Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

INS study of entrapped organic cations within the micropores of zeolite RTH

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Syntheses of the organic structure directing agents (SDAs)

The syntheses of RTH were carried out using two different SDAs, tri-isopropyl-methyl-phosphonium (TriIPMP) and tetra-isopropyl-phosphonium (TetIPP) cations (Figure S1).

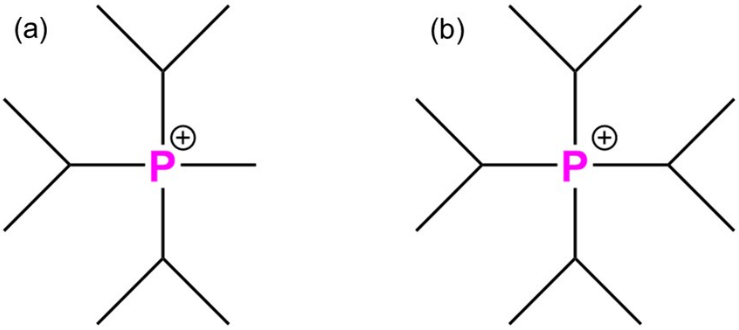

Figure S1. Structure of (a) tri-isopropyl-methyl-phosphonium cation (TriIPMP) and (b) tetra-isopropyl-phosphonium cation (TetIPP).

Synthesis of the SDA tri-isopropyl-methyl-phosphonium cation (TriIPMP)

In a typical synthesis (*Figure S2*), a solution of 25.52 g (179.80 mmol, 99% Aldrich) of iodomethane (b) in 50 ml of anhydrous acetonitrile was added dropwise under stirring into a solution of 17.6 g (119.88 mmol, 98% ABCR) of tri-isopropyl-phosphine (a) in 200 ml of anhydrous acetonitrile under a nitrogen atmosphere at the ice bath temperature. The resulting mixture was stirred at room temperature under a nitrogen flow for three days. The resulting solution was rotary evaporated until a white precipitate appeared and then, diethyl ether was added to completely precipitate the desired product. Finally, the solid was recovered by filtration, washed with a mixture of acetonitrile and diethyl ether and dried under vacuum. The product tri-isopropyl-methyl-phosphonium iodide (c) was obtained as a white powder with a yield over 98%.

Anhydrous acetonitrile was purchased to Alfa-Aesar (99%) and previously to its use was dried and deoxygenated by passage through commercial CuO columns and alumina under nitrogen.

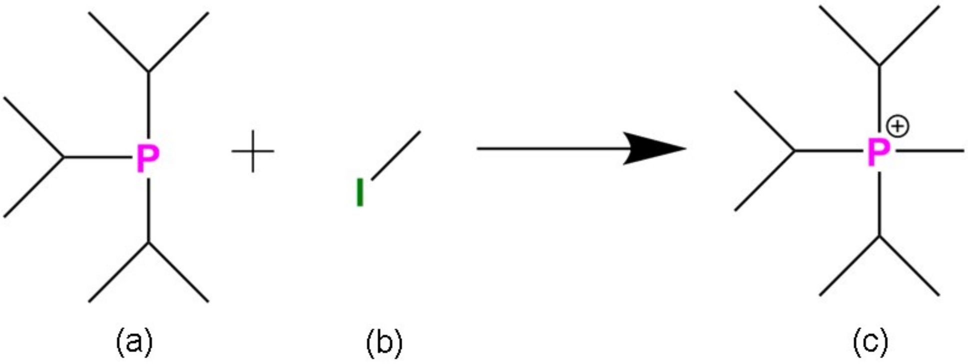

Figure S2. Schematic synthesis, using methyl iodide, of the organic structure directing agent tri-isopropyl-methyl-phosphonium (TriIPMP).

Then, the final product was suspended in water milli-Q and exchanged to the hydroxide form using an anionic exchange Amberlite IRN-78 resin in batch overnight, resulting in a 0.22 M solution.

