ICP-2: A New Hybrid Organo-Inorganic Ferrierite Precursor with Expanded Layers Stabilized by π - π Stacking Interactions

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Abstract. In this work we present the synthesis, characterization and molecular modeling of ICP-2, a new layered ferrierite precursor with expanded layers. ICP-2 is obtained in fluoride medium from aluminosilicate gels with low H₂O content, using the chiral cation (1R,2S)-dimethylephedrinium (DMEP) as the organic structure-directing agent; ICP-2 can also be obtained as the Al-free form. The combination of physico-chemical characterization of the material with molecular modeling indicates that ICP-2 is a layered material composed of ferrierite layers, where the organic cations play a dual

structural role through the formation of supramolecular aggregates. On the one hand, the organic cations stabilize the formation of the ferrierite layers with a core-shell structure, directing the formation of both the pseudo-10R channels (by supramolecular dimers aligned with the channel direction) and of the pseudo-cavities, with the trimethylammonium groups of DMEP fitting within. On the other hand, the aromatic rings of these organic cations in the pseudo-cavities develop π - π stacking interactions with equivalent cations in adjacent layers, holding together the ferrierite layers expanded at a distance of ~ 20 Å, hence preventing the formation of H-bonds between the inorganic layers. The diastereoisomer (1S,2S)-dimethylpseudoephedrinium instead cannot direct the formation of ICP-2, which is explained because of its distinct conformational space which fits worse in the core-shell structure of ICP-2.

1. Introduction

In recent years there has been a growing interest in 2-dimensional layered precursors of zeolites.¹⁻³ These materials are constituted by well-defined zeolite-like structures extended in only 2 dimensions (layers), with both sides of the layers usually terminated by silanols or siloxy groups, and the interlayer space occupied by organic cations which can lead to different stacking patterns of the layers. The stacking of these layers in the third direction is frequently stabilized by the development of H-bonds between the silanol/siloxy groups terminating the layers.⁴ Upon calcination, these layered materials can produce 3-dimensional zeolite frameworks through condensation of the silanol/siloxy groups triggered by the elimination of the organic molecules hosted in the interlayer space.

The interest in this type of materials is two-folded: on the one hand, the zeolitic layers of these materials are amenable to swelling and subsequent delamination, leading to

catalytic materials with very large external surface areas, thus greatly improving diffusion of reactants and products,³⁻⁹ as an alternative to the production of hierarchical mesoporous zeolites.¹⁰ Bulky reactants are then accessible to these catalytic sites, which would otherwise be unable to diffuse through 3D zeolite networks. These delaminated materials have led to new catalytic applications, including in reactions like cracking,⁵ alkylation,^{11,12} disproportionation,¹³ epoxidation^{7,14} and Beckmann rearrangement.¹⁵ Apart from such delamination procedures, these layered zeolites can also promote the formation of catalysts with high accessibility to the active sites through pillaring along the stacking direction,^{16,17} or through intercalation of organosilanes to the terminating silanol/siloxy groups in adjacent layers, yielding the so-called interlayered expanded zeolites (IEZ).¹⁸⁻²⁰ A second interest in these layered zeolites is that, under appropriate conditions, they can lead to new 3-dimensional zeolite frameworks through topotactic condensations,²¹ like the so-called ADOR strategy (Assembly, Disassembly, Organization, Reassembly), where a Ge-containing 3D-zeolite is transformed into a 2D-layered zeolite by dissolution of certain structural units, then being these layers reassembled to give new 3D-zeolite frameworks.²²⁻²⁴

In an attempt to produce chiral zeolite materials, we have been recently working in our group with (1R,2S)-ephedrine, (1S,2S)-pseudoephedrine and derivatives as chiral structure-directing agents (SDA) for the synthesis of microporous aluminophosphates.²⁵⁻

²⁹ These molecules were originally selected as SDA precursors since they contain two stereogenic centers and are enantiomerically-pure, imparting a strong asymmetric nature that could be potentially transferred to the inorganic framework. Moreover, they contain an aromatic ring which enables π - π -driven supramolecular aggregation, as well as H-bond donor and acceptor groups, both molecular features activating a rich supramolecular chemistry. In fact, a combined experimental and computational study

showed that the supramolecular chemistry associated to these molecules is strongly influenced by the conformational behavior, which is in turn dictated by the development of intramolecular H-bonds.²⁶ We also prepared the methyl- and dimethyl-derivatives of (1R,2S)-ephedrine, and they led to the crystallization of the AFI framework, but with a notably poorer π - π -driven supramolecular chemistry.³⁰ Due to the interest in the structure-direction of zeolite materials with these chiral molecules, we have now extended the study of the structure-directing behavior of (1R,2S)-dimethylephedrinium and its diastereoisomer (1S,2S)-dimethylpseudoephedrinium cations to the synthesis of aluminosilicate-based zeolites (see Scheme 1). Due to the limited stability of this cation, the synthesis has been performed in fluoride medium in order to avoid a basic pH that would enhance the degradation of the cation during hydrothermal crystallization. On the course of this synthesis study, we obtained a new material which, on the basis of physico-chemical characterization and molecular modeling, was identified as a new layered precursor of ferrierite with expanded layers, which we denoted as ICP-2 (ICP stands for *Instituto de Catálisis y Petroleoquímica*).

