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Supra-molecular assembly of aromatic proton sponges to direct the crystallization of extra-large-pore zeotypes

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The combination of different experimental techniques, such as solid ¹³C and ¹H magic-angle spinning NMR spectroscopy, fluorescence spectroscopy and powder X-ray diffraction, together with theoretical calculations allows the determination of the unique structure directing the role of the bulky aromatic proton sponge 1,8-bis(dimethylamino)naphthalene (DMAN) towards the extra-large-pore ITQ-51 zeolite through supra-molecular assemblies of those organic molecules.

1. Introduction

Bulky and rigid organic structure-directing agents (OSDAs) can be useful for the preparation of zeolites with large void volumes, and especially for the synthesis of extra-large-pore zeolites [1,2]. Using large and rigid OSDAs, different extra-large-pore zeolites presenting mono-directional 14-ring channels [3–5], multi-dimensional extra-large channels [6,7] and even mesoporous zeolites [8,9] have been synthesized. In these cases, the zeolite crystallization occurs through the interaction of single organic molecular units with the inorganic sources present in the synthesis gel. Bulky and rigid OSDAs must be soluble in the synthesis media (usually aqueous media), present high hydrothermal stability, and, more importantly, have strong non-bonded

Figure 1. Proton sponge DMAN.

interactions with the host inorganic matrix during nucleation–crystallization processes [10]. However, when the C/N ratio is increased above a certain value ($C/N > 14$), some solubility problems of these bulky OSDAs in aqueous media can appear precluding their structure-directing capacity [1,2].

Several years ago, a new organic structure-directing concept based on supra-molecular assemblies was introduced in the preparation of zeolites, and the pure silica small-pore large-volume A zeolite (LTA) was synthesized, breaking the paradigm that this zeolite could only be synthesized with high Al contents [11]. In this case, the bulky OSDA required to template the large LTA cavity and to allow minimization of framework negative charges was achieved by the supra-molecular self-assembly of two organic molecules presenting an aromatic ring, forming stable and soluble bulky dimers through π – π -type interactions [11]. Later, similar supra-molecular self-aggregation through π – π -type interactions of aromatic molecules, such as benzylopyrrolidine, was also described for the crystallization of the large-pore AIPO-5 zeotype [12,13].

Very recently, we introduced a new type of aromatic OSDA, i.e. an aromatic proton sponge (1,8-bis(dimethylamino)naphthalene (DMAN); figure 1), for the synthesis of the extra-large-pore ITQ-51 zeotype, whose structure presents 16-ring channels [14]. DMAN is a commercially available bulky aromatic diamine with the amine groups in close proximity, providing high basicity ($pK_a > 12.1$) by the repulsion of the close electronic lone pairs [15]. This high basicity would favour their protonation in the synthesis media, allowing organic–inorganic interactions during the nucleation–crystallization processes.

We will show here a combination of experimental and computational techniques in order to evaluate the structure-directing roles of these aromatic molecules, including their ability to be protonated and their self-aggregation as dimers in the synthesis gel and in the final as-prepared solid. The proton sponge dimers will allow the stabilization of the 16-ring extra-large pores of the ITQ-51 zeolite.

2. Experimental and computational details

(a) Synthesis

The synthesis procedure of ITQ-51 can be found in [14]. Aqueous solutions of DMAN were prepared by adding equimolecular amounts of the corresponding proton sponge and phosphoric acid. The ionic complex of DMAN with orthophosphoric acid was prepared by mixing 217.7 mg of H_3PO_4 (85 wt%, Sigma-Aldrich), 257.2 mg of proton sponge (99 wt%, Sigma-Aldrich) and 615.4 mg of water, and the resultant solution was lyophilized to remove the solvent.

(b) Characterization

The solid-state NMR spectra were recorded at room temperature on a Bruker AV 400 spectrometer. A ^{13}C magic-angle spinning (MAS) NMR cross-polarization spectrum was recorded at a sample-spinning rate of 5 kHz. A 1H MAS NMR spectrum was achieved with a spinning rate of 10 kHz at 400 MHz with a $\pi/2$ pulse length of 5 μs . ^{13}C and 1H NMR chemical shifts were referenced to adamantane and tetramethylsilane, respectively.