Safety note: especial precaution must be taken when handling phosphines owing to their very high toxicity.

Synthesis of the SDA tetra-isopropyl-phosphonium cation (TetIPP)

In a typical synthesis (Figure S3), a solution of 19.570 g (115.14 mmol, 99% Aldrich) of 2-iodopropane (a) in 100 ml of anhydrous acetonitrile was added dropwise under stirring into a solution of 12.300 g (76.76 mmol, 98% ABCR) of tri-isopropyl-phosphine (b) in 100 ml of anhydrous acetonitrile under a nitrogen atmosphere at the ice bath temperature. The resulting mixture was stirred and heated at 343 K under a nitrogen flow for five days. The resulting solution was rotary evaporated until a pale yellowish precipitate appeared and then, diethyl ether was added to completely precipitate the desired product. Finally, the solid was recovered by filtration, washed with a mixture of acetonitrile and diethyl ether and dried under vacuum. The product tetra-isopropyl-phosphonium iodide (c) was obtained as a pale yellowish powder with a yield over 80%.

Anhydrous acetonitrile was purchased to Alfa-Aesar (99%) and previously to its use was dried and deoxygenated by passage through commercial CuO columns and alumina under nitrogen.

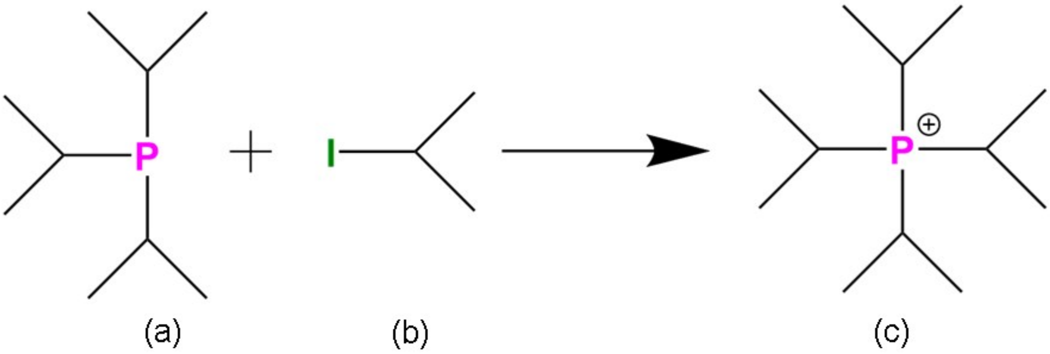

Figure S3. Schematic synthesis, using isopropyl iodide, of the organic structure directing agent tetra-isopropyl-phosphonium cation (TetIPP).

Then, the final product was suspended in water milli-Q and exchanged to the hydroxide form using an anionic exchange Amberlite IRN-78 resin in batch overnight, resulting in a 0.12 M solution.

Safety note: especial precaution must be taken when handling phosphines because their very high toxicity.

Synthesis of the zeolitic materials

The zeolite RTH was obtained as pure silica materials in fluoride media in order to decrease the structural defects which might affect to the INS measures. The phase selectivity remains the same regardless of the employed SDA.

Synthesis of zeolite RTH using tri-isopropyl-methyl-phosphonium cation (TriIPMP)

In a typical synthesis, 10.544 g (50.1 mmol) of tetra-ethyl-orthosilicate (TEOS, Aldrich) were added to 90.909 g of a 0.22 M (20.0 mmol) solution of the TriIPMP SDA. Then, the solution was stirred until the complete hydrolysis of TEOS and the evaporation of the necessary amount of water and ethanol, followed by the addition of 0.842 g (20.1 mmol) of a 48% solution of HF in water (Aldrich), to obtain a synthesis gel with the following molar composition:

$1\ SiO_2 : 0.4\ SDA(OH) : 5\ H_2O : 0.4\ HF$

The resulting gel was transferred to Teflon lined stainless-steel autoclaves and heated at 408 K at its autogenous pressure under tumbling (60 rpm) for 5 days. The solid was recovered by filtration and washed exhaustively with distilled water. The resulting solid was dried at 373 K overnight to obtain the as-made RTH zeolite.