Scheme 1. Molecular structures of the SDA cations used in this work.

2. Experimental and Computational Details

Synthesis of ICP-2

(1R,2S)-(-)-Dimethylephedrinium (DMEP) iodide was prepared through two consecutive methylation reactions of (1R,2S)-(-)-Ephedrine (Sigma-Aldrich, 98 %), following the same procedure as reported in our previous work.³⁰ The iodide salt was further transformed into the corresponding hydroxide (DMEPOH) through an anionic resin (Amberlite IRN-78, Aldrich), and concentrated up to ~24.0 wt %. A similar procedure was followed for the preparation of the diastereoisomer (1S,2S)-(+)-dimethylpseudoephedrinium (DMPsEP) hydroxide, starting in this case from (1S,2S)-(+)-Pseudoephedrine (Sigma-Aldrich, 98 %).

ICP-2 was discovered after a systematic study of the structure-directing efficiency of DMEPOH for the synthesis of Al-containing zeolite materials in fluoride medium. In particular, ICP-2 was prepared from a gel with composition 0.5 DMEPOH : 0.98 SiO₂ : 0.01 Al₂O₃ : 0.4 HF : 3 H₂O. In a typical synthesis, 5.57 g of tetraethylorthosilicate (Sigma-Aldrich, 98 %) and 0.109 g of aluminium isopropoxide (Alfa-Aesar, 98 %) were added to 11.75 g of DMEPOH aqueous solution (24.0 wt %). The mixture was kept under stirring at room temperature, allowing ethanol and water to evaporate until the desired composition was reached. 0.45 g of HF (Sigma-Aldrich, 48 %) was then added, and the mixture was finally homogenized with a spatula. The gel was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 14 cm³, which was heated statically at 120 °C under autogenous pressure for 5 days. The resulting solid was collected by filtration, washed with water and dried at room temperature.

In order to analyze the stability, as-made ICP-2 was thoroughly washed with ethanol under stirring for 2 hours at 40 °C, then filtered, washed with water and characterized by XRD. Calcination of ICP-2 was carried out at 550 °C (heating ramp of 2.9 °C/min with N₂ flow) in N₂ for 1 h and then in air for 20 hours.

Characterization of ICP-2

The obtained solids were characterized by powder X-Ray Diffraction (XRD), using a Philips X'PERT diffractometer with CuK_α radiation with a Ni filter. In-situ XRD experiments at increasing temperatures were performed in air from room temperature to 550 °C (heating rate = 10°/min), collecting XRD data at 50 °C intervals. Thermogravimetric analyses (TGA) were registered in air using a Perkin-Elmer TGA7 instrument (heating rate = 20 °C/min). UV-Visible diffuse reflectance spectra were registered using a UV-Vis Cary 5000 Varian spectrophotometer equipped with an integrating sphere using the synthetic polymer Spectralen as reference. CHN analyses were carried out with a LECO CHNS-932 elemental analyzer. Infrared measurements were carried out using an Attenuated Total Reflectance spectrophotometer (ATR, PIKETECHNOLOGIES), using quartz as detector. The nitrogen adsorption isotherm was recorded at 77 K in a Micromeritics ASAP 2420; surface areas were calculated by the BET method and pore volumes were determined at $P/P_0 = 0.1$. The samples were previously outgassed at 573 K. ^{13}C , ^{29}Si , ^{27}Al and ^{19}F MAS-NMR spectra were recorded with a Bruker AV 400 WB spectrometer, while spinning the samples at a rate of 10 kHz (further details are given in the Supporting Information). The morphology of the obtained crystals was studied using a Hitachi S3000N Scanning Electron Microscope. For the transmission electron microscopy studies, the powders were crushed, dispersed in ethanol, and dropped on a holey carbon grid. Images and selected area diffraction (SAED) patterns were taken with a JEOL 2100F.

Supramolecular aggregation of the DMEP cations in the solid materials was studied by fluorescence spectroscopy. Solid state UV-Visible fluorescence emission spectra were recorded in a RF-5300 Shimadzu fluorimeter. The fluorescence spectra were registered in the front-face configuration by a solid sample holder in which the samples were oriented 30 and 60° with respect to the excitation and emission beams, respectively.

Fluorescence spectra of the solid samples were recorded by means of thin films supported on glass slides elaborated by solvent evaporation from a dichloromethane suspension of the solid samples.

Computational Details

In an attempt to understand the structure of ICP-2 and the structure-directing behavior of DMEP (and DMPsEP), molecular simulations based on molecular-mechanics were performed. The molecular structures and packing of DMEP and their interactions with the zeolite framework are described with the pcff forcefield (with forcefield-assigned charges for the organic and water molecules), using the Forcite module, as implemented in Material Studio 7.0.³¹ This forcefield is based on CFF91, and has been extended so as to have a broad coverage of organic polymers, (inorganic) metals, and zeolites;³² we selected since it reproduced correctly the conformational behavior of the two cations in vacuum (as determined by DFT+D/B3LYP calculations with a 6-311++G(dp) basis set using the Gaussian09 code).³³ All calculations were performed under periodic boundary conditions (PBC), keeping the zeolite framework fixed during the calculations. The framework charges were initially fixed to -0.3 for O and 0.6 for Si. The positive charge of DMEP was compensated by the framework by uniformly reducing the Si atomic charge until neutrality. The organic cations were docked in the required configuration and geometry-optimised. The interaction energies were calculated by subtracting the energy of the organic cations in vacuum to the total energy of the systems; interaction energies are reported in kcal/mol. Further details of the particular models are given in the corresponding section.

