Impact of the crystal size of beta zeolite on the structural quality of zeolite templated carbons

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Abstract

The impact of the crystal size of the template zeolite on the textural properties of resulting Zeolite Templated Carbons was studied using nano- (20 nm) and micron-sized (5 μm) zeolite beta crystals. ZTCs were obtained for both nano- and micron-sized zeolite beta crystals, yet for the micron-sized sample the presence of supermicropores and small mesopores was detected, indicating a higher degree of structural defects during the templating process and hence in the final ZTC. The insights gained from nitrogen physisorption were confirmed by TEM, TGA and XPS. Despite, long range structural order, evidenced by X-ray powder diffraction (XRD) for both, nano- and micron-sized ZTCs was inferred. These results suggests that XRD patterns allow to evidence the well-ordered part of the sample but might not be the method of choice for characterizing the structural quality of ZTCs. Simulated XRD powder patterns allowed to propose a graphene-based nanoribbon structure grown in the zeolite pores as a satisfactory model for ZTCs in beta zeolite.

Keywords: Zeolite templated carbon, beta zeolite, crystal size, XRD simulation.

1. Introduction

Zeolite templated carbons (ZTCs) have firstly been reported in 1997 by Kyotani and co-workers.¹ In recent years an important revival of these structured carbon materials has been observed.² ZTCs were recently coined as microporous 3D-graphenes.³ Indeed, ZTCs seem to bridge the gap between the well-known activated carbons, microporous in nature, featuring highly disordered structures of cross-linked, randomly packed graphene sub-units, and pure two dimensional graphene sheets. Based on computational modelling, ZTCs were claimed to feature Schwarzite structure.⁴ This latter assumption has yet recently been questioned.⁵

ZTCs are synthesized within the microporosity of zeolites and can hence be described as the negative carbon replica of a give structure. The highest quality of ZTCs is achieved through the reaction of small carbon precursors (*e.g.* ethylene or acetylene), which diffuse and polymerize in the extended microporous zeolite networks. The pure ZTCs is achieved after dissolution of the inorganic scaffold classically using concentrated hydrofluoric acid solutions. The important growth in the field of ZTCs can be ascribed to their interesting properties resulting from the combination of tailored micropore topologies and electrical conductivity,⁶ which makes them potentially interesting candidates in a number of applications, including electrochemical capacitors,⁷ batteries,⁸ and hydrogen⁹ and methane storage.¹⁰

Different parameters, such as the zeolite framework and the nature of the counterion have been studied in the quest to achieve ZTCs.² Merely three zeolite systems have been identified to allow for synthesizing high quality ZTCs, *i.e.* FAU, EMT and *BEA, which can be ascribed to the presence of large interconnected micropores. Different cations permit for the formation of high quality ZTCs including protons, alkali, alkaline earth and rear earth metal cations. The presence of transition metals, such as Mn^{2+} and Cu^{2+} has been reported to allow for the development of ZTCs and simultaneous to their incorporation into the ZTC structure.¹¹

The impact of the crystal size of the zeolite template on the quality of the achieved ZTCs has so far only scarcely been approached. Yet, tailoring the particle size could have important implications as far as their mass transfer properties are concerned.¹² Garsuch *et al.*¹³ compared ZTCs from the templating of small (0.5 μm) and large (3 μm) zeolite Y crystals and observed superior micropore volume for ZTCs resulting from the small crystals compared to the ZTC resulting from the large crystals. The authors indicated that this might result from diffusion issues of the carbon precursor within the zeolite microporosity during polymerization process and assumed that this would lead to unfilled pores in the center of the large crystals, hence to hollow-centered ZTC particles. Parmentier *et al.*¹⁴ studied the effect of the crystal size of beta zeolite templates comprised between 0.1 and 1 μm . Yet, all of the resulting ZTCs presented merely a single XRD peak centered at $7.7^\circ 2\theta$, indicating rather low-quality materials. On the basis of molecular simulations, it was recently proposed that the structure of the ZTC forming within larger zeolite crystals would differ (less dense structure) to that developing within small crystals (denser structure).¹⁵ The authors compared zeolite crystals of 40 vs. 300 nm, which might not present a sufficiently important size difference to observe a real impact of the crystal size on structural quality. Indeed, independently of the crystal size ethylene does not face diffusion limitations in large pore zeolites.¹⁶ For larger zeolite crystals with increasing carbon deposition some diffusional constraints could arise. This would yet rather result in the development of defects in the carbon structure rather than to radically different ZTC structures.