Table 1. Crystallographic data for Rietveld refinement of as-prepared ITQ-51. GOF, goodness-of-fit; R_p , unweighted-profile R -factor; R_{wp} , weighted-profile R -factor; R_{exp} , expected R -factor; R_F , R -factor based on the F^2 ; SDA, structure-directing agent.

chemical formula	(C ₁₄ N ₂ H ₁₈ H) _{0.5} Al ₄ P ₄ O ₁₆
formula weight	2381.88
<i>a</i>	24.0445(11) Å
<i>b</i>	16.25415(63) Å
<i>c</i>	5.04846(20) Å
α	90°
β	91.5672(28)°
γ	90°
<i>V</i>	1972.31(14) Å ³
<i>Z</i>	4
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
CuK α_1	1.5406 Å
no. reflections	1380
no. parameters	117
no. restraints	384 T-O distances, rigid body for SDA and distance among the SDA and frameworks
R_p	0.0521
R_{wp}	0.0667
R_{exp}	0.0263
GOF	2.536
R_F	0.0281

Steady-state photoluminescence measurements were recorded on a Photon Technology International 220B spectrofluorimeter with Xe arc lamp light excitation and a Czerny–Turner monochromator, coupled to a photomultiplier. The solid samples were pressed between two Suprasil quartz cuvettes with a path length of 0.01 mm and placed at a 45° angle to both the excitation and emission monochromators. All measurements were carried out at room temperature.

(c) Refinement against powder X-ray diffraction data

The structural model underwent Rietveld refinement using Total Pattern Analysis Solution (TOPAS) with soft restraints for T–O bond distances and rigid body restraints for the OSDAs. The framework positions were fully occupied. There is one unique OSDA in the unit cell, with an occupancy of 0.5. All the atoms were refined isotropically and the atomic displacement parameters were restrained to be equal for similar atoms. The refinement of the ITQ-51 model was converged with $R_F = 0.0281$ and $R_{wp} = 0.0667$. The refinement detail is given in table 1.

(d) Computational methods

Several energetic contributions are widely acknowledged to be at play, such as electrostatic (long range) and van der Waals (short range) zeo-OSDA. A fundamental idea behind this approach is the fact that the location of the OSDA molecule is mainly dictated by short-range van der Waals forces between the OSDA and zeolite framework, the oxygen atoms of the zeolite being the most important in the interaction with the OSDA owing to their large size and anionic character.

In order to estimate the OSDA location within the micropore void, we use the following strategy: (i) one molecule of OSDA is located in the micropore of ITQ-51 and the minimum energy position is found through a simulated annealing-type procedure with repeated cycles of molecular dynamics runs followed by energy minimization; (ii) the unit cell of ITQ-51 is filled with different loadings of each particular OSDA and the optimum loading is calculated as that which minimizes the total energy; (iii) once the optimum loading is found, we use minimization algorithms for the full system. Then, we calculate the final contributions to the energy of the subsystems as shown in equations (2.1)–(2.3),

$$E_{\text{initial}} = E_{\text{frame}} + E_{\text{OSDA-OSDA}} + E_{\text{OSDA}} \quad (2.1)$$

and

$$E_{\text{final}} = E_{\text{frame}'} + E_{\text{frame}'-\text{OSDA}'} + E_{\text{OSDA}'-\text{OSDA}'} + E_{\text{OSDA}'} \quad (2.2)$$

A full electrostatic model has been considered with OSDA molecules containing a +1 charge. Owing to the fact that the positions of the counteranions are unknown, the compensating charge has been uniformly distributed across the framework atoms in order to have a neutral unit cell [16].

Therefore, it is expected that the energy difference between the final and initial states is owing to the SDA incorporation, which should be a negative, hence stabilizing, interaction. Some of the above terms will be positive, such as the energy difference regarding framework energy ($E_{\text{frame}'} - E_{\text{frame}}$) and OSDA energy ($E_{\text{OSDA}'} - E_{\text{OSDA}}$), and hence each of the individual moieties experiences an energy increase in the synthesis process. However, the interaction between the zeolite framework and the SDA molecules ($E_{\text{frame}'-\text{OSDA}'}$) should be sufficiently negative to compensate the previous energetic increase.

Combining equations (2.2) and (2.1), we obtain the final expression below, which shows quantitatively whether the synthesis is more or less feasible with the corresponding OSDA molecule. The more negative the value, the more favourable the synthesis.

$$\Delta E_{\text{synthesis}} = \Delta E_{\text{frame}} + E_{\text{frame}'-\text{OSDA}'} + \Delta E_{\text{OSDA-OSDA}} + \Delta E_{\text{OSDA}} \quad (2.3)$$

The calculations in steps (i), (ii) and (iii) have been performed using lattice energy minimization techniques [17] and the General Utility Lattice Program (GULP) code [18,19], employing a direct summation of the short-range interactions with a cut-off distance of 12 Å and using periodic boundary conditions. In this case, the symmetry has not been taken into account in order to allow the system to relax more freely, without any constraint; hence, only P1 symmetry has been considered. The rational functional optimizer technique was used as the cell minimization scheme with a convergence criterion of a gradient norm below 0.001 eV Å⁻¹. To account for the effect of the OSDA in the system, the force field described by Kiselev *et al.* [20] has been used for the intermolecular OSDA–zeolite and OSDA–OSDA interactions. For the AIPO system, a force field developed in a previous study was employed [21].