Due to the importance of the conformational behavior of the different ephedrine-derived diastereoisomers and its strong influence on the resulting supramolecular chemistry that we have already observed,²⁶ an initial conformational analysis was performed. The

conformational space of the cations was scanned by means of the Conformers Calculation Module in Materials Studio,³⁴ using a systematic grid scan search method and optimising the molecular structures for each set of dihedral angles. The stability of the different conformers was determined by ab-initio calculations, using the DFT+D/B3LYP methodology. The aggregation behavior of the two cations in water was studied by means of Molecular Dynamics (MD) simulations, using the Forcite code, in the same way as reported in our previous works.^{26,35} 16 organic cations and 16 Cl⁻ anions were included in the simulation cell together with 96 water molecules (in the same ratio as in the synthesis gel used for the synthesis of ICP-2), and 1000 ps of MD simulations in the NVT ensemble were then run at 298 K. The aggregation behaviour of the cations was studied by analysing the Radial Distribution Functions (RDF) of different sets of atoms [$g_{\alpha\beta}(r)$] (using only the last 500 ps of the MD simulations for production of data).

3. Results

A. Synthesis and characterization of ICP-2

In an attempt to promote the crystallization of chiral zeolite materials, we have performed an extensive study about the structure-directing efficiency of DMEPOH for the synthesis of Al-containing silica-based zeolites in fluoride medium. Results soon showed a rather limited hydrothermal stability of this cation at high temperatures, as we had observed previously in the synthesis of AlPO materials.³⁰ Only at 120 °C in fluoride (at nearly-neutral pH) medium did the DMEP cation resisted enough time to promote the crystallization of zeolitic materials. Under these conditions, a crystalline material, which we denoted as ICP-2, was obtained after 5 days of hydrothermal crystallization at 120 °C from a gel with a Si/Al ratio of 50. Slight variations of the Si/Al ratio and HF or

H₂O contents also led to ICP-2 but with slightly lower crystallinity (the same material was obtained with a composition of 0.5 DMEPOH : 0.98 SiO₂ : 0.01 Al₂O₃ : 0.5 HF : 5 H₂O).

Figure 1. XRD patterns of as-made ICP-2 (top), DMEP-PREFER (middle) and calcined (bottom) materials.

Figure 1 shows the XRD pattern of ICP-2 (top, black line), which is characterized by a very intense diffraction peak at low angle (at 4.4° 2θ, corresponding to a 'd' spacing of 20 Å) (no other diffractions at lower angles are found), and several other diffractions in the middle-angle region. TG analysis shows a very strong desorption of volatile compounds, with a total weight loss up to 43.5 % (Figure 2, black line). The organic content was lost mostly in two steps, at around 200° and between 450° and 700° C. CHN analysis showed a C/N ratio of 13, close to the nominal value for DMEP of 12; assuming that DMEP is intact, the C analysis indicated a DMEP organic content of 34.0 %. The weight loss (observed by TGA) between 90 °C (desorption at lower temperature

is due to physisorbed water) and 900 °C is 40.7 %, but only 34.0 % would be due to the organic content. This suggests a strong desorption of water occurring in this temperature range, possibly associated to condensation of silanol/siloxy groups (with consequent formation of water) at high temperatures. ^{13}C NMR of ICP-2 (Figure S1 in the Supporting Information, black line) showed that all the C resonances of DMEP are present (compare with liquid ^{13}C NMR of DMEP iodide in MeOD, blue line), confirming the resistance of the DMEP cations to the hydrothermal treatment and their intact incorporation within ICP-2. The XRD pattern of ICP-2 with such intense low-angle diffraction, together with the extremely large organic content, suggest that the structure of ICP-2 must be a layered framework with the interlayer space filled by the organic cations.

Figure 2. Thermogravimetric analyses (solid lines) of as-made ICP-2(Al) (black line), DMEP-PREFER (red line) and the pure-silica version of ICP-2 (blue) materials; derivatives are shown as dashed lines.

Fluorescence spectroscopy was used to analyze the supramolecular aggregation state of DMEP cations in ICP-2 (Figure 3). Phenyl ring gives a fluorescence band with a vibronic structure centered at 282 nm when the molecules are isolated (monomers). Supramolecular aggregation of phenyl-containing species through π - π stacking of their aromatic rings provokes a reorganization of the electronic levels which results in a strong red-shift of the fluorescence band.^{30,36} The fluorescence spectrum of ICP-2 showed the main fluorescence band at 360 nm, evidencing that the DMEP cations are involved in supramolecular aggregates through π - π stacking. The intensity of the signal at 282 nm is very low, suggesting a very minor (if at all) presence of DMEP cations as monomers in the material. The presence of supramolecular aggregates is also evidenced by UV-Vis absorption spectroscopy (Figure S2 in the Supporting Information) because of the presence of a shoulder at 300-400 nm characteristic of π - π stacking.

