

: Molecules as Efficient Organic Structure

Self-Assembled Aromatic Molecules as Efficient Organic Structure Directing Agents to Synthesize the Silicoaluminophosphate SAPO-42 with Isolated Si Species

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ABSTRACT: The use of self-assembled aromatic molecules through $\pi - \pi$ interactions has allowed the preparation of the silicoaluminophosphate (SAPO) form of the LTA, SAPO-42, with controlled Si content as isolated Si sites in the framework, and high thermal stability. Different SAPO-42 zeotypes can be synthesized with different acidity, morphology, and crystal size, depending on the selected quinolinium derived aromatic molecule as OSDA and the amount of fluoride content in the synthesis gels.



1. INTRODUCTION

LTA is a crystalline molecular sieve, whose structure is formed by large spherical cavities (~1.14 nm) interconnected by threedimensional small pores (~0.4 nm).¹ Since its discovery in 1961 by Barrer and Denny,² low silica LTA zeolite (Si/Al ratios lower than 2) has become an important industrial material with application as a drying agent or cation exchanger.³ Researchers have endeavored to rationalize the synthesis of LTA in an attempt to expand the number of applications of this zeolite to catalysis or gas separations. One of the big challenges was to increase the Si/Al ratio of the LTA zeolite to improve acidity, hydrothermal stability, and hydrophobicity. In this sense, Corma et al. proposed the use of bulky organic structure directing agents (OSDAs) formed by self-assembly of two aromatic organic molecules (MTPQ, see Figure 1) through $\pi - \pi$ interactions, to synthesize LTA in a wide range of framework Si/Al ratios, even in the pure silica form (ITQ-29).⁴



Figure 1. Aromatic organic molecules used as OSDAs for the synthesis of SAPO-42 materials: (a) 2,2-dimethyl-2,3-dihydro-1H-benzo[de]-isoquinoline-2-ium (DDBQ) and (b) 4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido [3.2.1-ij] quinolinium (MTPQ).

It appears that the synthesis of ITQ-29 zeolite is a very interesting example of the correlation between the shape and size of the OSDA and the framework cavity.⁵

In addition to the silicate and silicoaluminate forms of LTA, this material can also be prepared under other chemical compositions, such as aluminophosphate $(AIPO-42)^6$ and silicoalumiphosphate (SAPO-42).⁷ Silicoaluminophosphates (SAPOs) can be applied as heterogeneous acid catalysts since the insertion of isolated framework Si atoms by selective isomorphic substitution of Si by P atoms in their crystalline structures generates medium-strong Brønsted acid sites.⁸ Unfortunately, the ideal Si distribution as isolated Si species is not always accomplished, and large Si domains in the framework, named "Si islands", can also be present in SAPOs.⁹ In general, SAPOs with "Si islands" show lower acidity and hydrothermal stability than similar SAPOs with better Si distributions. For the particular case of SAPO-42 with LTA structure, very high contents of Si (SiO₂ between 15 and 35 wt %) were always required for its synthesis.¹⁰ This results in materials with large domains of "Si islands" and limited acidity and hydrothermal stability.

Very recently, Moscoso¹¹ and Schmidt et al.¹² have succeeded in the synthesis of SAPO-42 with low silicon content (SiO₂ less than 10 wt %). The OSDAs used for the preparation of these low-silica SAPO-42 materials are a combination of tetraethylammonium fluoride and diethanolamine¹¹ and a bulky and complex triquad,¹² respectively. In both cases, characterization describing silicon distribution and

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acidity of these SAPO-42 has not been reported. Moreover, SAPO-42 materials prepared using the bulky triquad OSDA were not stable after calcination treatments.¹²

In past years, we have worked on the synthesis of small pore SAPOs with large cavities and controlled silicon distributions as catalysts for the selective catalytic reduction (SCR) of NOx.¹³ Particularly, we have shown that the use of bulky self-assembled aromatic molecules as OSDAs (MTPQ, see Figure 1) has allowed the efficient synthesis of the small pore SAPO STA-6 with an excellent Si distribution, so the presence of large Si-rich domains was avoided.¹⁴ Having in mind that the pure silica LTA zeolite was achieved using the same bulky self-assembled aromatic molecule (MTPQ, see Figure 1), it could be envisioned that related OSDAs would show adequate properties to allow the synthesis of the small pore SAPO-42 zeotype with proper Si distributions.

Herein, we describe the synthesis of SAPO-42 using two aromatic organic molecules (MTPQ and DDBQ, see Figure 1), which are able to form soluble dimers in the synthesis media through $\pi - \pi$ interactions. Self-assembled paired MTPQ molecules allow the synthesis of SAPO-42 only when fluoride anions are present in the synthesis media, while self-assembled paired DDQB molecules are able to direct the crystallization of SAPO-42 only under fluoride-free conditions. We will also show that the presence of fluoride anions in the synthesized SAPO-42 zeotypes with LTA structure clearly influences the framework silicon distribution and, consequently, their acid properties.