For a more in-depth study of the interactions between the OSDA molecules, a full electron quantum approach based on new functionals containing dispersion terms has been used in order to obtain a more accurate picture of the intermolecular interactions and their role in the total OSDA–OSDA energy obtained. The functionals CAM-B3LYP [22] and LCWPBE [23], including dispersion, have been used. In all cases, the accurate triple zeta for valence electrons plus polarization function (TZVP) basis set [24] has been employed, and the results have been checked against basis set convergence by also using the further improved quadruple zeta valence electrons plus polarization function (QZVP) basis set. The GAUSSIAN09 software package was used for the optimization of the OSDA molecules using the density functional theory (DFT) approach outlined above.

The calculated unit cell parameters are: $a = 23.61$ Å, $b = 16.25$ Å, $c = 4.95$ Å, $\alpha = 90.0^\circ$, $\beta = 90.9^\circ$, $\gamma = 90.0^\circ$. The calculated stacking shows a relative rotation of the two SDA molecules of 155° , observing a tilt of 82° between the plane of the aromatic rings and the c (vertical) axis. This tilt is 74° in the experimental case. The combination of two opposite forces balanced could explain

Table 2. Comparison of experimental and calculated cell parameters of as-prepared ITQ-51.

parameter	calculated	experimental	difference (exp – calc)
<i>a</i>	23.61 Å	24.04 Å	+0.43 Å (1.8%)
<i>b</i>	16.25 Å	16.25 Å	+0.00 Å (0.0%)
<i>c</i>	4.95 Å	5.05 Å	+0.10 Å (2.0%)
α	90.0°	90.0°	
β	90.9°	91.6°	
γ	90.0°	90.0°	
volume	1897.67 Å ³	1972.31 Å ³	74.64 Å ³ (3.8%)
tilt	82°	74°	

the slight discrepancies between the calculated and the experimental OSDA orientations. In this sense, attractive OSDA framework interactions would drive the geometry towards a 90° tilt angle, while short-range repulsions due to the limited pore diameter lead to a larger tilt angle. It is suggested that the force field employed does not contain the appropriate balance between attractive and repulsive forces. Nevertheless, an overall reasonable correspondence of the calculated OSDA location has been found with loading and location similar to the experimentally observed (table 2).

3. Results

In previous work, we demonstrated by elemental analysis and solid ¹³C MAS NMR (see spectrum of the as-prepared ITQ-51 in figure 2) that the proton sponge DMAN remains intact within ITQ-51 crystals after the crystallization process [14]. However, despite the high proton affinity of DMAN molecules to form stable ionic species containing intramolecular [N...H...N]⁺ hydrogen bonding [15,25,26], the protonated nature of the occluded DMAN molecules within as-prepared ITQ-51 was not described. To properly analyse whether DMAN molecules are protonated or not, as-prepared ITQ-51 was characterized by solid ¹H MAS NMR spectroscopy. As seen in figure 3c, two main peaks are observed, corresponding to hydrogen bonds bound to the aliphatic and aromatic carbons, which are centred at approximately 2 and approximately 6.8 ppm, respectively. In addition to those large peaks, a small peak appears at 18.5 ppm. Interestingly, similar chemical shifts (approx. 17–18 ppm) have been described in the literature for the acidic proton shielded by the amino groups on different DMAN complexes with inorganic and organic acids [24–28]. The solid ¹H MAS NMR spectrum of commercially available DMAN only shows the two large peaks corresponding to protons bound to the aliphatic and aromatic carbons (figure 3a), but no signal at approximately 18.5 ppm is observed. However, if an ionic complex of DMAN is prepared with orthophosphoric acid (see Experimental and computational details) to force the protonated DMAN to form, the ¹H MAS NMR spectrum clearly shows the small band at 18.5 ppm (figure 3b), corresponding to the acidic proton between the amino groups, confirming that the DMAN is in a protonated form in the as-prepared ITQ-51.