Figure 3. Fluorescence spectroscopy of as-made Al-ICP-2 (black line) and DMEP-PREFER (red line) materials.

In an attempt to gain insights on the framework structure of ICP-2, an in-situ XRD study of the behavior of the material at increasing temperatures was undergone (Figure 4). ICP-2 is stable up to 100 °C, where there is no desorption of organics (only of physisorbed water, as observed by TGA in Figure 2). Above 100 °C, ICP-2 starts to intensively desorb organic material (see TGA in Figure 2), and this results in a collapse of the framework, as observed by the strong reduction of the intensity of the diffraction peak at 4.4° 2θ (Figure 4); however, a local order is preserved due to the remaining of several middle-angle diffractions (between 12° and 30° 2θ). When the temperature is increased to 250 °C (a very strong desorption of organics occurs between 200 and 250 °C, see TGA in Figure 2), a new low-angle diffraction raises at 6.7° 2θ (corresponding to a 'd' spacing of 13.1 Å, indicating a strong reduction of the basal space from 20 Å in

Figure 4. In-situ XRD patterns of Al-ICP-2 at increasing temperatures; *RT denotes the final material after cooling at room temperature.

ICP-2), while the medium- and high-angle diffractions remain. The XRD pattern of this new material (ICP-2_250C) resembles those of layered precursors of ferrierite (the so-called PREFER and other related materials).^{4,37-44} This material is stable up to 350 °C; during this temperature range (from 100 to 350 °C), a strong desorption of volatiles up to 25 wt % occurs (slightly more than half of the total volatile content) (Figure 2). Above 350 °C, the diffraction at 6.7° 2θ progressively shifts at increasing temperatures towards higher angles up to 550 °C, giving a final value of 9.0° 2θ, being the basal space reduced from 13.1 down to 9.8 Å. In this temperature range, the second strong desorption of volatile contents of 15.5 % occurs (Figure 2), concomitant to the reduction of the basal space. The XRD pattern of this final material corresponds to the FER

(ferrierite) framework. This FER material is stable when the temperature is dropped back to room temperature (Figure 4-dashed line).

All the characterization results so far suggest that ICP-2 must be a layered precursor of ferrierite, with fer layers as the inorganic framework, separated by DMEP cations residing in the interlayer space, arranged as an organic bilayer-like structure stabilized through π - π interactions between the aromatic rings (as evidenced by fluorescence spectroscopy). In line with this, a thorough washing of ICP-2 in ethanol (at 40 °C for 2 hours) transforms this material into the same PREFER-like material (hereafter called DMEP-PREFER) (Figure 1-bottom, red line) as the one observed during the high-temperature XRD experiments (upon heating ICP-2 at 250 °C: ICP-2_250C). This again suggests that the layers in ICP-2 are of the *fer* topology (since no relevant transformation of the internal structure of the inorganic layers is expected during this washing). Hence, both mild treatments, heating at 250 °C or washing with EtOH at 40 °C, transform ICP-2 into PREFER, leading to a decrease of the basal space from 20 to 13.1 Å while reducing the organic content to half. ^{13}C NMR (Figure S1 in the Supporting Information, red line) and CHN analysis again evidenced the integrity of DMEP cations within PREFER, with the organic content reduced from 34.0 (in ICP-2) to 18.3 % (in DMEP-PREFER). Fluorescence spectroscopy (Figure 3, red line) shows the presence of both monomers and supramolecular aggregates in DMEP-PREFER, which is also confirmed by the lower intensity of the shoulder in the UV-Vis spectra (see Figure S2 in the Supporting Information). Assuming a FER-like unit cell composition (with 4 additional O atoms to account for the layered interrupted FER framework, $\text{Si}_{36}\text{O}_{76}$), ICP-2 and DMEP-PREFER would contain 6.87 and 2.84 DMEP cations per unit cell. Direct calcination of this material also yields ferrierite (Figure 1, blue line).

Figure 5. SEM (top) and TEM (bottom) images of as-made ICP-2 and calcined materials.

Electron microscopy studies reveal plate-like particle morphology both for ICP-2 and the calcined ferrierite material. Figure 5-top collects scanning electron microscopy (SEM) micrographs, showing very thin plates of ICP-2 forming very open agglomerates. Upon calcination, the plates seem more condensed and thick yet maintaining the agglomerated nature. Transmission electron microscopy coupled with selected area electron diffraction (Figure 5-bottom) allowed observing individual thin plates of ICP-2. The electron diffraction pattern obtained from the area marked with a square in the image of ICP-2 (in the inset) could be indexed as ferrierite ‘bc’ plane.⁴³ Systematic electron diffraction analyses thus confirmed that the single plates of ICP-2

are formed by ferrierite sheets. Attempts have been made to identify the interlayer spacing present within single plates; however the material is extremely sensitive under the electron beam, which yields rather unreliable results for calculation of the basal space. The calcined material, already identified as ferrierite via XRD, show thicker and more stable plates under the electron beam.

