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Circumventing the direct textural characterization of presumed hierarchical zeolites: The case of surfactant-templated USY zeolites

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KEYWORDS : zeolite, surfactant-templating, hierarchical, zeolite-templated carbon, USY.

ABSTRACT

The presence of intracrystalline mesopores in hierarchical zeolites is often difficult to prove with standard and even advanced characterization techniques. Zeolite-templated carbons (ZTCs) develop within the zeolite microporosity and are hence a negative copy of their porous structure. Textural characterization of the ZTC allows for circumventing the difficulty in assessing the presence of intracrystalline mesoporosity in the presumed hierarchical zeolite. A set of surfactant-templated USY zeolites was prepared using surfactants with increasing chain lengths and the corresponding ZTCs were synthesized. The textural characterization of the hybrid materials (zeolite/ZTC) and of the ZTCs (after zeolite dissolution) achieved from surfactant-templated zeolites allowed to conclude the absence of intracrystalline tailored mesoporosity. Zeolites achieved upon surfactant-templating should hence rather be described as composite materials. The difficulty in assessing the composite nature of these surfactant-templated zeolites is due to the formation of the tailored mesoporosity within the larger (steamed) mesoporosity of the parent zeolite.

1. Introduction

The booming development of zeolite hierarchization strategies over the past 25 years is motivated by the possibility to achieve superior catalytic outputs resulting from the reduction of the diffusion path length.[1-10] The thorough characterization of the textural properties of such hierarchical zeolites is yet a rather challenging task.[11] It is indeed often difficult to distinguish a genuine hierarchical zeolite featuring intracrystalline mesoporosity and a composite material composed of a purely microporous and a mesoporous phase. Powder X-ray diffraction and transmission electron microscopy on ultramicrotomed samples are standard techniques used with the aim to describe the textural evolution upon zeolite hierarchization treatments. Such techniques, yet do not allow for proving the presence of intracrystalline mesopores, as they do not provide information on the connection of pores on different length-scales. Gas physisorption is a further frequently applied technique for the determination of the surface and porous properties of such materials.[12,13] Coasne and coworkers proved the impossibility to distinguish a truly hierarchical zeolite and a mechanical mixture of zeolite/mesopore material by gas physisorption.[14] Hysteresis scanning has emerged as strategy for inferring additional information on porosity connections and in particular allows for the quantification of the fraction of intracrystalline mesopores connected to the external pore surface through pore-necks (occluded mesopores).[15,16] This strategy is yet only applicable when the isotherm presents asymmetric hysteresis loops.

Hence, in many studies describing the textural properties of hierarchical zeolites, important ambiguity prevails on the intracrystalline nature of the mesopores. Among the different hierarchization strategies, zeolite surfactant-templating (firstly introduced as “riving”) has been reported as a versatile strategy allowing for the generation of tailored intracrystalline mesoporosity within zeolites.[17] This process is mainly described using beforehand

dealuminated Y zeolite and the prime example is the use of USY featuring a Si/Al ratio of 15 and relies on exposing the zeolite to an alkaline surfactant solution. The mechanism of the surfactant-templating process has been described as relying on the cleavage of Si-O-Si bonds through a basic attack, followed by the incorporation of positively charged surfactant molecules by intracrystalline diffusion and the assembly of surfactant molecules to form micelles, allowing for the generation of the mesophase. The reduction of the micropore volume in the mesostructured zeolite was reasoned on micropore disruption as a consequence of the formation of micelles. Likewise, a crystal expansion theory was put forward to explain the elimination of steamed mesoporosity (20 - 30 nm) in surfactant-templated zeolites.[18]

Numerous advanced characterization techniques were employed with the aim to evidence the intracrystalline mesopore nature of the surfactant-templated zeolites, such as rotational electron diffraction and electron tomography.[18-20] For the latter no distinction can be made between the presence of intracrystalline mesopores (*i.e.* mesopores connected with the micropores) and mesopores that are possibly embedded within the zeolite crystal. Indeed, important criticism of the zeolite surfactant-templating mechanism was expressed by Verboekend *et al.*,[21] who claimed that this process would rather yield into composite materials of zeolites and ordered mesoporous materials. Indeed, the development of composite materials composed of a MCM-41-like phase and of the parent zeolite has frequently been described when treating zeolites with basic surfactant solutions.[22] Ivanova and co-workers [23] coined this process for mordenite as recrystallization, which leads to a composite composed of the amorphous mesophase featuring zeolite fragments and the desilicated parent zeolite. Galarneau and co-workers surmised the development of a complex family of materials upon USY surfactant-templating.[24]

In the present contribution we present a novel approach that allows for circumventing the drawbacks of the direct textural characterization of presumed hierarchical zeolites. The

generation of a Zeolite-Templated Carbon (ZTC) and the characterization of its textural properties allows for identifying if the zeolite featured intracrystalline mesoporosity.