2. EXPERIMENTAL SECTION

2.1. Synthesis of the Organic Structure Directings Agents (OSDAs). 2,2-Dimethyl-2,3-dihydro-1H-benzo[de]isoquinoline-2ium (DDBQ). A total of 21.7 g (109.6 mmol) of commercial 1,8naphthalic anhydride was heated under reflux in an aqueous solution of *N*-methylamine (40 wt %) for 72 h. The mixture was cooled at room temperature, and the white solid obtained was filtered and dried under a vacuum to give *N*-methyl-1,8-naphthalimide (23.1 g, 100%). The spectral data were fully coincident with those described in the literature.¹⁵

¹H NMR (CDCl₃, 300.0 MHz): $\delta_{\rm H}$ 8.5 (d, *J* = 9 Hz, 2H, Ar–H), 8.1 (d, *J* = 9 Hz, 2H, Ar–H), 7.7 (t, *J* = 9 Hz, 2H, Ar–H), and 3.5 (s, 6H, 2xNCH₃). ¹³C NMR (CDCl₃, 75.5 MHz): $\delta_{\rm C}$ 164.5 (2×C=O), 133.9, 131.6, 131.2, 126.9, 122.6 (Ar–C), and 27.0 (NCH₃).

Then, 23.4 g (111.0 mmol) of N-methyl-1,8-naphthalimide was added in small portions to a stirred solution of 14.8 g (388.0 mmol) of LiAlH₄ and 100.0 mL of AlCl₃ THF complex (0.5 M in THF; 50.0 mmol) in 600 mL of anhydrous THF, cooled in an ice bath, and maintained under N₂. The mixture was stirred for 30 min at room temperature before being refluxed for 7 h, and then, it was stirred at room temperature overnight. The temperature was decreased with an ice bath, and the excess of LiAlH₄ was quenched by the slow addition of 10 mL of H₂O. After 30 min, the formed salts were filtered and washed with THF and ethyl acetate, providing 14.9 g (73%) of the desired amine as yellow oil after evaporation under a vacuum. The spectral data were fully coincident with those described in the literature.¹⁵

¹H NMR (CDCl₃, 300.0 MHz): $\delta_{\rm H}$ 7.7 (d, *J* = 6 Hz, 2H, Ar–H), 7.4 (t, *J* = 6 Hz, 2H, Ar–H), 7.2 (d, *J* = 6 Hz, 2H, Ar–H), 3.9 (s, 4H, 2×CH₂), and 2.6 (s, 6H, 2×NCH₃). ¹³C NMR (CDCl₃, 75.5 MHz): $\delta_{\rm C}$ 133.5, 133.1, 127.9, 126.1, 125.6, 121.9 (Ar–C), 58.7 (2×CH₂), and 45.6 (NCH₃).

Finally, 50.0 mL (803.2 mmol) of methyl iodide was slowly added to a solution of 14.9 g (81.4 mmol) of 2-methyl-1,3-dihydrobenz-[d,e]isoquinoline in 75 mL of MeOH. The mixture was stirred for 1 week, and no precipitate was observed. The solution was concentrated to dryness, and the resulting solid was washed with acetonitrile, filtered, and dried, providing 18.3 g (69%) of the desired ammonium salt as a white powder.

The spectral data. ¹H NMR (DMSO-d6, 300.0 MHz): $\delta_{\rm H}$ 8.0 (d, J = 9 Hz, 2H, Ar–H), 7.6 (t, J = 9 Hz, 2H, Ar–H), 7.5 (d, J = 9 Hz, 2H, Ar–H), 5.0 (s, 4H, 2×CH₂), and 3.2 (s, 6H, 2×NCH₃). ¹³C NMR (DMSO-d6, 75.5 MHz): $\delta_{\rm C}$ 132.1, 128.6, 126.6, 124.9, 124.8, 124.3 (Ar–C), 63.4 (2×CH₂), and 51.1 (2×NCH₃). Anal. Calcd for C₁₄H₁₆IN: C, 51.71; H, 4.96; N, 4.31. Found: C, 52.2; H, 5.17; N, 4.35.

To obtain the hydroxide form of the organic cation, 9 g of the iodide salt was dissolved in water, and thus, 30 g of resin Dower SBR was added. The mixture was maintained overnight under stirring, and after filtration, the hydroxide form of the organic cation was obtained.

4-Methyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3.2.1-ij]quinolinium (MTPQ). The synthesis of MTPQ has been described previously.⁴ To prepare the corresponding hydroxide form of the organic cation, 8.52 g of the iodide salt was dissolved in water, and 27 g of resin Dower SBR was added. The mixture was maintained under stirring overnight. The solution was filtered, and the hydroxide form of the organic cation was obtained.