Once the protonated nature of DMAN molecules in the as-prepared ITQ-51 has been confirmed, the next step was to understand the directing roles of the aromatic proton sponge molecules during the zeolite crystallization process. As described above, the supra-molecular chemistry has been rarely described in the structure direction of crystalline microporous materials, with π – π -type interactions of aromatic molecules being the only examples reported [11–13]. However, if the chemical structure of the DMAN molecule is considered, this proton sponge molecule shows a suitable size, rigidity, thermal stability and hydrophobicity (aromatic naphthalene group) to be a potential candidate to form bulky dimers by supra-molecular self-assembled OSDAs.

Figure 2. Solid ^{13}C MAS NMR of as-prepared ITQ-51 molecular sieve (a) and liquid ^{13}C NMR of proton sponge DMAN (b).

Figure 3. Solid ^1H MAS NMR spectra of DMAN (a), of the complex of DMAN with orthophosphoric acid (b), and of the as-prepared ITQ-51 molecular sieve (c).

It has been described that, during the synthesis of LTA when self-assembly through π - π -type interactions of aromatic molecules occurs, the fluorescence spectrum shows an intense shift of the emission band towards higher wavelengths by the strong interaction of the aromatic rings [11]. Having that in mind, we have prepared two aqueous solutions of DMAN at different concentrations, 5×10^{-4} M and 3 M, in order to study the fluorescence emission spectra of the diluted and concentrated solutions. The idea behind this is that DMAN molecules would remain

Figure 4. UV-vis spectrum of DMAN in aqueous solution.

Figure 5. Height-normalized fluorescence emission spectra of DMAN aqueous solutions at different concentrations and as-prepared ITQ-51 solid, measured at different excitation wavelengths (270, 285 and 300 nm). The arrow indicates the second-order emission.

as monomers in highly diluted conditions while dimerization may occur under concentrated conditions. It is important to note that this DMAN concentration is the same as that required in the preparative gel for the synthesis of ITQ-51. As the UV-vis spectrum of DMAN in aqueous solution shows a band centred at 285 nm (figure 4), the photoluminescence study of both DMAN aqueous solutions was performed at the excitation wavelengths of 270, 285 and 300 nm. As can be observed in figure 5, both diluted and concentrated DMAN solutions present similar fluorescence emission spectra with a main fluorescence band centred at 475 nm. This result clearly indicates that self-interactions of DMAN molecules through π - π -type interactions of aromatic molecules do not occur in either the diluted or concentrated solutions of DMAN, and, therefore, it can be expected

Figure 6. Liquid ^1H NMR spectra of an aqueous solution of DMAN at 5×10^{-4} M (a), at 3 M (b), and solid ^1H MAS NMR spectrum of the as-prepared ITQ-51 zeotype (c).

Figure 7. Observed (blue), calculated (red) and difference (black) PXRD profiles for the Rietveld refinement of the as-prepared ITQ-51 ($\lambda = 1.5406$ Å). The higher angle data have been scaled up (inset) to show the good fit between the observed and calculated patterns.

that dimers of DMAN molecules by π - π stacking will not be formed during the synthesis of ITQ-51. Indeed, the fluorescence emission spectrum of the as-prepared ITQ-51 solid shows a shift of the fluorescence band towards a lower wavelength (approx. 415 nm; figure 5), which could be attributed to a particular interaction of DMAN molecules in the confined space of the ITQ-51. Nevertheless, it can be asserted that neither in the synthesis gel nor in the final solid is there self-aggregation of DMAN molecules through π - π -type interactions.

Figure 8. The structure of experimental as-prepared ITQ-51 zeolite viewed along [001] (a), and viewed along [010] (b). For clarity, the OSDAs in the channels on the edges of the unit cell were removed.

However, when both aqueous solutions of DMAN were studied by liquid ^1H NMR spectroscopy, intense chemical shifts were observed for the hydrogen bound to the aliphatic and aromatic carbons, which depend on the concentration of DMAN (figure 6). The diluted DMAN solution shows peaks ranging from 7.9 to 7.6 ppm for the protons associated with the aromatic carbons and a peak centred at 3 ppm for the protons associated with the aliphatic carbons (figure 6a). On the other hand, the concentrated DMAN solution shows signals at 6.8–6.3 and 1.9 ppm, for the protons associated with the aromatic carbons and aliphatic carbons, respectively (figure 6b). These changes in the chemical shifts of more than 1 ppm in the liquid ^1H NMR spectra depending on the DMAN concentration would be associated with some self-interactions of DMAN molecules under concentrations similar to those used during the zeolite synthesis. Interestingly, the ^1H MAS NMR spectrum of the as-prepared ITQ-51 shows two broad peaks centred at 6.9 and 2.4 ppm (figure 6c), which resembles the ^1H NMR spectrum of the concentrated DMAN solution. Particular issues related to the confinement of DMAN molecules within the ITQ-51 structure could be the reason for the slightly different chemical shifts. Thus, we could conclude from the ^1H NMR spectroscopy that a self-interaction of DMAN molecules may occur in the synthesis gel and in the final as-prepared ITQ-51 solid, but it cannot be unequivocally ascertained from the characterization results obtained so far.