2. Experimental part

2.1 Materials

The zeolite used for this study was the commercial USY zeolite (CBV720, Si/Al = 15, proton form) supplied by Zeolyst International. The zeolite was calcined at 550 °C for 6 hours before use. The surfactants cetyltrimethylammonium bromide (CTAB, 98%, C16) and dodecyltrimethylammonium bromide (98%, C12) as well as the sodium hydroxide (99%) were purchased by Sigma-Aldrich and used as received. Hydrofluoric acid (Fisher Scientific, 49% in water), boric acid (Sigma-Aldrich, 99%), sodium bicarbonate (Sigma-Aldrich, 99%), ethylene (> 99.99%, Air Liquide) and N₂ (> 99.995%, Air Liquide) were used as received.

2.2 Zeolite surfactant-templating

According to the methodology previously described,[19] 5.49 mmol of the surfactant (C12 or C16) was dissolved in 25.2 mL of NaOH 0.38 M, followed by the addition of 4.0 g of CBV720. The mixture was stirred during 20 min and then heated to 80 °C under autogenous pressure for 24 h. Thereafter, the solid was recovered by filtration and abundantly washed with distilled water and overnight dried at 80 °C. The obtained solid was further calcined at 550 °C for 6 hours. The achieved materials were named USYC12 and USYC16.

2.3 Synthesis of Zeolite-Templated Carbons (ZTC)

1.5 g of the calcined parent and surfactant-templated zeolites was introduced into a cylindrical quartz reactor containing a frit, and placed in a tubular furnace. After heating during 1 hour at 150 °C under nitrogen flow (150 mL min⁻¹) the temperature was risen to 790 °C for one hour. The gas was then switched to a mixture of ethylene in N₂ (6.67vol%) for four hours. The furnace temperature was then gradually risen to 890 °C under pure nitrogen and kept at this temperature for two hours. Finally, the temperature of the oven was cooled to room temperature and the hybrid material (containing both the zeolite and carbon material) was recovered. The hybrid materials were named H-USY, H-USYC12 and H-USYC16.

In order to recover the ZTC, 1 g of the hybrid material was treated under mixing with 10 mL of HF solution in a Teflon beaker at room temperature for four hours for zeolite dissolution. In order to neutralize the fluoride anions, 60 mL of a saturated aqueous solution of boric acid was added to the beaker and the pH was raised to 5 by adding a saturated aqueous solution of sodium bicarbonate. The final ZTC was recovered by filtration, abundantly washed with hot distilled water and dried overnight at 80 °C. The ZTCs were named C-USY, C-USYC12 and C-USYC16.

2.4 Characterization

Materials were characterized by X-ray diffraction (XRD) realized on an Empyrean PAN analytical with Cu-K α emission ($\lambda = 1.54 \text{ \AA}$) in the range 2θ 0.5–5° and 2θ 5–50°. Nitrogen physisorption isotherms at 77 K were measured on a Micromeritics TRIFLEX instrument. Before the analysis, the samples were degassed at 350 °C for 12 h. Pore size distribution was calculated by DFT using a cylindrical pore model for zeolites and hybrid materials while an NLDFT model available on SAIEUS for carbon materials with heterogeneous surface was used for the ZTCs. The micropore volume was calculated by *t*-plot method using a reference

or non-porous silica[26] and carbon.[27] Transmission electronic microscopy (TEM) was carried out using a JEOL 2100 microscope (200 kV with a LaB6 source equipped with a Gatan Ultra scan camera) and scanning electronic microscopy (SEM) using a JEOL JSM-790CF instrument.

3. Results and Discussion

3.1 Characterization of the parent and the surfactant-templated zeolites

Pristine USY zeolite was subjected to a basic treatment in the presence of the surfactants cetyltrimethylammonium bromide (C16) or dodecyltrimethylammonium bromide (C12), giving rise to the samples USYC12 and USYC16.

