in reference [20] (supplementary information) for samples prepared under ultrasonication for a shorter time (i.e., ≤ 1 h) with ZSM-5/ NH_4F w/w ratio = 1/8. This evidenced the reproducibility of the obtained results and that ultrasonication can be easily replaced by increasing the treatment time. Our study also evidenced that results obtained by Qin et al. could be reproduced even if the amount of treated zeolite is strongly increased (up to 4 times). Our results also showed the superior advantages of this NH_4F treatment in preserving the intrinsic properties of zeolites compared to the biased chemical etchings reported in the literature.

2.2 *Study of the influence of the weight concentration of ammonium fluoride*

In the first part of this study, it has been shown that it is possible to modulate the secondary zeolite porosity by solid:liquid ratio in the etching system. However, in all cases, the initial concentration of the ammonium fluoride solution was very high (40 wt%). The high concentration might strongly influence the dissolution kinetics of the zeolite and, thus, on the porosity of the final material. In this second part, the influence of this parameter has been studied by varying the NH_4F weight concentration from 40 to 2%. 1g of zeolite was treated for 2h (or less) at 323 K with a solution containing from 8 to 0.25 g of NH_4F and 12 g of water (for more details, see Table 1).

2.2.1 *Structure of modified ZSM-5*

The influence of the treatment on the crystallinity of the zeolites has been followed by XRD. Figures 6(a) and S4(a) show the X-Ray diffraction pattern of parent $\text{NH}_4\text{-ZSM-5}$ and fluoride etched samples after 2h of treatment. Whatever the amount of the initially employed NH_4F , no differences in XRD patterns of the treated samples was observed. It can be concluded that this parameter's variation does not induce alteration in the crystallinity of the MFI structure. Furthermore, the absence of peaks related to aluminum and silicon fluoride also evidenced that, in agreement with the conclusion of section 2.1.1., a careful washing of the treated zeolite avoids the presence of such compounds. It can also be noted that samples obtained after etching times of 0.5, 1.0 and 1.5 h are equally well crystallized and free of secondary phases independently of the initial weight concentration of NH_4F in the solution.

Analysis of pristine and etched NH₄-ZSM-5 by ²⁷Al MAS NMR (Figure 6(b) and Figure S4(b)) shows that whatever the initial concentration of the NH₄F etching solution (from 40 to 2 wt%), the local environment of Al atoms was preserved. Indeed, the peak at 55 ppm, attributed to tetrahedral Al, accounts for more than 98 % of the Al atoms for pristine and etched zeolites. In addition, normalization of the ²⁷Al MAS NMR spectra to the same weight of dry NH₄-ZSM-5 evidences the preservation of the aluminum loading as the same amount of sample containing the same amount of aluminum and thus independently of the etching conditions.

In conclusion, as for the variation of the weight of zeolite to treat, the variation of the NH₄F weight concentration of the etching solution does not alter the long range order in zeolite and the local environment of Al atoms.