In the present contribution we investigate the templating ability of nano-sized (20 nm) with that of micron-sized (5 μm) zeolite beta by high resolution nitrogen physisorption and careful evaluation of electronic microscopy images and XRD patterns of the resulting ZTCs. Together with gathered insights from TEM, ATG and XPS this allowed us to identify defect development in the larger micropore range for the micron-sized ZTC. The development of

structural defects does not impede the observation of XRD long-range structural order. The observation of the XRD reflections could further be reasoned by computational simulation, by taking into consideration a ZTC structural model based on a nanoribbon network.

2. Experimental section

2.1 Materials

Hydrofluoric acid (48% in water, Sigma-Aldrich), sodium bicarbonate (Sigma-Aldrich, 99%), boric acid (Sigma-Aldrich, 99%), tetrapropylammonium hydroxide solution (TEAOH, Sigma-Aldrich, 35% in H_2O), tetraethylorthosilicate (TEOS, Sigma-Aldrich, 98%), aluminium (Fluka, 99%), ethylene (Air liquid, >99.5%) and nitrogen (Air liquid, 99.995%) were purchased and used as received.

2.2 Zeolite templates N- and M-BEA

Nano-sized beta zeolite (N-BEA) was purchased from PQ corporation with the reference CP811 BL-25 (H^+ form). Micron-sized beta zeolite (M-BEA) was synthesized by an adapted protocol from the literature.¹⁷ To 8.830 g of TEAOH solution was added 0.081 g aluminium and the mixture was stirred at RT until complete dissolution. Thereafter, 7.810 g of TEOS were added and stirred until complete evaporation. 4.610 g water and 1.300 g hydrofluoric acid were added to the solid residue and the mixture was stirred during 4 h at RT to obtain a white gel. The gel was transferred to a Teflon lined stainless steel autoclave and heated at 170 °C during 8 days. After cooling to room temperature, a solid was obtained by filtration which was washed abundantly with demineralized water and dried at 80 °C during 12 h prior to calcination at 550 °C for 8 h. The sample was proton exchanged through suspending 1 g of

the powder in 100 mL of 1 M NH_4NO_3 solution at 80 °C for 2 h. After filtration and washing with deionized water, the solid was dried for 8 h at 80 °C and two additional exchange cycles were performed. The sample was thereafter calcined at 500 °C for 4 h.

2.3 Synthesis of N- and M-ZTCs

The synthesis of ZTCs was carried out in a setup as previously described.¹² 1 g of the zeolite was placed on the frit in the quartz reactor and the reactor was introduced into a tubular oven. In order to remove any traces of water the zeolites were activated at 700 °C under nitrogen flow (150 mL min^{-1}) before rising the temperature to 800 °C and switching the gas to a composition of 7vol% ethylene in nitrogen. After 4 h of treatment the gas flow was switched to nitrogen and the temperature was risen to 900 °C for 2 h. After cooling to RT the residue was transferred to a Teflon beaker and treated with 20 mL HF for 4 h. The solution was neutralized with 120 mL of a saturated solution of Boric acid and 120 mL of a saturated solution of NaHCO_3 . After filtration and washing with distilled water a black powder was obtained, which was dried at 80 °C during 12 h. The ZTCs recovers from N- and M-BEA zeolite templates were named N- and M-ZTC, respectively.