2.2. Synthesis of the Silicoaluminophosphate Materials. In a typical zeotype synthesis procedure, the required amount of orthophosphoric acid (85 wt %, Aldrich) was added to the aqueous solution of the hydroxide form of the OSDA. Then, the alumina source (75 wt %, Condea) was introduced, keeping the gel under stirring for 5 min. A silica source (Ludox AS40, 40 wt %, Aldrich) was also introduced into the synthesis gel, leaving the mixture under stirring for 20 min. If required, HF was finally added to the gel, and the resultant mixture was stirred for 20 min. The gel was transferred to a Teflon-lined stainless steel autoclave with a free volume of 3 mL and heated at the appropriate temperature under static conditions for 5 days. Crystalline products were filtered and washed with abundant water and dried at 100 °C overnight. The samples were calcined in a tube furnace following the next temperature program: the samples were heated at 600 °C using a 1 °C/min ramp under flowing N2. The temperature was held for 8 h under flowing air, and finally, the samples were cooled to room temperature under flowing N2.

2.3. Characterization. Powder X-ray diffraction (PXRD) measurements were performed with a multisample Philips X'Pert diffractometer equipped with a graphite monochromator, operating at 45 kV and 40 mA, and usig Cu K α radiation (λ = 0.1542 nm).

The chemical analyses were carried out in a Varian 715-ES ICP-Optical Emission spectrometer, after solid dissolution in $HNO_3/HCl/$ HF aqueous solution. The organic content of the as-made materials was determined by elemental analysis performed with a SCHN FISONS elemental analyzer. Thermogravimetrical analysis was performed using a Mettler Toledo thermo-balance.

The morphology of the samples was studied by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope and by field emission scanning electron microscopy (FESEM) using a ZEISS Ultra-55 microscope.

MAS NMR spectra were recorded at room temperature with a Bruker AV 400 spectrometer. ²⁹Si NMR spectra were recorded with a spinning rate of 5 kHz at 79.459 MHz with a 55° pulse length of 3.5 μ s and repetition time of 180 s. ²⁹Si chemical shift was referenced to tetramethylsilane. ¹⁹F was measured at 376.28 MHz using a Bruker probe with 2.5-mm-diameter zirconia rotors spinning at 25 kHz. The ¹⁹F spectra were collected using pulses of 4.5 μ s corresponding to a flip angle of $\Pi/2$ rad and a recycle delay of 100 s to ensure the complete recovery of the magnetization.

NH₃-TPD experiments were carried out in a Micromeritics 2900 apparatus. A calcined sample (100 mg) was activated by heating to 400 $^{\circ}$ C for 2 h in an oxygen flow and for 2 h in an argon flow. Subsequently, the samples were cooled to 176 $^{\circ}$ C, and NH₃ was adsorbed. The NH₃ desorption was monitored with a quadrupole mass spectrometer (Balzers, Thermo Star GSD 300 T) while the temperature of the sample was ramped at 10 $^{\circ}$ C/min under a helium flow. Total ammonia adsorption was measured by repeated injection of calibrated amounts of ammonia at 176 $^{\circ}$ C until saturation. Ammonia

desorption was recorded by means of the mass 15, since this mass is less affected by the water desorbed.

UV-vis spectra were obtained with a PerkinElmer (Lambda 19) spectrometer equipped with an integrating sphere with $BaSO_4$ as a reference.

Steady-state photoluminescence measurements were performed in a Photon Technology International (PTI) 220B spectrofluorimeter having Xe arc lamp light excitation and a Czerny–Turner monochromator, coupled to a photomultiplier. The solid samples were pressed between two windows of 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.

Textural properties were determined by N_2 adsorption isotherms measured at 77 K with a Micromeritics ASAP 2020.

3. RESULTS AND DISCUSSION

3.1. Synthesis of SAPO-42 Material Using DDBQ Organic Molecule as OSDA. Since the high silica LTA zeolite (ITQ-29) has been synthesized using bulky self-assembled dimers formed by the interaction of two MTPQ molecules (see Figure 1) through $\pi - \pi$ interactions,⁴ it could be expected that this aromatic molecule would direct the crystallization of the SAPO form of the LTA, SAPO-42. However, under the typical SAPO conditions, MTPQ allows the selective crystallization of the STA-6 material instead of the SAPO-42.¹⁴ Despite the similarities between STA-6 and SAPO-42 structures, both present small pores and large cavities, STA-6 cavities (9.6 × 9.6 Å, see SAS cavity in Figure 2b) are slightly



Figure 2. Large cavities present in the SAPO-42 (A) and STA-6 (B) structures.

smaller than those of SAPO-42 (11.4×11.4 Å, see LTA cavity in Figure 2a). Thus, the preferential structure directing effects of the π -stacked dimers of MTPQ toward the STA-6 cavities forced us to design new OSDAs that favor the stabilization of the LTA cavity. Having in mind the different size of both cavities, we have used aromatic molecules slightly larger than MTPQ as potential OSDAs to stabilize the LTA cavities and, consequently, to favor the crystallization of SAPO-42. In this sense, a bulky aromatic molecule containing naphthalene groups, such as 2,2-dimethyl-2,3-dihydro-1H-benzo[de]isoquinoline-2-ium (DDBQ, see Figure 1a), has been prepared to study its templating directing role for the synthesis of silicoaluminophosphate materials.