Figure 6. ^{27}Al (top) and ^{29}Si (bottom) MAS NMR of as-made ICP-2 (black line), DMEP-PREFER (red line) and calcined (blue line) materials.

The inorganic composition of the fer-like layers was analyzed by NMR. ^{27}Al NMR of ICP-2 (Figure 6-top, black line) showed a single band at 52 ppm, characteristic of tetrahedral Al embedded in the fer layers;^{6,7,38,45} the absence of resonances at ~ 0 ppm evidenced the lack of extra-framework octahedral Al. Similar bands characteristic of

tetrahedral Al are observed in DMEP-PREFER (red line) and FER calcined materials (blue line). In the latter sample, a certain amount of extraframework octahedral Al is produced during the calcination treatment. ^{29}Si NMR of ICP-2 (Figure 6-bottom, black line) shows several well-defined resonances, one centered at -111 ppm (with a shoulder at -114 ppm), which can be assigned to SiQ4 species in the fer layers, and another intense signal at -103 ppm, which can be ascribed to SiQ3 species (in silanol/siloxy groups), confirming that ICP-2 is an interrupted framework;^{6,8,38} the high intensity and resolution of this band suggests a well-defined position of the Si-O_x dangling bonds. In addition, ICP-2 shows also a band at -106 ppm, which could be due to Si(1Al) Q4 species. ^{29}Si NMR of DMEP-PREFER shows similar bands (red line), although slightly shifted with respect to ICP-2, at -112 ppm (SiQ4) and a broader band centered at -104 ppm, which might involve both SiQ3 and Si(1Al) Q4 species. Calcination of these FER-precursors does not lead to two well-resolved ^{29}Si NMR bands (blue line) as reported previously,⁸ but instead leads to a broad band centered at -111.5 ppm with several components, similar to that of the calcined FER materials obtained by the co-template synthesis route;^{42,43} this might indicate a particular spatial distribution of the Al sites. The presence of silanol groups in ICP-2 was confirmed by ATR-IR which showed a band at 960 cm⁻¹ characteristic of silanol groups (Figure S3 in the Supporting Information). As expected, the intensity of this band was notably reduced in PREFER-DMEP and further in the calcined FER material, due to the progressive condensation of the dangling bonds.

^{19}F NMR (not shown) revealed a series of signals at around -124 ppm which are likely due to the common presence of hexafluorosilicate (SiF_6^{2-}) or $\text{SiO}_x\text{F}_{(6-x)}$ species accompanying these materials when prepared in fluoride medium.^{38,46,47} However, signals around -59 ppm typical of fluoride in [5⁴] cavities of the FER framework are not

observed, suggesting that fluoride is not part of the ICP-2 framework, the same as occurred for the original PREFER material.³⁸

Finally, the textural properties of the ferrierite material obtained after calcination of ICP-2 were analyzed by N₂ adsorption/desorption isotherm, and were compared with those of a ferrierite material obtained by calcination of PREFER, as reported in the literature⁹ (hereafter called FER-prefer). The BET surface area of our material is 388 m²/g, notably higher than that of FER-prefer (277 m²/g), with a notably higher external surface area in our material due to inter-crystalline volume (149 m²/g compared to 52 m²/g of FER-prefer). Nonetheless, the micropore volume of our calcined material was only slightly lower (0.100 cm³/g compared to 0.113 cm³/g for FER-prefer). The high BET surface of calcined ICP-2 might be associated to the particular crystal size and morphology of our material, as observed by SEM (Figure 5), which might improve diffusion of reactants and products.

We tried to obtain ICP-2 in the absence of Al, and indeed we succeeded and produced the all-silica version of ICP-2 (Si-ICP-2, Figure S4 in the Supporting Information). Surprisingly, calcination of this Al-free version of ICP-2 did not produce a FER material but only amorphous. Indeed, XRD at increasing temperatures revealed that Si-ICP-2 first transformed into the PREFER derivative, the same as in the Al-version, but this was not further transformed into the pure-Si version of FER, but rather into an amorphous material (Figure S5 in the Supporting Information). Comparison of the organic weight losses (see TGA in Figure 2) showed a distinct organic desorption pattern of ICP-2 as a function of the presence of Al: part of the organic material is strongly retained and is only desorbed at the high temperature of 600 °C in Al-ICP-2 because of the presence of Al and the formation of acid sites during the thermal treatment (black line). In contrast, the Al-free version of ICP-2 desorbs a higher amount

of organics at lower temperatures because of the absence of acid sites (blue line). Therefore, such desorption of organics at lower temperatures might lead to a collapse of the framework at temperatures too low as to enable a reorganization of the material to promote the topotactic condensation to produce a FER material. In contrast, the presence of Al provokes a strong retention of the organic pillars, and Al-ICP-2 only collapses at very high temperatures which enable the reorganization into the final FER material by topotactic condensation.

We finally tried to produce ICP-2 but using (1S,2S)-dimethylpseudoephedrinium (DMPsEP), the diastereoisomer of DMEP (1R,2S). Surprisingly, despite their very similar molecular structure, DMPsEP was not able to produce ICP-2 under the same synthesis conditions than DMEP, and only amorphous materials were observed.