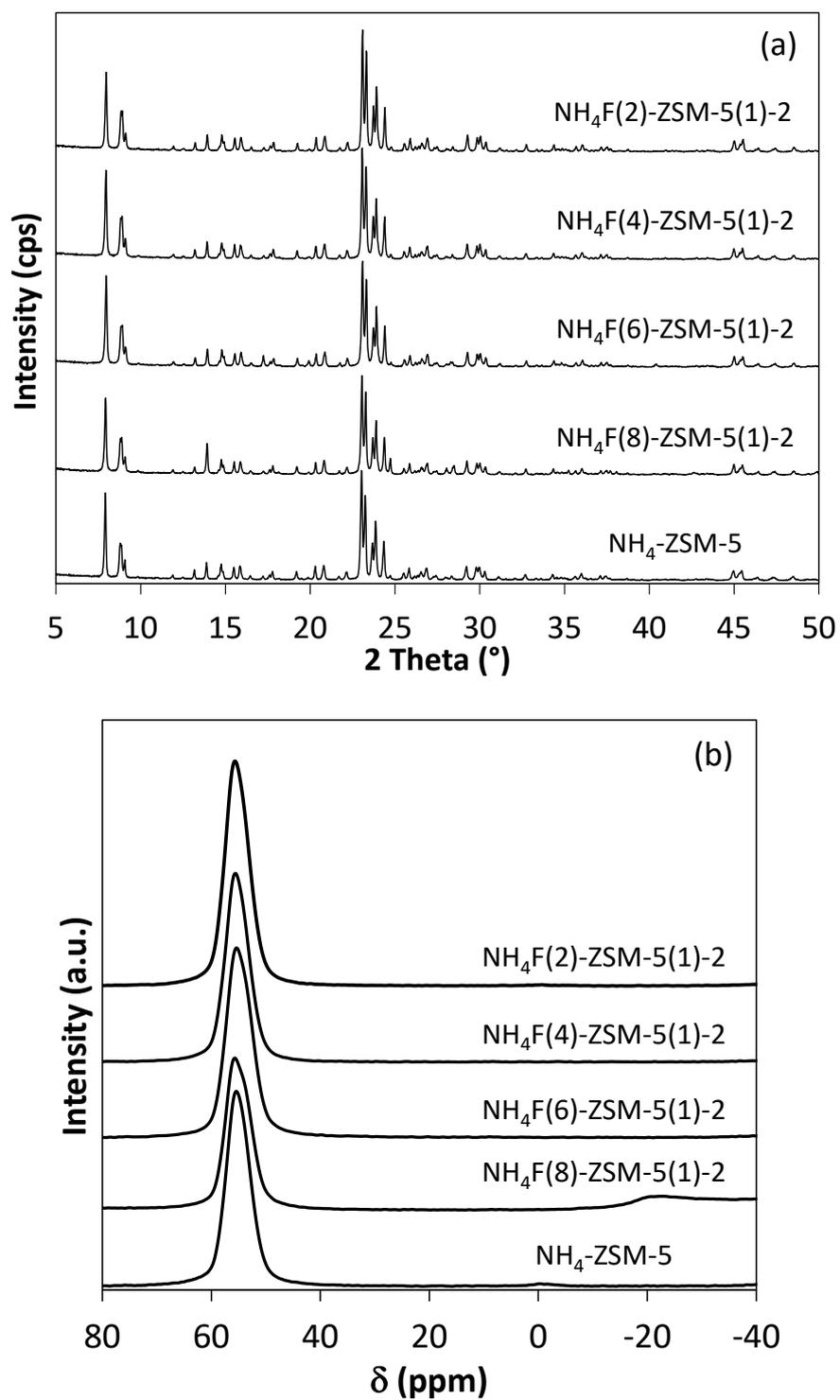


Figure 6: (a) XRD patterns and (b) ^{27}Al MAS NMR spectra of the parent $\text{NH}_4\text{-ZSM-5}$ and of samples etched 2 h in a solution containing from 8 to 2 g of NH_4F and 12g of water. Amount of zeolite used: 1 g.

2.2.2 Composition of the etched samples and yield of the post-treatment

Table 3 summarizes the evolution of the initial F/(Al+Si), as well as the maximum yield of post-treated ZSM-5 and the Si/Al atomic ratio in the etched samples as a function of the amount of NH₄F used. In this second set of experiments, the initial F/(Al+Si) has been varied from 12.4 to 0.4. Between 12.4 and 6.2, the amount of NH₄F is sufficient to fully mineralize the zeolite into AlF₆³⁻ and SiF₆²⁻ ions. The theoretical mineralization yield for a lower ratio falls to 7%. Fortunately, even for the highest amount of NH₄F, the treatment time is not sufficient to reach the maximum yield of dissolution of the zeolite. When the initial F/(Al+Si) atomic ratio decrease from 12.4 to 3.1, the yield of etched ZSM-5 sharply increases from 10 to 81%. For a lower F/(Al+Si) ratio, the yield still progresses to reach 95%. If this high value seems to be a good point, it is important to remember that such treatment aims to create extra porosity via the partial dissolution of the zeolite. So, a high yield is the sign of a low extent of dissolution and thus may be the absence of secondary porosity. This point will be then developed in the following.