For this purpose, an initial experimental design was established to study the following synthesis variables: P/Al, Si/(Al+P) and H₂O/(Al+P). The values for P/Al, Si(Al+P), and H₂O/(Al+P) molar ratios were [1, 0.9, 0.8], [0, 0.052, 0.11], and [30, 50], respectively. The syntheses were carried out at 175 °C for 5 days under static conditions in a fluoride-free system.

The silicon-free aluminophosphate form of LTA, AlPO-42, was achieved under very diluted synthesis conditions ($H_2O/TO_2 = 50$, see experiment LTA-1 in Figure 3a), but the PXRD pattern of this sample reveals the presence of a small amount of a dense phase as an impurity (see LTA-1 in Figure 4a). If silicon is introduced in the synthesis mixture under similar diluted gels, the dense phase is obtained as a pure crystalline phase (see Figure 3a). However, the preparation of gels under more concentrated conditions ($H_2O/TO_2 = 30$) allows the crystallization of the pure SAPO-42 material when the Si/(Al +P) is fixed at 0.11 (see LTA-2 in Figure 3a), and a mixture of an unstable lamellar phase and SAPO-42 is obtained when the Si amount is decreased (Si/TO₂ = 0.05, see phase diagram in Figure 3a).

The PXRD pattern of LTA-2 confirms the absence of other crystalline impurities, but some amount of amorphous material is also present in the sample, as reveals the slight curvature of the PXRD pattern background (see LTA-2 in Figure 4a). The existence of the amorphous phase in the LTA-2 sample is confirmed by scanning electron microscopy (SEM), where the presence of small crystallites with irregular morphologies



Figure 3. Phase diagrams achieved using DDBQ as OSDA at 175 °C for 5 days under static conditions.



Figure 4. PXRD patterns of LTA materials in their as-prepared (a) and calcined (b) forms. For comparison purposes, the simulated PXRD pattern of the pure silica form of LTA has been added.

characteristic of amorphous materials is observed (see Figure 5a).

To improve the crystallinity of the SAPO-42, a small amount of preformed crystals of SAPO-42 were introduced as seeds in the synthesis gels (~5 wt %). Two different Si contents (Si/ $TO_2 = 0.08, 0.11$) and gel concentrations (H₂O/TO₂ = 30, 50) have been selected to study the effect of the SAPO-42 seeds. Two SAPO-42 materials, LTA-3 and LTA-4, have been obtained when the synthesis gels are more concentrated (see phase diagram in Figure 3b). The PXRD patterns of LTA-3 and LTA-4 materials indicate high crystallinity and the absence of impurities (see Figure 4a). Both samples present similar crystal sizes of ~1 μ m with irregular rhombohedral morphology (see Figures 5b and 5c).

Chemical analyses on LTA-3 and LTA-4 reveal a similar silicon content in both samples [Si/(Al+P) ~ 0.1]. However, a significant difference in the aluminum content (0.66 and 0.54 for LTA-3 and LTA-4, respectively, see Table 1) is clearly observed in these two SAPO-42 samples. Theoretically, SAPOs should show Al mole fractions close to 0.50, because the preferential isomorphic substitutions involve Si and P atoms. Thus, the high Al mole fraction observed for LTA-3 (~0.66) could be explained by the presence of octahedral Al₂O₃ species that have not been inserted in framework positions during the synthesis. Moreover, the large amount of octahedral Al₂O₃ species in extra-framework positions could also explain the relatively low micropore volume observed for LTA-3 (~0.12

cm³/g, see Table 2). In contrast, SAPO-42 containing a mole fraction of Al close to 0.5 (see LTA-4 in Table 1) shows a significantly higher micropore volume (\sim 0.27 cm³/g, see Table 2), which is comparable to the values reported for the high-silica LTA polymorphs.⁴

The amount of the organic occluded within the LTA-4 material after the crystallization procedure was determined by thermogravimetric analysis (TGA). As seen in Table 3, the total weight loss between 200 and 750 °C, which is assigned to the organic moieties occluded within the microporous molecular sieves, was almost 22 wt %. On the other hand, elemental analysis of the as-prepared LTA-4 material reveals a C/N ratio of 12.5. It is important to note that the theoretical C/N value for the DDBQ molecule is 14, indicating that most of the aromatic molecules entrapped within the micropore structure (almost 90%) remain stable after zeotype crystallization (see Table 1). Additionally, the stability of the aromatic OSDA molecules within the as-prepared LTA-4 has also been studied by ¹³C NMR spectroscopy. As shown in Figure 6, the solid state ¹³C MAS NMR spectrum of the as-prepared LTA-4 material shows similar chemical shifts to those of the liquid ¹³C NMR spectrum of the organic DDBQ molecule, confirming the stability of the aromatic molecules occluded in the crystalline solids.