2.4 Characterization

Nitrogen physisorption was carried out using a Micromeritics 3FLEX at -196 °C. 50 mg of the sample was out-gassed prior to each experiment during 12 h at 350 °C. The micropore volume was calculated through t -plot method. The thickness of the nitrogen layer was calculated using reference isotherms recorded for (i) a non-porous silica (used for the t -plot of

the template zeolites, **Table S1**) and (ii) graphene (used for the t -plot of the ZTCs, **Table S2**). The pore size distributions and the cumulative pore volumes were determined using non-linear density functional theory (NLDFT) models available on SAIEUS. For the zeolites an NLDFT model developed for zeolitic materials was applied. For the ZTCs a 2D-NLDFT model developed for carbon materials with heterogeneous structure was used.

Powder diffractograms were collected using a PANalytical Empyrean X-ray diffractometer using CuK α radiation (1.54059 Å), for 2θ ranging from 5° to 50°. XRD of ZTCs were recorded in quartz capillaries at the DiffAbs line at the Synchrotron SOLEIL using 18 KeV and XPAD S140 (CIRPAD) detector. XPS was carried out on a Kratos Axis Ultra DLD using a Al mono source. Transmission electronic microscopy (TEM) was performed using a JEOL 2100 instrument (operated at 200 kV with a LaB₆ source and equipped with a Gatan Ultra scan camera). Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-790CF microscope. Thermogravimetric analysis was performed using a SDT Q600 by heating the samples in a N₂/O₂ (4:1) gas stream (100 mL min⁻¹) with a ramp of 10 °C min⁻¹ to 900 °C. The Si/Al ratio of the template zeolites was determined using ICP-OES analysis, through using a Perkin Elmer Optima 2000 DV instrument.

2.5 Atomistic simulation and XRD powder patterns

The patterns were calculated in terms of the Debye model of diffraction through the Debyer Software.^{18,19} The model provides an observable intensity function which depends on the atomic arrangement, without taking into account periodic conditions, as follows:

$$I_{debye} = \sum_m \sum_n \frac{f_m(s) f_n^*(s) \sin(2\pi s d_{mn})}{2\pi s d_{mn}}$$

Where s corresponds to the scattering vector $s = \frac{2 \sin \theta}{\lambda}$, f is the scattering amplitude and d_{mn} represents to the distance between the atoms m and n .

In order to achieve a description with higher accuracy of the experimental result additional correction were introduced:

$$I_{calc} = \frac{A(\theta)P(\theta)I_{debye}}{R^2}$$

Where $A(\theta)$ represents an absorption factor, which is usually neglected, $P(\theta)$ is the Lorentz Polarization's factor and R corresponds to the goniometer radius. These parameters were introduced and discussed in a previous work.²⁰

For the XRD simulation we prepared a model based on the zeolite framework (BEA) filled with carbon nanoribbons. This model was further submitted to a classical molecular dynamics (MD) simulation using a universal force field, as implemented in LAMMPS²¹ under an NVT ensemble at $T=300$ K for a total time period of 60 ps with a time step of $\Delta t = 1$ fs. After the MD simulation we removed the zeolite framework and obtained the pure carbon nanoribbons arrangement utilized for the further analysis. Hydrogen atoms were neglected due to their very low scattering factor. In order to achieve a reasonable accuracy with the experiments, unit cell parameters were compressed ~5% in the a , b axis resulting in a tetragonal crystalline arrangement with: $a=b=1.20$ nm $c=2.62$ nm. In order to take the size dependent profile of the XRD pattern into account, a “real size system” consisting of a crystallite domain model of about 20 x 20 x 20 nm was constructed in order to be consistent with the experimental information.

3. Results and Discussion

3.1 Characterization of nano- and micron-sized zeolite templates

The texture of the template zeolites was studied through recording high resolution nitrogen physisorption isotherms at 77 K. The shape of the isotherm of M-BEA is of type I, characteristic for a purely microporous material (**Figure 1a**). For the N-BEA the isotherm shows a large uptake in the low relative pressure region as for M-BEA, yet an important adsorption at relative pressures greater than 0.8 is monitored, which is due to intercrystalline adsorption, typically observed for small zeolite crystals below 100 nm. For both materials a microporous volume of $0.23 \text{ cm}^3 \text{ g}^{-1}$ was calculated, which is the expected value for beta zeolite,²² and indicates that the textural properties of both materials are similar and further proves the absence of extraframework species that could hinder or block microporosity. Indeed, the NLDFT pore size distribution is identical for both zeolite templates and presents a neat peak centred in the microporous region (**Figure 1b**).