The parent USY zeolite features a type I nitrogen physisorption isotherm for low relative pressure (**Figure 1a**), characteristic of microporous materials. A slight increase of the nitrogen uptake at high relative pressures (>0.8) indicates the presence of large mesopores, which results from the steaming process applied by the manufacturer. The presence of a H4 hysteresis loop can be ascribed to cavitation, probably due to the presence of occluded mesopores. Pore size distribution of the parent zeolite indicates the presence of **FAU** micropores centered at 1 nm and supermicropores at 2 nm, which can be ascribed to defects caused by the steaming treatment. As far as the samples achieved after surfactant-templating are concerned, significant changes in the shape of the nitrogen physisorption isotherms are observed, which can be described as a combination of type I at low relative pressure (<0.2) and type IV (capillary condensation regime), indicating the presence of both micropores and tailored mesopores (**Figure 1b**).[25] When comparing the isotherms from the parent zeolite and the surfactant-templated samples, a decrease in the nitrogen uptake is noticed for low relative pressures (< 0.2). This behavior results from a decrease of the microporous volume

from 0.25 to 0.13 cm³ g⁻¹ for the parent USY and the surfactant-templated zeolites, respectively. The reduction of micropore volume was previously reasoned to result from the disruption of microporosity.[26] A further explanation might be the absence of supermicropores in the surfactant-templated samples. Mesopore size distribution is a function of the alkyl chain length of the surfactant used in the process, this is moreover confirmed by the position of the peaks developing in the small angle XRD patterns (**Figure S1**). These results compare well with what was previously reported.[27]

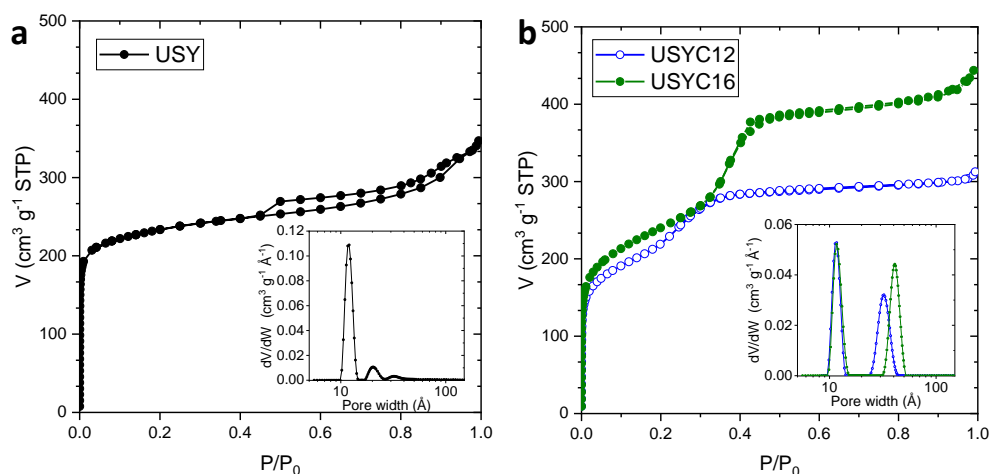


Figure 1. Nitrogen physisorption isotherms at 77 K of parent USY (a), USYC16 and USYC12 (b). The insert in each graph presents the pore size distribution.

The observation of the electron microscopy images allows for fostering the conclusions derived from nitrogen physisorption (**Figure 2** and **Figure S4**). The images reveal the absence of steamed mesoporosity in the surfactant-templated zeolites (**Figures 2c,d**). The removal of the steamed mesoporosity during surfactant-templating treatment was previously reasoned to result from zeolite expansion by the accommodation of intracrystalline micelles.[18]