The number of DDBQ molecules per LTA cavity in the asprepared LTA-4 material can be calculated from the TGA results (see LTA-4 in Table 3) and the structural information on the LTA framework; i.e., each unit cell has one cavity, and it is composed of 24 T atoms. Thus, it was calculated that it should be almost two DDBQ molecules per cavity for LTA-4 (see Table 1). This result would indicate that DDBQ aromatic molecules could act as paired-OSDAs during the crystallization of the SAPO-42 materials. However, further characterization is required to confirm or reject the paired nature of the aromatic DDBQ molecules.

In our original work on the synthesis of the high silica LTA zeolite, the state of aggregation of similar aromatic molecules both in the synthesis gels and final crystalline products was proven by fluorescence spectroscopy.⁴ An intense shift of the emission band toward higher wavelengths in the fluorescence spectrum was observed and was related to $\pi - \pi$ interactions of the aromatic rings of the supramolecular self-assembled molecule.⁴ Here, the photoluminescence study with DDBQ has been performed at the excitation wavelength of 284 nm, since the UV-vis spectrum of DDBQ in aqueous solution shows its maximum at this wavelength (see Figure 7a). Then, aqueous solutions of DDBQ with two extreme concentrations $(1.10^{-4} \text{ and } 1 \text{ M})$ have been prepared as a control for the spectroscopic study. The highly diluted aqueous solution of DDBQ (1.10^{-4} M) is expected to be mostly formed by monomeric species, whereas the concentrated aqueous solution of DDBQ (1 M) should favor the presence of dimeric selfassembled species. It is important to note that the 1 M concentration of the aqueous solution of DDBQ is comparable to the real concentration of the aromatic organic molecules in the synthesis gels (see Figure 3). The fluorescence spectrum of the diluted solution shows a main fluorescence band centered at 325 nm, and the concentrated solution shows a broad fluorescence band ranging from 400 to 440 nm (see Figure 8). The fluorescence spectrum of the as-prepared LTA-4 material clearly shows the presence of a broad band between 400 and 450 nm (see Figure 8c), similarly to the spectrum of the concentrated aqueous solution of DDBQ (see Figure 8b).



Figure 5. SEM images of the different SAPO-42 materials: LTA-2 (a), LTA-3 (b), LTA-4 (c), LTA-5 (d), and LTA-6 (e).

Table 1. Chemical and Elemental An	lysis of SAPO-42 Materials S	ynthesized Using DD	BQ and MTPQ as OSDAs ^a
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	sample	Si ^b	\mathbb{P}^{b}	Al^b	Si/(Al+P)	wt % N	wt % C	$(C/N)_{real}$	OSDA/cavity
	LTA-3	0.11	0.23	0.66	0.12				
	LTA-4	0.10	0.36	0.54	0.10	1.61	17.34	12.5	2.1
	LTA-5	0.04	0.46	0.50	0.04	1.51	16.39	12.6	2.2
	LTA-6	0.05	0.43	0.52	0.05	1.65	16.87	11.9	2.3
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^{*a*}The estimated standard deviation (esd) of the analytical measures for Si, P, and Al is ± 0.002 , and for wt % N and wt % C is ± 0.005 . ^{*b*}Mole fractions (Si + Al + P = 1).

Table 2. Physico-chemical Properties of the SynthesizedSAPO-42 Materials^a

Table 3. Thermogravimetric Analysis (TGA) of the As-Prepared SAPO-42 Materials

				acidity concentration (mmol NH ₃ /g)		
sample	BET surface area (m²/g)	microp. area (m²/g)	microp. volume (cm ³ /g)	weak	mild	strong
LTA-3	384	245	0.12			
LTA-4	575	558	0.27	0.270	0.000	1.432
LTA-5	618	614	0.30	0.172	0.000	0.000
LTA-6	609	589	0.29	0.042	0.272	0.086

^{*a*}The estimated standard deviation (esd) of the analytical measures for BET surface area and the micropore is ± 5 and for micropore volume is ± 0.01 .

	loss of weight		
sample	<200 °C	200–750 °C	
LTA-3			
LTA-4	4.6	21.6	
LTA-5	2.2	22.9	
LTA-6	3.3	23.7	

Thus, it can be proposed that aromatic DDBQ molecules within the as-synthesized materials are forming self-assembled dimers through $\pi - \pi$ interactions, and these supramolecular assemblies are acting as bulky OSDAs.