As previously reported in the literature [20,30] and as previously observed for the first set of samples, NH₄F etching has no significant effect on zeolite composition. Indeed, the Si/Al atomic ratio (Table 3) presents similar values, close to parent zeolite.

Table 3: Initial F/(Al+Si) atomic ratio of the NH₄F/ZSM-5/water suspension, maximum yield of etched zeolite (% Y_{max}) and Si/Al atomic ratio and porosity of parent and NH₄F treated ZSM-5.

Samples	F/(Al+Si) _{ini} ^a	% Y _{max}	Si/Al ^b	S _{BET} m ² g ⁻¹	S _{Ext} ^c m ² g ⁻¹	V _{micro} ^c cm ³ g ⁻¹	V _{meso} ^d cm ³ g ⁻¹
NH ₄ -ZSM-5	-	-	17	325	14	0.16	0.03
NH ₄ F(8)-ZSM-5(1)-2	12.4	10	13	299	40	0.14	0.23
NH ₄ F(6)-ZSM-5(1)-2	9.3	16	18	325	39	0.15	0.34
NH ₄ F(4)-ZSM-5(1)-2	6.2	29	18	345	34	0.16	0.22
NH ₄ F(2)-ZSM-5(1)-2	3.1	81	18	339	34	0.16	0.13
NH ₄ F(1)-ZSM-5(1)-2	1.5	83	17	347	37	0.16	0.09
NH ₄ F(0.5)-ZSM-5(1)-2	0.8	94	17	325	39	0.15	0.06
NH ₄ F(0.25)-ZSM-5(1)-2	0.4	95	17	346	19	0.17	0.03

(a) Initial atomic ratio in the NH₄F/ZSM-5/H₂O suspension; (b) ICP-OES analysis; (c) t-plot analysis;

(d) V_{meso} = V_{tot} - V_{micro}

2.2.3 Influence of the etching condition on the generation of the mesoporosity

According to Figures 7(a, b) and S5(a), N₂ isotherms of etched ZSM-5 present a hysteresis loop in the 0.45-1 range of P/P°, which indicates that NH₄F weight concentration is an effective parameter to create mesopores of various diameter.

For the highest NH₄F concentration (from 40 to 25 wt. %), the hysteresis loops are mainly observed at P/P° higher than 0.9 (Figure 7(b)), which is characteristic of large mesopores. This is confirmed by the pore size distribution (Figure 7(c)), showing the wide distribution of “large” mesopores. However, figure 7(c) also shows that decreasing the concentration of NH₄F induces a decrease in the mean pore diameter from 55 to 35 nm.

For lower NH₄F concentration (from 14.3 to 2.0 wt. %), N₂ isotherms show hysteresis loops at lower P/P° (between 0.95 and 0.45), indicating smaller mesopores (Figure 7(b) and Figure S5(a)). Indeed, Figure 7(c) and Figure S5(b) show the narrower distribution of medium mesopores. In addition, decreasing NH₄F concentration induces the decrease of the mean pore diameter from 16 nm (14.3 wt. % NH₄F) to 13 nm (7.7 wt. % NH₄F) to above 5 nm (4.0 wt. % NH₄F) and further to below 5 nm (2.0 wt. % NH₄F).

Quantitative analysis of the N₂ isotherms (Table 3) shows a slight increase of BET surface area as well as external surface area (~ 20 m²/g for both) and thus without noticeable modification of the microporous volume. The mesoporous volume increase with increasing NH₄F concentration up to 0.34 g cm⁻³ and then decrease for the highest concentration. It can be noted that all these values are in agreement with those obtained for the first set of experiments and the ones obtained by Qin et al. [20].