B. Computational model of ICP-2

Due to the poor quality of the XRD pattern of ICP-2, which prevents an XRD crystallographic study, we attempted to unravel the structure of the material with the aid of molecular simulations. The characterization results found so far indicate that ICP-2 is a layered material composed of *fer* layers separated by an organic bilayer with the DMEP cations filling this interlayer space (~ 6.9 DMEP/u.c.), arranged as supramolecular aggregates stabilized through π - π interactions. Based on this information, we now applied molecular simulations in order to unravel the arrangement of the organic molecules within the interlayer space.

Our model of the inorganic framework consisted of the same *fer* layers (taken from the FER framework), which were separated away by interrupting through the FER cavities to give a basal space of 19.81 Å (corresponding to a FER ‘a’ unit cell parameter of 39.62 Å, assuming that the low-angle diffraction at $4.4^\circ 2\theta$ corresponds to 200 *hkl*);

additional O atoms were added to saturate Si atoms where the framework was cut. This gives place to interrupted layers with alternated pseudo-cavities and pseudo-10R-channels, which upon topotactic condensation will produce the FER framework.

1 DMEP cation was initially introduced in this layered framework in two different locations, with the trimethylammonium moiety sited in the pseudo-cavity or in the pseudo-10R-channel. Energy results indicate a higher stability for the cation residing in the pseudo-cavity (see Figure S6 in the Supporting Information), probably because of a stronger confinement of the trimethylammonium group.

Figure 7. Two views (left and right) of the location of 2 DMEP cations in the FER pseudo-cavities in configuration A (top) or B (bottom). Dashed yellow rectangles highlight supramolecular π - π interactions between DMEP cations in the organic bilayer.

We then incorporated a second DMEP cation (one on each adjacent layer) forming supramolecular aggregates (as evidenced by fluorescence spectroscopy) in the pseudo-

cavities. After an intensive computational search, two stable arrangements for DMEP dimers were obtained, being the stability of both very similar (Figure 7). In configuration A (top), the two DMEP cations composing the supramolecular aggregates are in the same pseudo-cavity, with the aromatic rings roughly perpendicular to the [010] axis, while in configuration B (bottom), the two DMEP cations composing the dimers are in consecutive pseudo-cavities in adjacent layers, with the aromatic rings roughly parallel to the [010] axis. Under both arrangements, the layers are held together through π - π type interactions between the aromatic rings (yellow dashed rectangles in Figure 7). These DMEP arrangements account for 4 SDAs/u.c., so we still need to include ~ 2.9 cations in the void space of the pseudo-10R-channels, and these again must be forming supramolecular aggregates.

After an intensive search, our simulations showed that the most stable arrangement of DMEP aggregates in the pseudo-10R channels involves these cations forming supramolecular dimers aligned with the [001] axis, one on each of the adjacent *fer* layers, giving an additional packing of 2.67 DMEP cations (indeed, 8 SDAs arranged as 4 dimers in 1x1x3 supercells), which together with the molecules in the pseudo-cavities give a total DMEP content of 6.67 SDAs/u.c., in close agreement with the experimental value of 6.87; this would give a unit cell composition for Si-CP-2 of $[(\text{DMEP})_{6.67} \text{Si}_{36}\text{O}_{76}\text{H}_{1.33}]$, where 6.67 of the 8 Si-O dangling bonds are siloxane groups to compensate for cationic charges, and 1.33 are SiOH groups (in the case of Al-ICP-2, the amount of siloxane groups is reduced according to the incorporation of Al). Figures 8 and 9 show the proposed location of DMEP cations in ICP-2, with DMEP in the cavities in the two possible configurations previously described (A and B, see Figure 7); the calculated interaction energies were very similar, -455.6 and -451.3 kcal/mol per u.c. for configurations A and B, respectively. DMEP cations play two complementary structural

Figure 8. Most stable arrangement of DMEP cations in ICP-2 layered material in configuration A (top) or B (bottom). Dashed yellow rectangles highlight supramolecular π - π interactions between DMEP cations in the organic bilayer. Two types of DMEP dimer locations are present, in the pseudo-cavities which held together the *fer* layers through π - π type interactions (blue dashed circle) and in the pseudo-10R-channels (green dashed rectangle); see Figure 9 for details.

roles: on the one hand, as previously described, 4 DMEP cations (per u.c.) site in the pseudo-cavities (in configuration A or B) (highlighted in blue dashed circles in Figure 8, and detailed in Figure 9-left), with the trimethylammonium groups inside the pseudo-cavities, holding the layers together through the establishment of π - π type interactions

Figure 9. Details of the arrangement of DMEP cations in configuration A (top) and B (bottom), with the two types of positions of the organic cations in the pseudo-cavities, holding the layers together through π - π interactions (left, blue dashed circles in Figure 8), and in the pseudo-10R-channels (right, green dashed circles in Figure 8) remarked as sticks.

between DMEP cations in adjacent layers (dashed yellow rectangles in Figure 8). On the other hand, 2.67 DMEP cations (per u.c.) site forming dimers aligned with each of the pseudo-channels (highlighted in green dashed rectangles in Figure 8, and detailed in Figure 9-right); in this case, there is no intermolecular connection between the molecules in adjacent layers, and their structural role is to fill the pseudo-channels. In

both types of locations, DMEP cations always arrange as supramolecular dimers with π - π stacking interactions (see Figure S7 in the Supporting Information for a detail), as experimentally evidenced by fluorescence spectroscopy. The simulated XRD pattern of our model for ICP-2 is reasonably similar to that experimentally obtained, considering the low crystallinity of the obtained ICP-2 material and the probable occurrence of a certain degree of disorder in the layers which prevented further XRD analysis (see Figure S8 in the Supporting Information).