Figure 1. a) Nitrogen physisorption isotherms at 77 K of N- (black squares) and M-BEA (empty green circles). The insert presents the isotherm with logarithmic P/P_0 scale. b) NLDFT pore size distribution of N- (black squares) and M-BEA (empty green circles).

The morphology of the zeolites was investigated by electron microscopy. The N-BEA presents agglomerates of crystals of approximately 10 – 20 nm in size. As far as the M-BEA

is concerned truncated bipyramidal shape of crystals with smooth faces could be deduced from SEM images. The cut-off extremities of the bipyramids yet present rough surfaces, which indicates polycrystalline nature of the sample. The size of the crystals estimated from SEM images is 6 μm in length and 4.5 μm in width.

Figure 2. TEM images of N-BEA (a, b) and SEM image of M-BEA (c).

The XRD powder patterns for both N- and M-BEA present the typical reflections of the *BEA framework. The full width at half maximum (FWHM) is larger for N-BEA, which indicates the presence of smaller crystalline domains in this sample. Using the Debye-Scherrer equation the coherent crystal size was calculated, which amounts to 22 and 106 nm for N- and M-BEA, respectively. This compares well to what is observed from the TEM images for the N-BEA sample. Yet, as far as the M-BEA is concerned much larger crystals are inferred from the SEM images (5 μm). For large zeolite beta crystals some peaks present large peak broadening, indeed the intergrowth of polymorphs allows only for sharp peaks in $h = 3n$ and $k = 3n$.²³ Yet, even for these latter the calculated coherent crystal domain is smaller compared to the observation from SEM, which can be explained by lattice imperfections which are frequent in beta zeolites and to the polycrystalline nature of the sample.²⁴ From the

positions of the (320) and (008) reflections the lattice parameters of the polymorph A were calculated which are slightly larger for M-BEA, which is in agreement with the slightly higher Si/Al ratio of this material (**Table 1**).

Figure 3. XRD powder patterns of N-BEA (black) and M-BEA (green).

Table 1. Textural, structural and chemical properties of nano- and micron-sized zeolite templates.

	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Si/Al ratio	D (nm) ^a	CCD (nm) ^b	Lattice parameters a, b (nm)	Lattice parameter c (nm)
N-BEA	0.23	678	12.9	20	22	1.264	2.626
M-BEA	0.23	628	14.0	5000	106	1.267	2.627

^aZeolite particle size measured from electronic microscopy images.

^bCoherent crystal size. Calculated from XRD powder peaks corresponding to (320) and (008) reflections.

3.2 Nano- and micron-sized Zeolite Templated Carbons

N- and M-BEA were used as templates for the synthesis of N- and M-ZTCs. For both samples the amount of carbonaceous residue in the zeolite is similar and amounts to 22.9 and 21.1% for N- and M-BEA, respectively (**Figure S1**). This indicates that the apparent density of

carbonaceous species is slightly lower for the micron-sized crystals and amounts to 1.29 and 1.16 g cm⁻³ for N- and M-BEA, respectively. This finding strongly suggests the presence of structural defects for the M-ZTC sample.