Safety note: Autoclaves must be opened in a fume-hood to avoid exposition to gaseous phosphines that must be formed during the hydrothermal synthesis of zeolites.

Synthesis of zeolite RTH using tetra-isopropyl-phosphonium cation (TetIPP)

In a typical synthesis, 10.522 g (49.9 mmol) of tetra-ethyl-orthosilicate (TEOS, Aldrich) were added to 166.667 g of a 0.12 M (20.0 mmol) solution of the TetIPP SDA. Then, the solution was stirred until the complete hydrolysis of TEOS and the evaporation of the necessary amount of water and ethanol, followed by the addition of 0.833 g (20.0 mmol) of a 48% solution of HF in water (Aldrich), to obtain a synthesis gel with the following molar composition:

$1\ SiO_2 : 0.4\ SDA(OH) : 5\ H_2O : 0.4\ HF$

The resulting gel was transferred to Teflon lined stainless-steel autoclaves and heated at 408 K at its autogenous pressure under tumbling (60 rpm) for 10 days. The solid was recovered by filtration and washed exhaustively with distilled water. The resulting solid was dried at 373 K overnight to obtain the as-made RTH zeolite.

Safety note: Autoclaves must be opened in a fume-hood to avoid exposition to gaseous phosphines that must be formed during the hydrothermal synthesis of zeolites.

Chemical analysis of the materials

The chemical and elemental analyses of the as-made RTH, as well as the chemical analyses of the SDAs, are shown in Tables S1 and S2.

Table S1. Chemical and elemental analyses of the as-made RTH zeolite obtained with the TriIPMP SDA.

		Theoretical values	Free SDA[a]	As-made RTH
Chemical analyses (wt%)	Si	-	-	39.3
	P	-	9.37	2.6
	Si/P [b]	-	-	16.1
	C	-	39.56	10.5
	C/P [b]	10	10.9	10.3

[a)] Chemical analyses for the free SDA were obtained before anionic exchange.

[b)] Molar ratio.

Table S2. Chemical and elemental analyses of the as-made RTH zeolite obtained with the TetIPP SDA.

		Theoretical values	Free SDA[a]	As-made RTH
Chemical analyses (wt%)	Si	-	-	38.3
	P	-	8.55	2.7
	Si/P [b]	-	-	15.9
	C	-	43.77	12.75
	C/P [b]	12	13.2	11.9

[a)] Chemical analyses for the free SDA were obtained before anionic exchange.

[b)] Molar ratio.

Structural characterization of the materials

The crystallinity of the obtained materials was measured by the powder X-ray diffraction technique, employing a PANalytical X´Pert PRO diffractometer with a PANalytical X´Celerator detector, measuring with the Cu K_α X-ray radiation ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5444$ Å, $I_2/I_1 = 0.5$), with a 240 mm length goniometer, a tube voltage and intensity of 45 kV and 40 mA, respectively, at room temperature (298 K), and a scan range from 2.0º to 40.0º (2θ), with a scan step size of 0.020 (2θ), and a counting time of 35 s/step. The materials obtained show a high crystallinity, with very small differences between them (Figure S4).