The transformation by ethanol-washing (or thermal treatment) of ICP-2 into DMEP-PREFER involves a strong reduction of the organic content in the interlayer space, with a concomitant approximation of the *fer* layers; besides, the DMEP cations are now occluded both as monomers and dimers (Figure 3). Hence, on the basis of the proposed model for ICP-2, we suggest that DMEP-PREFER is formed upon extraction of approximately half of the DMEP cations forming dimers in the pseudo-channels, which will remain as supramolecular dimers, and approximately half of the cations residing in the pseudo-cavities, which will now be occluded as monomers. This should give an organic content of 3.33 DMEP/u.c., which is reasonably close (though slightly larger) to the experimental value of 2.87 DMEP/u.c., and giving a unit cell composition of $[(\text{DMEP})_{3.33} \text{Si}_{36}\text{O}_{76}\text{H}_{4.66}]$ (in the absence of Al). We also modeled this system (with a basal space of 13.2 Å, following the experimental ‘d’ spacing of $6.7^\circ 2\theta$), and observed that the new framework structure is compatible with such an arrangement of the organic molecules (Figure 10): supramolecular aggregates (evidenced by fluorescence spectroscopy) can only be hosted in the 10-ring channels, where the most stable orientation in this framework involves a rotation of 90° of the organic cations around the ‘c’ axis, while the cavities have now only room to host DMEP monomers, in good agreement with the experimental observations.

Figure 10. Two views (top and bottom) of the arrangement of DMEP cations in DMEP-PREFER, with the two types of locations for DMEP cations, arranged as monomers in the cavities (white dashed circles) or as dimers along the 10R channels (yellow dashed circles).

We finally incorporated the diastereoisomer, DMPsEP, in the same positions as those for DMEP, and geometry-optimized the system. The calculated interaction energies were -452.8 kcal/mol per u.c. for configuration A, very similar to that for DMEP (-455.6 kcal/mol); on the contrary, the interaction energy for DMPsEP in configuration B was rather lower, -414.6 kcal/mol per u.c. (compared to -451.3 kcal/mol for DMEP). The fact that our experiments showed that DMPsEP does not lead to the crystallization of ICP-2 might point to configuration B as being the arrangement required for the formation of ICP-2 during the crystallization process.

Figure 11. Top: relative energies (DFT+D3/B3LYP, in kcal/mol) of different conformers of DMEP (left) and DMPsEP (right); bottom: RDF between aromatic C atoms (left) and between the aromatic C atoms with the substituent attached (cp0) and N atoms (right) for solutions of DMEP (blue) and DMPsEP (red).

We then analyzed the conformational behavior of the two diastereoisomers in vacuum. Conformational analysis (DFT+D/B3LYP level) showed three related stable conformers for the two diastereoisomers (Figure 11-top): conformer 1, the most stable one for both diastereoisomers, had the bulky ammonium group in ‘anti’ position from the aromatic ring. In contrast, conformers 2 and 3 had the bulky ammonium moiety closer (in ‘gauge’ position) to the aromatic ring. Conformer 2, which is more stable for DMEP ($\Delta E = 2.5$ kcal/mol for DMEP and 4.0 kcal/mol for DMPsEP), has the aromatic ring in ‘anti’ to the H atom. Conformer 3, which has the aromatic ring in ‘anti’ position to the methyl groups, is more stable for DMPsEP in this case ($\Delta E = 1.9$ kcal/mol for DMPsEP and 4.1 kcal/mol for DMEP). We note that the conformer that produces ICP-2 (with DMEP) is exclusively conformer 1, with the two bulky groups (ring and trimethylammonium) in ‘anti’ position, away from each other.

We then studied the conformational behavior of the two diastereoisomers in aqueous solution (at the same concentration as in the synthesis gel of ICP-2: 1R:6H₂O). RDF of the aromatic C atoms (Figure 11-bottom-left) shows a peak at ~ 6 Å, indicative of π - π stacking, which is slightly more intense for DMPsEP. The occurrence of conformer 1 or conformers 2 and 3 can be monitored by plotting the RDF between the aromatic C atom with the substituent attached (cp0) and the N atom: in conformer 1, this distance is 3.9 Å for both diastereoisomers, whilst in conformers 2 and 3, this distance is 3.2-3.4 Å. The intramolecular cp0-N RDF (Figure 11-bottom-right) shows that DMEP occurs almost exclusively as conformer 1 (peak at 4 Å), whilst DMPsEP occurs as a mixture of conformer 1 (peak at 4 Å) and conformers 2 and 3 (peaks at 3.4 Å). Together with the low interaction energy of DMPsEP in ICP-2 under configuration B, these conformational behaviors in water could also explain that DMPsEP does not direct the formation of ICP-2, since only conformer 1 is able to drive its crystallization.