The shape of the nitrogen physisorption isotherm at 77 K of the resulting ZTCs recalls for both samples that of the zeolite template (**Figure 4a**), indicating that the textural and morphological features of the achieved ZTCs are similar to that of the respective zeolite crystals. From the 2D-NLDFT pore size distribution (**Figure 4b**) and from the cumulative pore volume (**Figure 4c**) important differences for the N- and M-ZTC can be observed. For N-ZTC the cumulative pore volume increases constantly up to 1.3 nm before reaching a first plateau. Only after 2 nm further increase in nitrogen uptake is observed, which can be ascribed to the development of multilayers of the adsorbent and interparticle condensation. For this sample a uniform pore size distribution in the micropore region is observed, centred at 0.9 nm and results in an overall micropore volume of 0.87 cm³ g⁻¹. As far as M-ZTC is concerned, steady increase in cumulative volume was observed up to 0.81 cm³ g⁻¹ (up to 1.3 nm). Cumulative pore volume increases thereafter with different tendency and reaches 1.11 cm³ g⁻¹ at 2 nm. Hence from the PSD two different contributions in the micropore range could be resolved, one which is identical as for the N-ZTC (at 0.9 nm) and a second, larger contribution centred at 1.6 nm. This finding allows to deduce for M-ZTC 73% of the micropore volume corresponds to smaller micropores (identical pore-size as for the nano-sized sample, N-ZTC). The remaining 27% of micropore volume is due to larger supermicropores. This observation strongly indicates the presence of structural defects within the M-ZTC sample that might result from more important diffusion restrictions of the carbon precursor during the polymerization of ethylene in the extended micropore network (long diffusion path length) of the M-BEA.

Figure 4. a) Nitrogen physisorption isotherms at 77 K of N- (black squares) and M-ZTC (empty green circles). The insert presents the isotherm with logarithmic P/P_0 scale. b) 2D-NLDFT pore size distribution of N- (black squares) and M-ZTC (empty green circles). c) Cumulative pore volume of N- (black squares) and M-ZTC (empty green circles).

For both N-ZTC and M-ZTC perfect morphological control of the zeolite templates was observed. N-ZTC particles of approximately 20 nm could be deduced in TEM, which present similar aspect compared to the zeolite template and feature homogenous distribution of micropores within individual carbon particles (**Figure 5**). The absence of graphitic carbon species on the surface of individual ZTC particles was further assessed, indicating that no turbostratic carbon formed during the synthesis. As far as M-ZTC is concerned, it presents very similar appearance as the zeolite template, *i.e.* individual particles of approximately 5 μm in length featuring truncated bipyramidal morphologies with cut-off extremities. Detailed observation of the M-ZTC particles reveal flacid edges compared to the zeolite crystals. From TEM images on ultramicrotomed images of M-BEA the transcription of the zeolite skeleton can be observed from the electron clear spots (micropores). Careful observation of the image further suggests the presence of regions in the sample of lower structural order, which might be the structural defects inferred from nitrogen physisorption. The presence of hollow regions

in the M-ZTC sample was not observed, different to what was suggested by Garush *et al.* using a 3 μm FAU template.¹³

Figure 5. Electronic microscopy images of N-ZTC (top) and M-ZTC (bottom).

Further differences between N- and M-ZTC were inferred from the recorded TGA and XPS data. From the mass loss curves of the N-ZTC only one major contribution was observed centred at 486 °C (**Figure 6b**). As far as the M-ZTC is concerned two contributions could be observed. The first at 486 °C (equal as for N-ZTC) and a second at higher temperatures (515 °C). This observation suggests two different structured types of carbons present in M-ZTC one resulting from the templating of the zeolite microporosity (low temperature combustion) and one from possible defect zones (high temperature carbon). To further elucidate the chemical composition of the achieved ZTCs these were characterized through XPS (**Figure 6c**). Both samples, N-ZTC and M-ZTC, present very similar spectra, dominated

by the C_{1s} and O_{1s} photoelectron peaks (**Figure S2**). A slight difference in the position of the C_{1s} peak was observed for N-ZTC and M-ZTC, which is centred at 284.5 and 284.8 eV, respectively. Pure graphene features a characteristic C_{1s} peak at 284.4 eV (aromatic sp² carbon). The peak shifts to higher energies with increasing sp³ character of the sample (typically observed for graphene featuring structural defects).²⁵ This suggests that the M-ZTC features a higher degree of sp³ hybridized carbon, which is in agreement to the assumption of enhanced structural defects in this sample.

Figure 6. a) TGA mass loss curves of N-ZTC (black) and M-ZTC (green). b) DTA curves as function of temperature for N-ZTC (black) and M-ZTC (green). c) X-ray photoelectron C_{1s} peak of N-ZTC (black) and M-ZTC (green). The blue curve represents the measured background.