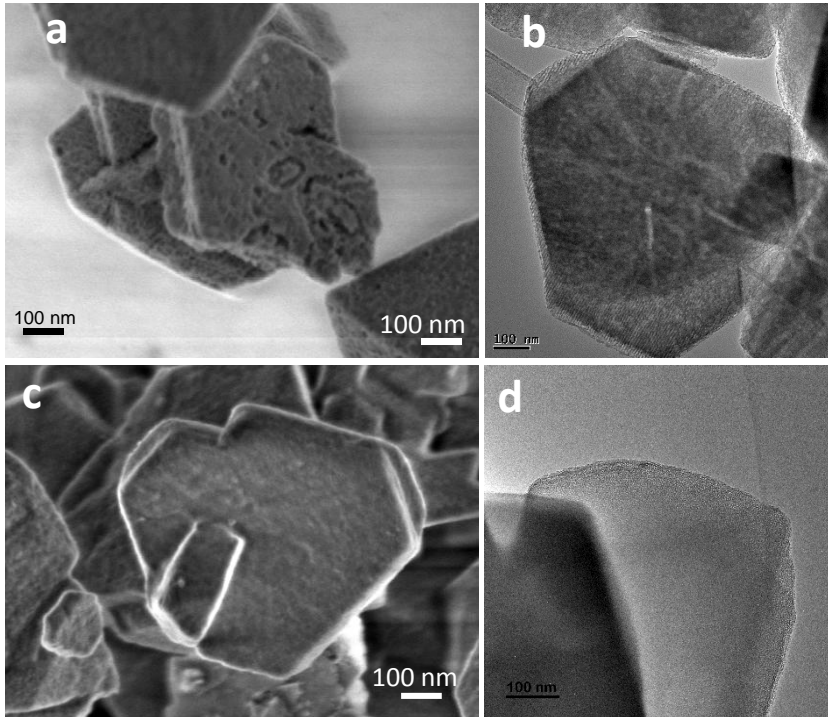


Figure 2. SEM and TEM images of parent USY (a-b) and USYC12 (c-d).

3.2 Characterization of hybrid materials

The pristine USY and the two surfactant-templated zeolites were then used for the synthesis of ZTCs. The zeolites were treated with diluted ethylene at 790 °C for 4 hours and then heat treated at 900 °C under N₂ before cooling to RT. The achieved materials were name H-USY, H-USYC12 and H-USYC16.

The nitrogen physisorption isotherms for USY feature a similar shape for the hybrid samples (H-USY) compared to that of the zeolite sample (USY) (**Figure 3a**). It is yet to observe the absence of micropore filling in the low-pressure range, which results from complete obstruction of the micropores with carbon. It is known from previous studies that only the micropore system of the zeolite is obstructed during the synthesis of ZTCs using **FAU** structured zeolites.[27] The nitrogen uptake at high relative pressure (>0.8) is similar to what

was observed for USY zeolite, indicating that the steamed mesopores are not filled with carbon. As far as the hydride materials for the surfactant-templated zeolites are concerned, these equally present the absence of micropore filling (**Figure 3b**). It is further possible to observe a capillary condensation step in the isotherms of these samples, indicating the presence of tailored mesoporosity in the hybrid materials (**Figure 4b**). Indeed, the mean mesopore sizes calculated for the hybrid materials are in good agreement with those observed in the surfactant-templated zeolites and are close to 3 and 4 nm for H-USYC12 and H-USYC16, respectively.

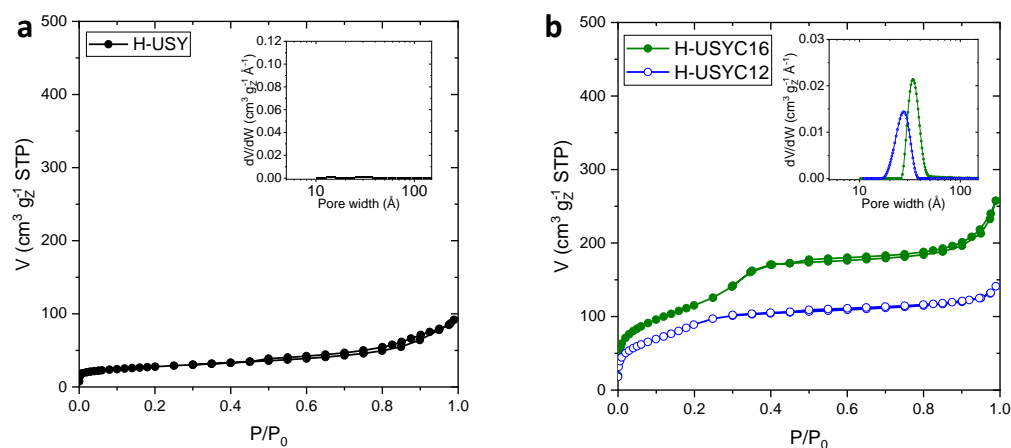


Figure 3. Nitrogen physisorption isotherms at 77 K of parent H-USY (a), H-USYC16 and H-USYC12 (b). The isotherms were corrected by taking into consideration the amount of carbonaceous species inferred from TGA (**Table S1**). The insert in each graph presents the pore size distribution.