4. Discussion

The use of the chiral DMEP cation has allowed for the discovery of a new type of layered materials with expanded layers directly from crystallization, precursor to the FER framework. Apart from the ferrierite precursors (PREFER and the like),³⁷⁻⁴³ several other materials built from the same *fer* layers but with alternative linkages have been obtained;^{4,48,49} in these materials a close interaction between the adjacent layers (usually through H-bonds) is established, in contrast to our layered material where the large size of the organic bilayer forces the *fer* layers to sit further away, thus preventing H-bond interactions between layers.

Figure 12. Details of the stabilization of the different structural elements of the *fer* layers by the different configurations of the DMEP cations in ICP-2, and detail of the pillaring of the layers through π - π -interactions (dashed yellow rectangles).

The crystallization of ICP-2 occurs because DMEP cations play a dual structural role during the crystallization process (Figure 12); in fact, the intimate structural relationship between the organic cation and the inorganic framework is manifested by the fact that a very similar organic cation, the (1S,2S)-diastereoisomer, cannot produce the material. The structure-directing role of DMEP is two-folded: on the one hand, the pseudo-10R-channels of the *fer* layers are filled by DMEP supramolecular dimers aligned with the

channel direction, providing stabilization to this structural element. On the other hand, the pseudo-cavities of the *fer* layers are stabilized through confinement of the trimethylammonium group, which nicely fits within the void space of this topological item, as we previously demonstrated for tetramethylammonium,⁴⁵ and leaving pending aromatic rings exposed. One can realize the core-shell structure of these layers, where the *fer* layers compose the inorganic core and are surrounded by a shell of the organic cations, which stabilizes the system by providing a protective shield against hydrolysis during the hydrothermal treatment, a role that has been previously proposed.⁵⁰ On the other hand, the exposed aromatic rings allow a self-assembly with other adjacent layers in the medium through stacking of their aromatic rings driven by π - π -type interactions, giving the final ICP-2 material. This type of self-assembly process is enabled by the particular molecular structure of DMEP, which has a hydrophobic self-assembling aromatic ring on one side, separated by a long-enough alkyl chain from a hydrophilic positively-charged trimethylammonium head which resembles the chemical structure of typical zeolite SDA cations.

This type of π - π supramolecular interactions has been previously used by us^{35,36,51,52} and others⁵³⁻⁵⁹ to promote the formation of large supramolecular dimers in an attempt to produce large structure-directing agents that will drive the crystallization of large-pore zeolites. Moreover, a similar concept as the one exposed here for ICP-2 has been previously reported for the production of single-crystalline mesostructured MFI zeolite nanosheets.^{60,61} In addition, similar organo-inorganic layered materials with the interlayer space composed by an organic bilayer have been reported previously by us^{62,63} and others.⁶⁴ The strategy of using these simple SDA cations with quaternary ammonium groups (typically directors of zeolite units) separated by a long-enough alkyl chain from a self-assembling aromatic ring (typically directors of π - π -stacked organic

bilayers) should be extendable to the production of other layered zeolite materials with the layers already expanded, which could be precursors to zeolitic catalytic materials with large external surface areas or further transformed into 3D zeolite frameworks.

Conclusions

In this work we present the synthesis and characterization of ICP-2, a new crystalline layered material crystallized in the presence of chiral (1R,2S)-dimethylephedrinium (DMEP) as the organic structure-directing agent. Physico-chemical characterization of ICP-2 indicates a large basal space of ~ 20 Å and an extremely large organic content of 34 %, with the aromatic cations incorporating as supramolecular aggregates stabilized through π - π interactions. ICP-2 can be easily transformed in PREFER (ferrierite precursor) by washing with ethanol or heating at moderate temperatures (200 °C), and then to ferrierite by calcination (at 550 °C). The Al-free version of ICP-2 could also be produced, but this did not lead after calcination to FER materials. Surprisingly, the diastereoisomer (1S,2S)-dimethylpseudoephedrinium did not drive the crystallization of ICP-2. On the basis of the characterization and a subsequent molecular modeling study, we propose a structure for ICP-2, where the inorganic layers have the same structure as those of PREFER, with a core-shell structure where the shell is composed of the organic cations arranged as supramolecular dimers surrounding the inorganic cores in two different locations, aligned with the pseudo-channels and with the trimethylammonium groups in the pseudo-cavities. These core-shell *fer* layers are expanded to a basal distance of 19.81 Å, and the layers are held together through the development of π - π stacking interactions between the aromatic rings of the cations sitting in the pseudo-cavities. The weak nature of these inter-layer interactions makes ICP-2 an easily un-assemblable material, which can then be transformed into catalysts or other zeolite

frameworks through topotactic condensations. As a final comment, worth is remarking the potential of molecular modeling to assist in the structure-solution of new materials when poorly-crystalline phases are obtained.

Supporting Information

MAS-NMR details, ^{13}C CP MAS-NMR, UV-Vis Absorption, ATR-IR spectroscopy, additional XRD patterns and additional molecular pictures are reported as Supporting Information.

Conflict of interest

There are no conflicts to declare.

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TOC Graphic

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