Figure 8 presents TEM image of the pristine and treated ZSM-5. Figures 8(b) to 8(h) clearly evidenced that decreasing NH₄F concentration strongly influences the creation of mesopores. Indeed, for the most concentrated etching solution (i.e. sample NH₄F(8)-ZSM-5(1)), TEM images evidenced the fragmentation of the ZSM-5 crystal and/or the formation of large mesopores channels as well as numerous “rectangular” mesopores (Figure 8(b)). When decreasing the concentration of the etching solution from 33.3 to 7.7 wt. % (i.e., samples NH₄F(6)-ZSM-5(1) to NH₄F(1)-ZSM-5(1)), TEM images still reveal fragmentation of the ZSM-5 and the creation of mesopores, however, the pore diameter clearly decrease (Figure 8 (c to f)). In addition, if numerous “rectangular” voids are observed on sample NH₄F(6)-ZSM-5(1), their number decreases with the concentration of the etching solution used (Figure S6(a to d)).

Finally, for samples prepared with the less concentrated solution (i.e $\text{NH}_4\text{F}(0.5)\text{-ZSM-5}(1)$ and $\text{NH}_4\text{F}(0.25)\text{-ZSM-5}(1)$), only a few mesopores were observed (Figure 8 (g and h)).

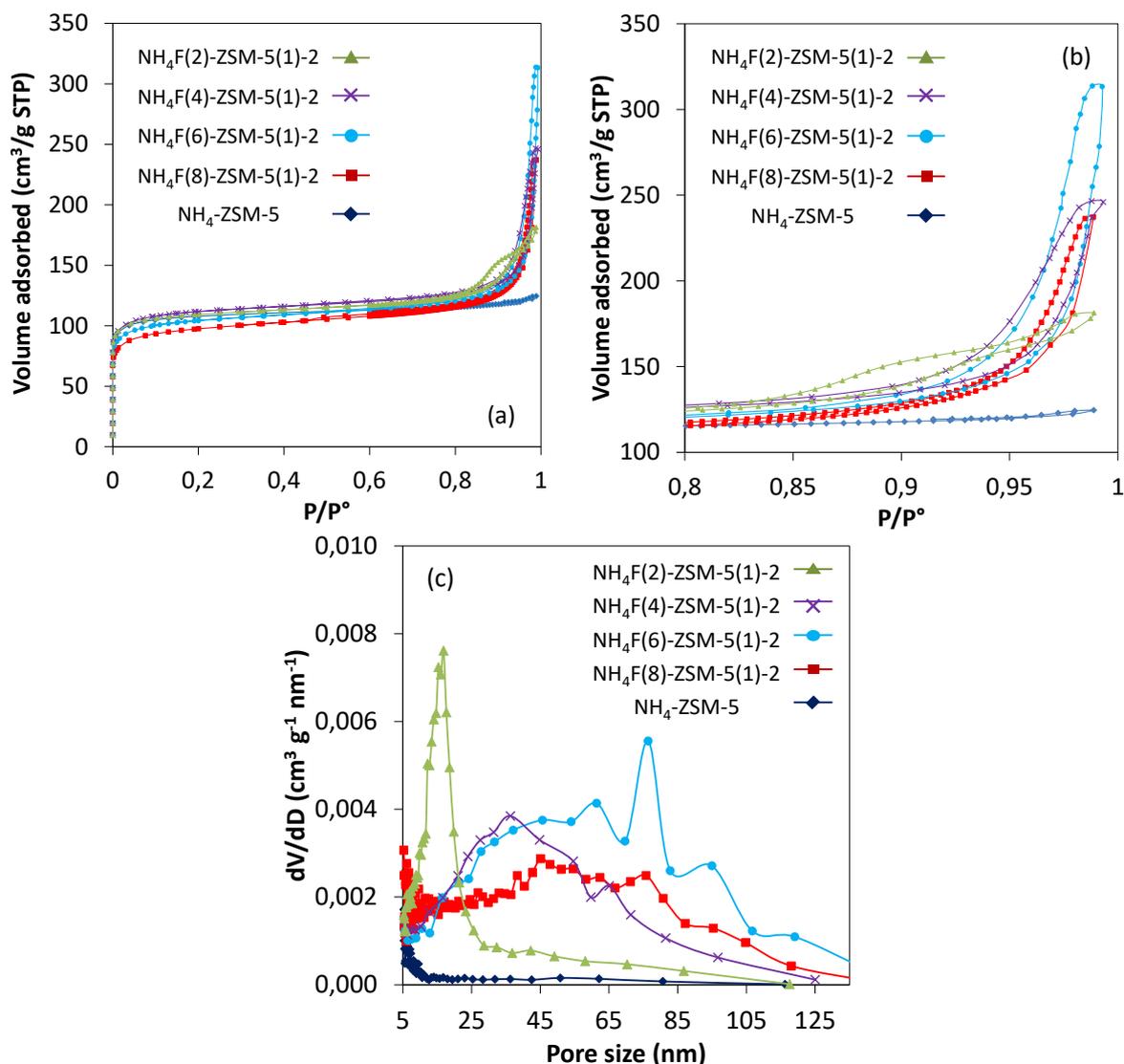


Figure 7: (a, b) N_2 adsorption isotherms and (c) BJH pore size distributions of the parent $\text{NH}_4\text{-ZSM-5}$ and the samples etched in a solution containing from 8 to 2 g of NH_4F and 12 g of water. Amount of zeolite used: 1 g.