Figure 6. Solid ¹³C CP MAS NMR of as-prepared LTA-4 (top) and liquid ¹³C NMR of DDBQ OSDA (bottom).



Figure 7. UV–vis spectra of the aromatic DDBQ (a) and MTPQ (b) OSDAs in aqueous solution.



Figure 8. Photoluminescence spectra ($\lambda_{ex} = 284$ nm) of (a) diluted aqueous solution of DDBQ at 1.10^{-4} M, (b) concentrated aqueous solution of DDBQ at 1 M, and (c) as-prepared LTA-4 material.

To our delight, the crystalline structure of the LTA-4 material remains stable after calcination in air at 580 °C, as reveals the PXRD pattern (see LTA-4_calc in Figure 4b). This is interesting because a recent report describing the synthesis of

similar SAPO-42 materials with low Si content using bulky triquads as OSDAs shows that these materials were not stable

after the calcination treatments.¹² Si Distribution and Surface Acidity.²⁹Si MAS NMR spectroscopy has been used to investigate the coordination of



Figure 9. ²⁹Si MAS NMR spectra of SAPO-42 materials.

the Si species in the LTA-4 material. As seen in Figure 9, the ²⁹Si MAS NMR spectrum mainly exhibits a strong band at -93 ppm, which has been assigned to Si(4Al) species or isolated Si atoms,¹⁶ a shoulder peak centered at -97, which has been assigned to Si(1Si3Al), and finally, a minor band centered at -110 ppm, which corresponds to undesired silicon islands (less than 10%).¹⁵ The large presence of isolated silicon species, which are selectively formed by the isomorphic substitution of Si⁴⁺ atoms by P⁵⁺ atoms in the zeolitic framework, must provide strong acidity to the SAPO. Thus, in order to evaluate the acidic properties of the LTA-4 material, the calcined sample has been characterized by temperature-programmed desorption of ammonia (NH₃-TPD). The different desorption temperatures indicate the different acidic strength of the acid sites present in the material. Indeed, two well-defined desorption peaks can be found in the LTA-4 sample (see Figure 10). The first peak centered at 200 °C corresponds to weak acid sites, mainly attributed to P-OH hydroxyl groups,¹⁷ and the second peak centered at 330 °C would indicate the presence of strong acid sites, which would correspond to the acidic protons associated with the presence of isolated silicon species in the zeolitic framework.17 The amount of strong acid sites is much higher than weak acid sites, as could expected by the high silicon distribution achieved within the LTA-4 material (see²⁹Si MAS NMR in Figure 9). The areas under the desorption temperature peaks allow the quantification of each acid site, giving 1.43 and 0.27 mmol NH₃/g for strong and weak acid sites, respectively (see LTA-4 in Table 2).



Figure 10. Temperature-programmed desorption of ammonia of calcined SAPO-42.

3.2. Synthesis of SAPO-42 Material Using MTPQ Organic Molecule as OSDA in Fluoride Medium. In addition to the organic directing effects of the paired-OSDAs to fill and stabilize the large cavity of the LTA structure, the introduction of fluoride anions in the synthesis media as inorganic structure directing agents can influence the nucleation and crystallization processes involved in the synthesis of the LTA. It is well-known that fluoride anions are able to stabilize some small cages present in zeolites, as for instance double-4-rings (D4Rs),¹⁸ which are also present in the LTA structure. Indeed, the synthesis of the high-silica form of the LTA (ITQ-29) requires the combination of bulky paired OSDAs (MTPQ) and fluoride anions to stabilize the large cavities and the D4R cages of the LTA structure, respectively. The presence of fluoride anions in the synthesis media not only favors the crystallization of the high-silica LTA structure due to the stabilization of the D4R cages but also helps to control the charge distribution within the crystalline structure by preferential location of fluoride anions within the D4Rs, allowing the preparation of the high-silica and even pure silica LTA polymorphs.

We have shown above that the use of self-assembled DDBQ dimers, whose size is slightly higher than the size of MTPQ dimers, is able to direct the crystallization of SAPO-42 with low Si content and highly distributed Si species under fluoride-free conditions. However, the introduction of fluoride anions in the synthesis gel of the optimized SAPO-42 material could produce significant alterations in its physicochemical properties, such as crystal size, silicon distribution, and acid strength, among others.

Thus, the synthesis of the SAPO-42 zeotype in a fluoride medium using DDBQ molecules as OSDA was first attempted. For this purpose, similar synthesis conditions to that described above for the optimum SAPO-42 under fluoride-free conditions were selected in this part of the work but in fluoride media: $[P/AI = 0.8, Si/(AI+P) = 0.11, MTPQ/(AI+P) = 0.5, HF/(AI+P) = 0.5, H_2O/(AI+P) = 10]$ at 175 °C for 5 days. Unfortunately, an unstable lamellar material was obtained under these synthesis conditions.