3.3 Characterization of the ZTCs

After dissolution of the zeolite with HF solution the final ZTCs, named C-USY, C-USYC12 and C-USYC16, were achieved. A complete weight loss of the ZTC by TGA confirms the total dissolution of the zeolite from all samples (**Figure S2**). The achieved ZTCs present high structural order, as indicated by the peak in the XRD pattern centered at $6.6^\circ 2\theta$ (**Figure S3**),

indicating the achievement of high quality ZTCs for all samples.[28] As expected, the nitrogen physisorption isotherm of the C-USY is of type I (**Figure 4a**). Surprisingly, the isotherms of C-USYC12 and C-USYC16 present identical shapes to that achieved for C-USY (**Figure 4b**), foregrounding the absence of tailored mesoporosity in the ZTCs achieved from surfactant-templated USY samples. An equal pore size distribution of the ZTCs resulting from USY and the surfactant-templated zeolites can be observed featuring a mere contribution in the micropore region with a shoulder, suggesting the presence of supermicropores; typically observed for ZTCs achieved from micron-sized crystals.[29] Independently of the chain length of the surfactant, the micropore volume of the ZTCs is similar and amounts to approximately $0.7 \text{ cm}^3 \text{ g}^{-1}$. By revenge, C-ZTC features a higher micropore volume of almost $1.0 \text{ cm}^3 \text{ g}^{-1}$. The reduced micropore volume in the surfactant-templated zeolites hence impacts the micropore volumes in the resulting ZTCs.

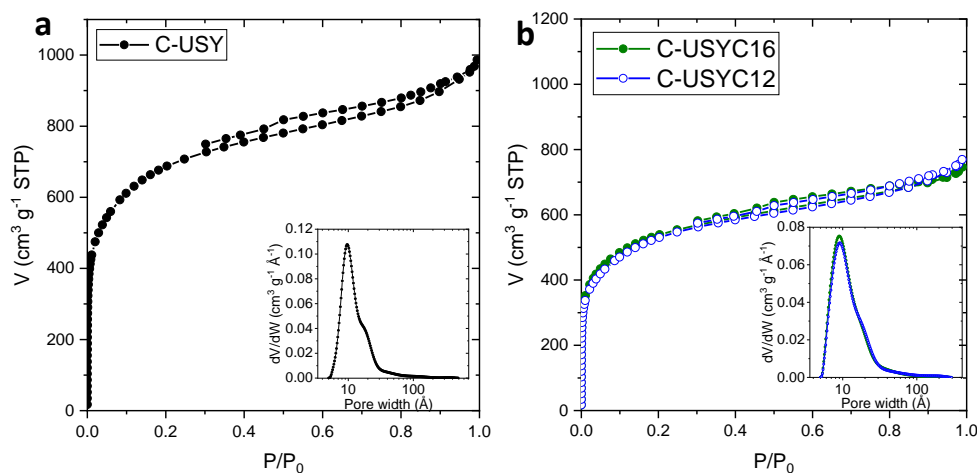


Figure 4. Nitrogen physisorption isotherms at 77 K of C-USY (a), C-USYC16 and C-USYC12 (b). The insert in each graph presents the pore size distribution.

From the SEM and TEM images it can be observed that the ZTC resulting from the USY parent zeolite (C-USY) clearly presents the textural features of the steamed mesoporosity,

which indicates the transcription of the textural properties of the zeolite template to the ZTC (**Figure 5a,b**). As far as the C-USYC12 is concerned both SEM and TEM images indicate the presence of larger mesopores, conspicuously similar to the steamed mesoporosity in USY zeolite (**Figures 5c,d**). Equal observations were made for C-USYC16 (**Figure S3b**).

The presence of steamed mesoporosity in the ZTCs resulting from surfactant-templated zeolites, hence indicates that the former was never eliminated but rather masked due to its obstruction. The most manifest conclusion to these observations is that the steamed mesoporosity is filled with an amorphous micelle-induced mesophase during zeolite surfactant-templating (**Scheme 1**).