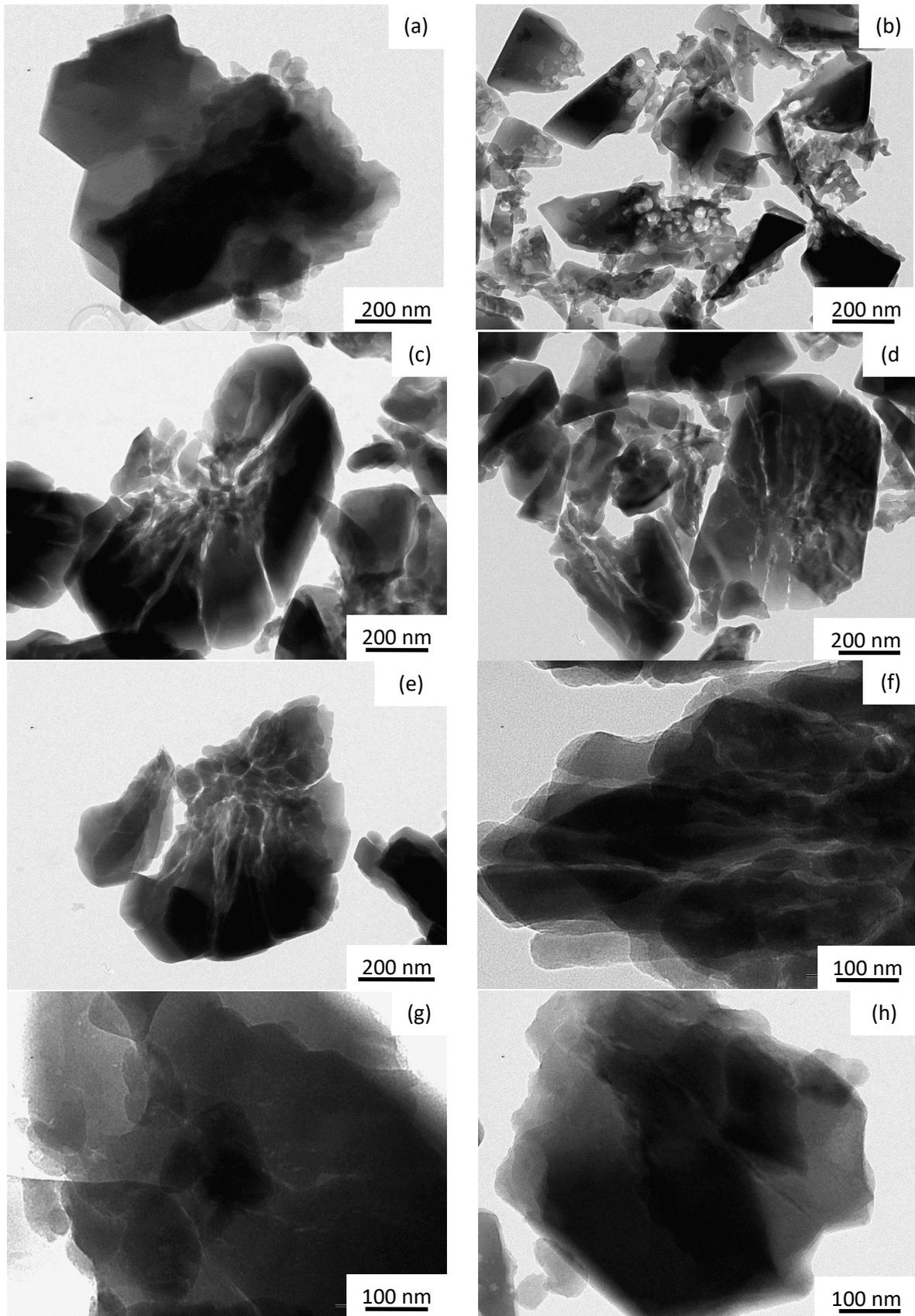


Figure 8: TEM monitoring of the dissolution of MFI as function of the weight concentration of NH_4F etching solution for 2h – (a) $\text{NH}_4\text{-ZSM-5}$; (b) $\text{NH}_4\text{F(8)-ZSM-5(1)-2}$; (c) $\text{NH}_4\text{F(6)-}$

ZSM-5(1)-2; (d) NH₄F(4)-ZSM-5(1)-2 ; (e) NH₄F(2)-ZSM-5(1)-2 ; (f) NH₄F(1)-ZSM-5(1)-2 ; (g) NH₄F(0.5)-ZSM-5(1)-2 and (h) NH₄F(0.25)-ZSM-5(1)-2

It can be concluded that the variation of the weight concentration of NH₄F in the etching solution allows the creation of hierarchical ZSM-5 with tuneable pore size from large to small mesopores without modification of the microporous volume and without alteration of the local and long range order of zeolite crystals.

3 Conclusions

Post-treatment of ZSM-5 by fluoride solution is already known to be an efficient way to obtain hierarchical zeolite with large mesopores and/or macropores [18–21]. Among fluoride post-treatment, the use of concentrated NH₄F solution has shown its efficiency by preserving Si/Al ratio, crystallinity, and micropore volume of the zeolite [20]. Herein we further optimized the NH₄F etching using less concentrated solutions and milder treatment conditions.

The set of experimental results has shown that it is possible to soften the post-treatment conditions by playing with three synthesis parameters:

- (i) Decreasing the NH₄F/ZSM-5 wt/wt ratio from 8 to 2 still allow the generation of mesopores of different diameter (from 27 to 55 nm).
- (ii) Decreasing the duration of the etching from 2 to 0.5 hours allows more precise control of the textural properties of the hierarchical ZSM-5. Indeed, by simultaneously play with NH₄F/ZSM-5 wt/wt ratio and etching duration, it is possible to vary the mesoporous diameter from 11 to 55 nm and the mesoporous volume from 0.10 to 0.28 cm³ g⁻¹.
- (iii) Decreasing the initial NH₄F weight concentration from 40 to 2 wt. %, also allows precise control of mesopores generation. By playing with this parameter is possible to tune the pore diameter from large mesopores (55 nm) to a small one (below 5 nm).

It is important to underline that, in agreement with previous results [20,21,23], all this post-treatment does not affect the zeolite composition (i.e., Si/Al ratio) and crystallinity, and retains the microporous volume of the parent zeolite.

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