While changes in synthesis conditions may help to direct the synthesis toward the desired SAPO-42, we decided first to use the slightly smaller aromatic molecule MTPQ that can also fit well the cavity size and shape, as OSDA to attempt the synthesis of the SAPO-42 under fluoride conditions. We decided to use this OSDA on the basis that previous work showed that paired self-assembled MTPQ molecules for the synthesis of silicoaluminophosphate materials under fluoride-free conditions result in the crystallization of the STA-6 zeotype.¹⁴ However, since D4R cages are not present in the crystalline framework of STA-6 but in the LTA, it could be expected that the introduction of fluoride anions in the synthesis gel would favor the crystallization LTA with respect to STA-6.

The initial synthesis conditions selected to attempt the synthesis of the SAPO-42 under fluoride conditions using MTPQ as OSDA were [P/Al = 0.9, Si/(Al+P) = 0.05, MTPQ/ (Al+P) = 0.5, HF/(Al+P) = 0.5, H₂O/(Al+P) = 10] at 175 °C for 5 days. The resultant solid shows the characteristic PXRD pattern of SAPO-42 (see LTA-5 in Figure 4a), confirming the preferential directing effects of fluoride anions toward zeotypes containing D4R cages. The average crystal size for the LTA-5 sample is ~4 μ m (see Figure 5d), which is much larger than the crystal sizes obtained previously for other SAPO-42 materials synthesized under fluoride-free conditions (see Figure 5b and c).

The elemental analysis of the as-prepared LTA-5 solid reveals that the C/N molar ratio is very close to 13 (see Table 1), indicating that almost 90% of the MTPQ molecules remain intact after the SAPO-42 crystallization. The amount of aromatic molecules per cavity was calculated, as above, from the thermogravimetric analysis (see Table 3) and the structural information on SAPO-42. It results to be ~2 OSDAs/cavity (see Table 1). Then, as before, the photoluminescence study of control MTPQ aqueous solutions and as-prepared LTA-5 solid has been performed at the excitation wavelength of 265 nm (see UV-vis spectrum in Figure 7b). As can be seen in Figure 11, the as-prepared LTA-5 material shows a broad band in the photoluminescence spectrum at 400-440 nm that can be assigned to the presence of self-assembled MTPQ dimers through $\pi - \pi$ interactions of the aromatic rings. In conclusion, fluorescence and elemental analyses confirm the bulky paired nature of the aromatic MTPQ molecules acting as OSDA.

The crystallinity of the LTA-5 material remains intact after calcination at 580 °C in the air (see the PXRD pattern of LTA-5_calc in Figure 4b). Moreover, N₂ adsorption of calcined LTA-5 gives high micropore volume (0.30 cm³/g) and micropore area (614 m²/g), revealing good quality of the SAPO-42 material prepared.

Si Distribution and Surface Acidity. The ²⁹Si MAS NMR spectrum of the LTA-5 material exhibits a main signal at -111 ppm, which is characteristic of Si-rich domains in SAPO materials (see LTA-5 in Figure 9). This result suggests that, under these synthesis conditions, the paired-MTPQ OSDA is not able to preferentially direct the Si atoms as isolated Si species in SAPO-42. If this is so, other anionic species must be introduced within the zeolitic framework or some structural defects must be created in the zeolite to properly balance the two positive charges of the occluded OSDA molecules per cavity. The ¹⁹F MAS NMR spectrum (Figure 12) shows a main signal at -95 ppm, which has been assigned to F⁻ within D4Rs.^{6a} The quantification of the signal assigned to F⁻ in the D4R (1.6 wt % of F⁻) indicates that the negative charge



Figure 11. Photoluminescence spectra ($\lambda_{ex} = 284 \text{ nm}$) of a diluted aqueous solution of MTPQ at 5.10^{-4} M (a), concentrated aqueous solution of MTPQ at 3 M (b), as-prepared LTA-5 material (c), and as-prepared LTA-6 material (d).



Figure 12. ¹⁹F MAS NMR of as-prepared LTA-5 and LTA-6 samples.

introduced by the fluoride anions per unit cell is almost 2. Therefore, the two positive charges provided by the selfassembled paired-MTPQ molecules per unit cell fit well with the two negative charges introduced by fluoride anions. This high interaction between the OSDA molecules and the fluoride anions precludes the preferential location of silicon as isolated species.