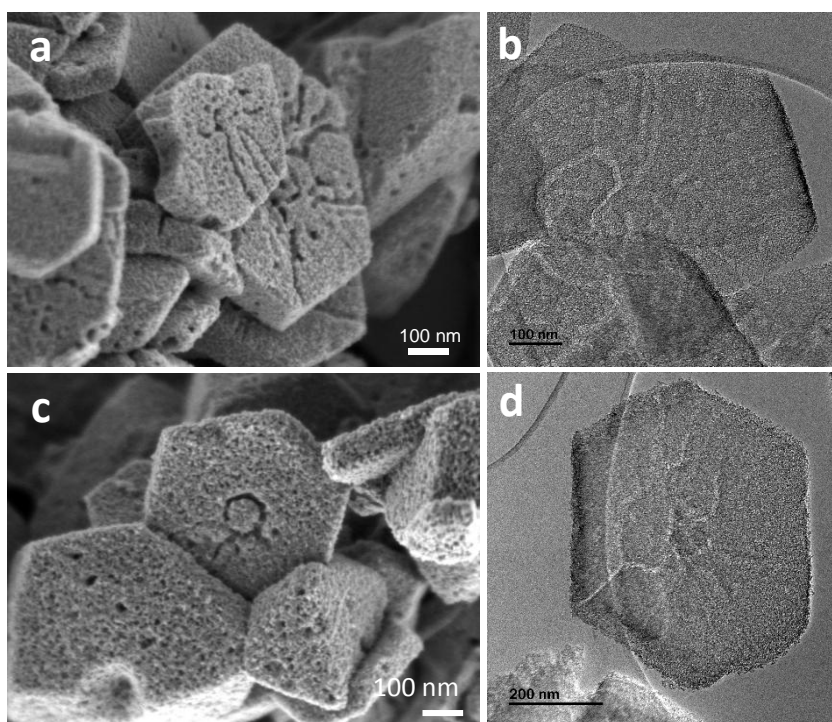
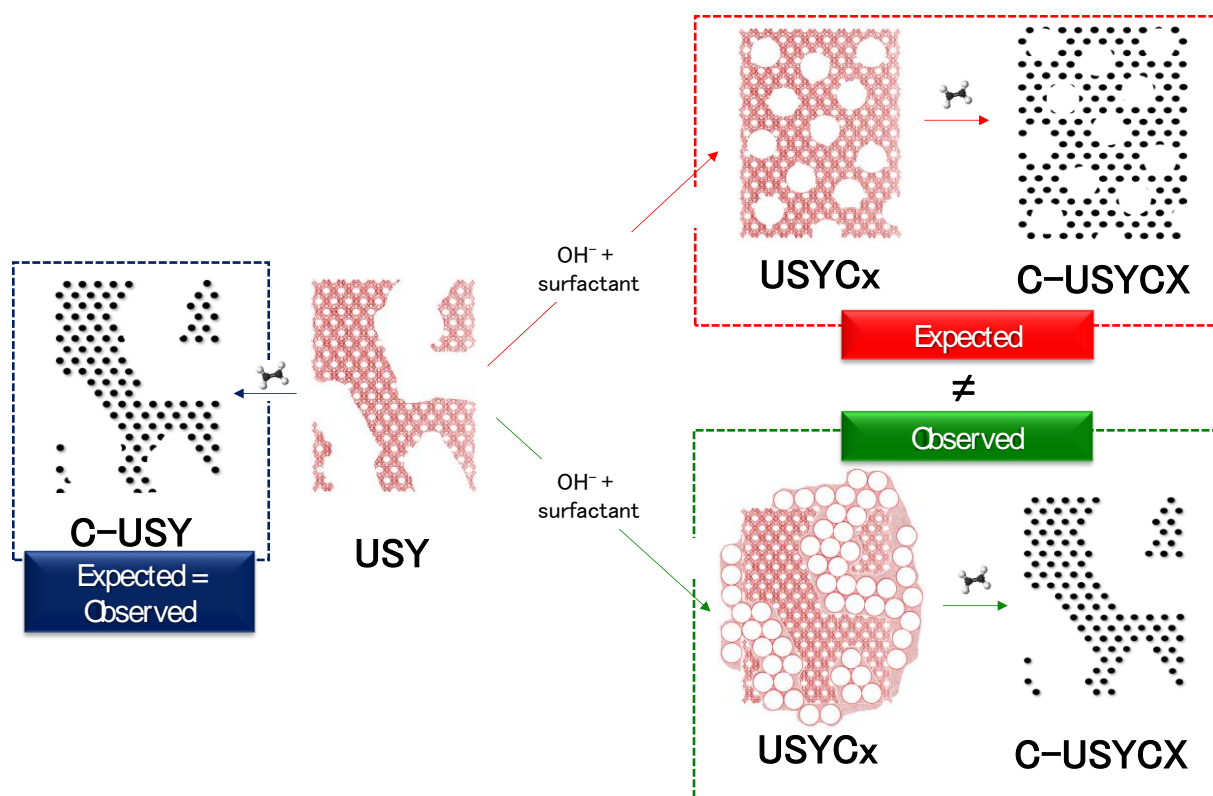


Figure 5. SEM and TEM images of C-USY (a,b) and C-USYC12 (c,d).