Despite the clear evidence of structural defects present in the M-ZTC sample, the XRD powder patterns present long range structural order peaks for both the nano- and micron-sized sample (**Figure S3**). This result suggests that XRD allows only to evidence the well-ordered part of the samples, as previously indicated by Parmentier and co-workers.²⁶

In order to achieve a higher quality resolution of the peaks they were recorded using synchrotron radiation at 18 keV (**Figure 7**). Three reflection peaks can be observed centred at 3.58, 5.95 and 6.73 °2theta.

The majority of studies in the literature only report one or two peaks for carbon replicas of beta zeolite (usually at 7.7 and 15.0° 2 θ using CuK α radiation).²⁷⁻²⁹ The first of these peaks was ascribed as high intensity “basal peak” and the second reflection was related to high level zeolite-type ordering.

Figure 7. XRD powder patterns of N-ZTC (black) and M-ZTC (green) recorded using synchrotron radiation with 18 KeV.

Despite the important number of atomistic models reported for ZTC derived from FAU structure,⁵ only very little was published for ZTCs resulting from beta zeolites. Solely Oliveira and co-workers proposed a model for ZTCs resulting from beta zeolites through the generation of an intergrown three-dimensional carbon nanotube network.³⁰ The development of such a nanotube-based structure within zeolite channels is yet highly unrealistic. Detailed studies on the coking mechanism in zeolite beta indicate the favoured development of anthracene and pyrene-based molecules.³¹ It is therefore rather reasonable to consider the ZTCs developed within beta zeolite to feature a graphene-based nanoribbon network.

In order to achieve further insights of the long-range pore-to-pore ordering revealed by XRD powder patterns were simulated considering the ribbons to form a crisscrossed long order structure (Figure 8 and Figure S4). The simulated XRD pattern matches the experimental patterns rather well (Figure 9). According to our model the main signals located at $2\theta = 3.61^\circ$, 5.59° and 6.73° could be ascribed to length correlation between nanoribbons corresponding to lattice planes (011), (103) and (201), respectively. The assignment is based on the zeolite template model obtained by molecular dynamics excluding the Si and O atoms. By using the same model, including just carbon nanoribbons, we estimated the free volume of the zeolite to correspond to $820 \text{ \AA}^3$ in the main unit cell that allowed us to estimate a micropore volume of $0.31 \text{ cm}^3 \text{ g}^{-1}$.³² This value is higher when compared to the experimental one ($0.23 \text{ cm}^3 \text{ g}^{-1}$), which might be due to the possible interconnections among carbon nanoribbons that were not taken into account in our model.

Figure 8. Crystalline model of nanoribbon in BEA structure as model for N-ZTC projected in different planes.

Figure 9. XRD pattern of N-ZTC (black) and simulated XRD pattern (red) considering fitted background (blue) determined by Debye's method.

4. Conclusion

Micron and nano-sized ZTC using beta zeolite as template were prepared. Nitrogen physisorption isotherms at 77 K reveal the presence of larger micropores, which indicates the presence of structural defects for the micron-sized ZTC. These results were supported by TGA and XPS measurements. These defects probably occur during synthesis and are related to mass transfer issues of the carbon precursor within the extended micropore system of the micron-sized zeolite. Despite the presence of defects long-range structural XRD order could be evidenced, indicating important diffraction domains even in the micron-sized ZTC. The presence of diffraction peaks is often taken as indication for the high quality of ZTC structure. XRD merely allows to evidence the well-ordered part of the sample and hence indicates that XRD results should be taken with caution for interpreting structural quality of ZTCs. Simulated XRD powder patterns allowed to propose a graphene nanoribbons structure grown in the zeolite pores as a suitable model for the zeolite template carbons.

Supporting Information

Reference *t*-plots for non-porous silica and graphene, TGA of hybrid materials, XPS spectra, XRD patterns of ZTCs using CuK α radiation and the crystalline model of nanoribbons without the BEA structure are available as supporting information.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the European Union (ERDF) and "Région Nouvelle Aquitaine". The authors further acknowledge SOLEIL for provision of synchrotron radiation facilities and we would like to thank Cristian Mocuta for assistance in using beamline DiffAbs.

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