3.3. Synthesis of SAPO-42 Material Using MTPQ Organic Molecule as OSDA with Stoichiometric Amount of Fluoride in the Synthesis Gel. In order to improve Si isolation, a synthesis has been designed where the amount of fluoride introduced in the synthesis is that required to only fill one D4R per unit cell (D4R/u.c.). Then, if we assume that two positive charges per unit cell have been introduced by the self-assembled dimeric OSDA and one of those positive charges will be balanced by one fluoride anion entrapped within a D4R, the other positive charge should be able to locate, at least, one Si atom in isolated form in the unit cell of SAPO-42. Working under the same synthesis conditions as for the LTA-5 sample, but decreasing the theoretical HF/(AI+P) ratio to 0.05, would correspond to the presence of one fluoride anion per unit cell

(note that the LTA structure is composed of 24 T atoms per unit cell).

The PXRD pattern of the resultant material indicates the formation of the SAPO-42 material (see LTA-6 in Figure 4a). With respect to the crystal size of the LTA-6 sample, Figure 5e shows a mixture of crystals with different shapes (tetragonal and cubic) and sizes (ranging from 2 to 5 μ m). The chemical composition of different crystals has been measured by EDX, and similar chemical compositions were found that correspond well with that of the bulk sample (see bulk chemical analysis of LTA-6 in Table 1). Thus, despite the presence of different crystal morphologies, the chemical distribution within the whole sample is homogeneous. As occurred above for the LTA-5, sample LTA-6 also shows the presence of two aromatic organic molecules per cavity forming a supramolecular selfassembled bulky dimer by $\pi - \pi$ interactions of the aromatic rings (see chemical analyses in Table 1 and photoluminescence study in Figure 11d).

Si Distribution and Surface Acidity. The LTA-6 sample has been studied by ¹⁹F MAS NMR spectroscopy to determine the coordination and the amount of the fluoride anions in the asprepared solid. The ¹⁹F MAS NMR spectrum of the LTA-6 sample has a single signal centered at -95 ppm (see LTA-6 in Figure 12), indicating that all the fluoride anions present in the silicoaluminophosphate LTA-6 are occluded inside D4Rs. The amount of fluoride anions is 0.8 wt % of F⁻, giving almost 1 F⁻/ u.c. Thus, if we know that there are two positive charges provided by the OSDA per unit cell (see Table 1) and there is almost one of these positive charges properly balanced by one fluoride anion, it should be another positive charge that would be able to selectively place the Si species in isolated form.

To confirm this point, the coordination of the silicon species in the LTA-6 sample has been characterized by ²⁹Si MAS NMR spectroscopy. As can be seen in Figure 9, the presence of a main peak centered at -93 ppm reveals the preferential formation of isolated Si species. Interestingly, ICP analysis indicates that the amount of Si/TO₂ is 0.05, corresponding to \sim 1.2 Si atoms per u.c. (note that there are 24 atoms per u.c.), which is the expected amount of potential Si species to be properly balanced by the OSDA.

The crystalline nature of the LTA-6 sample is preserved after being calcined in the air at 580 °C (see PXRD pattern of LTA-6_calc in Figure 4b). N₂ adsorption reveals high volume and micropore area (see Table 2).

Finally, the acid properties of the calcined LTA-6 have been evaluated by NH_3 -TPD. As seen in Figure 10, the LTA-6 sample shows three overlapped desorption peaks centered at 200, 250, and 340 °C, indicating the presence of weak, medium, and strong acid sites, respectively. The amount of the different acid sites can be estimated integrating the area under the ammonia desorption peaks. Following this methodology, the concentration of each acid site could be estimated, obtaining 0.04, 0.27, and 0.09 mmol NH_3/g for weak, mild, and strong acidities (see Table 2). The amount of desorbed ammonia for the LTA-4 sample is significantly higher than for the LTA-6 sample, probably due to the higher content of isolated Si atoms in LTA-4 (see Table 1 and Figure 9).

The catalytic activity and hydrothermal stability of the small pore SAPO-42 materials synthesized along the present work with different acid strength will be evaluated for different industrially relevant chemical processes, such as methanol-to-olefins (MTO) or selective catalytic reduction (SCR) of NOx.¹⁹

4. CONCLUSIONS

The synthesis of the silicoaluminophosphate form of the LTA, SAPO-42, with low silicon content, a very large amount of isolated Si sites, and high thermal stability, has been accomplished by using bulky OSDAs formed by the self-assembling of two aromatic organic molecules through $\pi-\pi$ interactions in fluoride as well as in fluoride free synthesis conditions. Two different quinolinium derived aromatic molecules, MTPQ and DDBQ, are able to direct the crystallization of the SAPO-42 material. The rational combination of self-assembled aromatic molecules and the presence or not of fluoride anions, as well as the amount of fluoride content, allows synthesizing SAPO-42 materials with different crystal sizes, morphologies, silicon distributions, and acid strength, depending on the synthesis conditions.

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Notes

The authors declare no competing financial interest.

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