To confirm or reject the formation of DMAN dimers, a structural model of the as-prepared ITQ-51 material has been developed using powder X-ray diffraction (PXRD) data. The structural model underwent Rietveld refinement using TOPAS [29] with soft restraints for T–O bond distances and rigid body restraints for the OSDAs. The framework positions were fully occupied. There are only two OSDAs in each unit cell, and they are distributed in four different sites, with an occupancy of 0.5 each. All the atoms were refined isotropically and the atomic displacement parameters were restrained to be equal for similar atoms. The refinement of the ITQ-51 model converged to $R_F = 0.0281$ and $R_{WP} = 0.0667$. The refinement details are given in figure 7 and table 1. From the structural solution, it is observed that the OSDAs are located in the middle

Figure 9. Views of the calculated unit cell of ITQ-51 with four OSDA molecules.

of the 16-ring channels with a rotation angle of 74° from the channel axis (figure 8a) and form stacking OSDA dimers (figure 8a,b).

A computational study has also been performed to further support the dimer formation (see Experimental and computational details). In the optimized geometry of ITQ-51-OSDA (figure 9a), it can be observed that the OSDA molecules are not perpendicular to the channel axis. As the OSDA molecule is wider ($9.2 \text{ \AA}$) than the channel width ($7.7 \text{ \AA}$), the OSDA has to rotate (figure 9b). This deviation from an ideal angle of 90° seeks to maximize the OSDA framework attraction and also maximize the OSDA–OSDA interaction.

As described in the crystallographic structure model, the OSDA molecules adopt stacking inside the zeolite which is not very different from that calculated in the gas phase, in spite of the fact that the pore size/shape represents a constraint for the optimization of the OSDA dimer (see details in Experimental and computational details and table 2). Calculations at the level of first principles using DFT indicate a stabilization energy in the gas phase of $4.1 \text{ kJ (mol-of-dimer)}^{-1}$. The present OSDA dimer interactions are mainly driven by electrostatic and van der Waals interactions (see Experimental and computational details and table 3). Regarding the geometries of the OSDA dimers in the zeolite framework, figure 10 shows in detail that the bulky methyl groups are on opposite sides of the neighbour OSDA, with the aromatic rings parallel to each other. The OSDA–OSDA distance in the optimized ITQ51-OSDA system is $4.99 \text{ \AA}$. Taking into account that the planes of the naphthalene moieties of each SDA molecule are not parallel, an exact distance cannot be defined and this should only be taken as an approximation.

Figure 10. OSDA dimers within the ITQ-51 zeolitic framework. The calculated distance between the two OSDA molecules through the naphthalene planes is 4.99 Å.

Table 3. Stabilization energy (kJ mol^{−1}) of the OSDAs in the ITQ-51 zeotype. The values have been calculated for the optimum loading, which includes four OSDA molecules in a 1 × 1 × 2 unit cell of ITQ-51. With these values, a total stabilization energy of −409 kJ is obtained according to equation (2.3) ($\Delta E_{\text{synthesis}} = \Delta E_{\text{frame}} + E_{\text{frame}'-\text{OSDA}'} + \Delta E_{\text{OSDA}-\text{OSDA}} + \Delta E_{\text{OSDA}}$).

$\Delta E_{\text{synthesis}}$	ΔE_{frame}	$E_{\text{frame}'-\text{OSDA}'}$	$\Delta E_{\text{OSDA}-\text{OSDA}}$	ΔE_{OSDA}
−409	+80	−364	−145	+20

4. Conclusion

We have demonstrated by experimental and computational techniques the unique self-assembly role of the aromatic proton sponges in the synthesis of the extra-large-pore ITQ-51 zeolite. In this sense, the design of new OSDAs allowing the control of their supra-molecular chemistry can provide an efficient tool to direct the synthesis of new microporous materials, especially those presenting extra-large-pore structures.

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