Scheme 1. Representation of the USY template zeolite and its resulting ZTC (blue part), the representation of USYCx and its resulting ZTC as expected (red part), and the representation of USYCx and its resulting ZTC as observed (green part). (X represents the carbon chain length of the surfactant).

4. Conclusion

From the presented results it can be concluded that the characterization of ZTCs resulting from hierarchical zeolite systems allows to assess the presence of intracrystalline mesoporosity in the template zeolite. The described strategy hence permits for distinguishing truly hierarchical zeolites from composite materials. Surfactant-templating of zeolites is a particularly complex case and is frequently described to allow for the formation of intracrystalline tailored mesoporosity. By simple textural characterization of the ZTCs resulting from surfactant-templated zeolites, the composite nature could be demonstrated. The complexity in directly assessing the composite nature in surfactant-templated zeolites results from the formation of the mesophase within larger mesoporosity of the USY zeolite. The

formation of ZTCs reveals hence as a very efficient tool for circumventing the difficult direct textural characterization of presumed hierarchical zeolites. It should be noted that high quality ZTCs can currently be achieved using **FAU**, **EMT** and ***BEA** structured zeolites, hence the presented methodology is likely to be applied on hierarchical zeolites featuring these structures.

ASSOCIATED CONTENT

Supporting Information

XRD patterns of zeolites, TGA mass loss curves and XRD patterns of ZTCs, and SEM and TEM images of USYC16 and C-USYC16 are available free of charge.

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Author Contributions

Thibaud Aumond: Conceptualization, Data Curation, Formal analysis, Investigation, Methodology, Resources, Supervision, Validation, Visualization, Writing - Original Draft. **Iane M. S. Souza:** Data Curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing - Original Draft. **Sophie Morisset:** Data Curation, Formal analysis, Resources. **Yannick Pouilloux:** Funding acquisition. **Sibele B. C. Pergher:** Funding acquisition, Validation. **Alexander Sachse:** Conceptualization, Data Curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing - Review & Editing.

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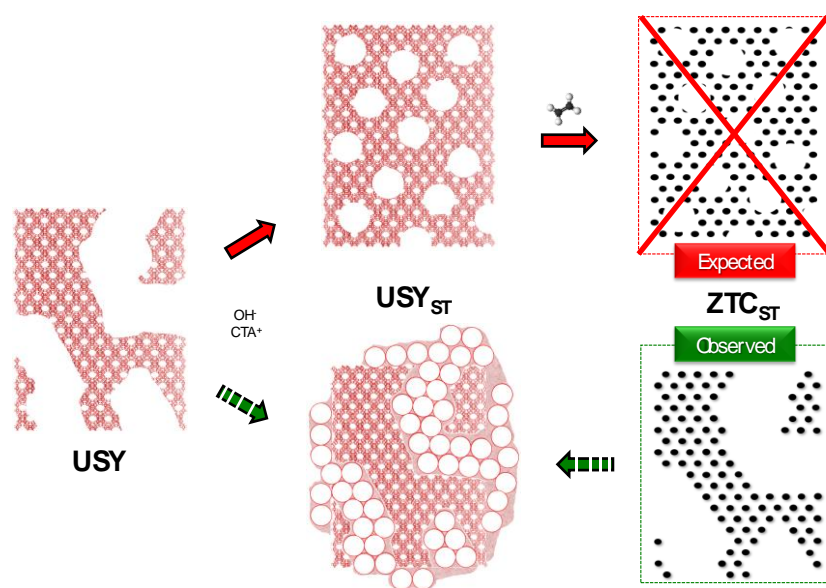
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The synthesis of Zeolite-Templated Carbons (ZTCs) reveals a powerful tool for circumventing the difficult direct textural characterization of potentially hierarchical zeolite. Intracrystalline mesoporosity in hierarchical zeolites can be assessed if these are transcribed to the resulting ZTC.