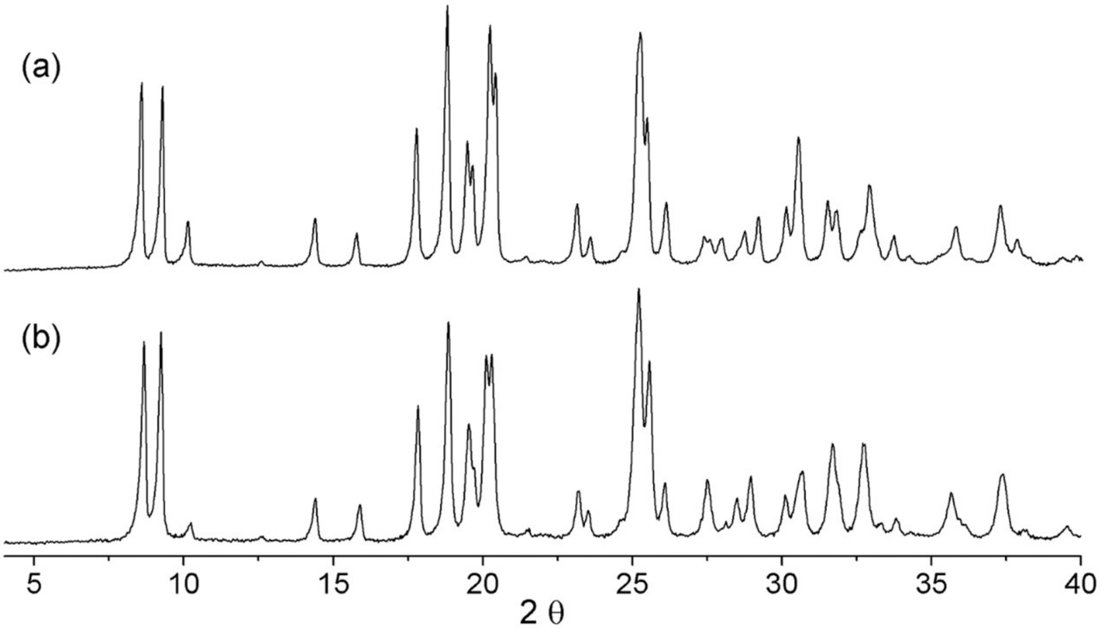

Figure S4. XRD patterns of: (a) zeolite RTH obtained with TriIPMP; and (b) zeolite RTH obtained with TetIPP.

The main difference between the two materials relies on a small displacement in some diffraction peaks, which implies different crystallographic cell parameters for each one of the obtained RTH zeolites depending on the employed SDA.

Table S3. Crystallographic cell parameters of the RTH zeolites synthesised in this study (optimized using the Treor peak indexing method), the first RTH describe in literature, and the idealized structure.

Material	a (Å)	b (Å)	c (Å)	α (º)	β (º)	γ (º)	Cell volume (Å^3)
RTH (TriIPMP)	9.7843	20.6105	9.6532	90	96.75	90	1933.16
RTH (TetIPP)	9.7365	20.4151	9.6518	90	96.93	90	1904.39
Reference RTH(a)	9.659	20.461	9.831	90	96.58	90	1930.13
RTH idealized	9.762	20.530	9.996	90	96.90	90	1988.85

a) Vortmann, S., Marler, B., Gies, H. and Daniels, P. *Microporous Materials*, **4**, 111-121 (1995).

The chemical stability of the SDAs in the as-made material was checked by ^{31}P and ^{13}C MAS-NMR in the as-made materials (Table S4), and by liquid NMR for the free SDAs. The samples were prepared by solution of the SDA salts (before the anionic exchange) in deuterium oxide.

Table S4. Single pulse MAS-NMR acquisition conditions.

Nuclei	I	Natural abundance (%)	ν_L at B_0=9.4T	Pulse angle (rad)	Pulse length (µs)	Time between pulses (s)	δ reference	Spinning speed (kHz)
^{31}P	1/2	100	165.8	1/2	5	20	H_3PO_4	10
^{13}C	1/2	1.108	100.6	1/4	6	30	Adamantane	5
^{19}F	1/2	100	376.3	1/2	4.5	100	$CFCl_3$	25, 15

The ^{13}C (Figure S5) and ^{31}P NMR (Figure S6) show that the SDAs remain stable in the zeolites after the hydrothermal synthesis conditions.

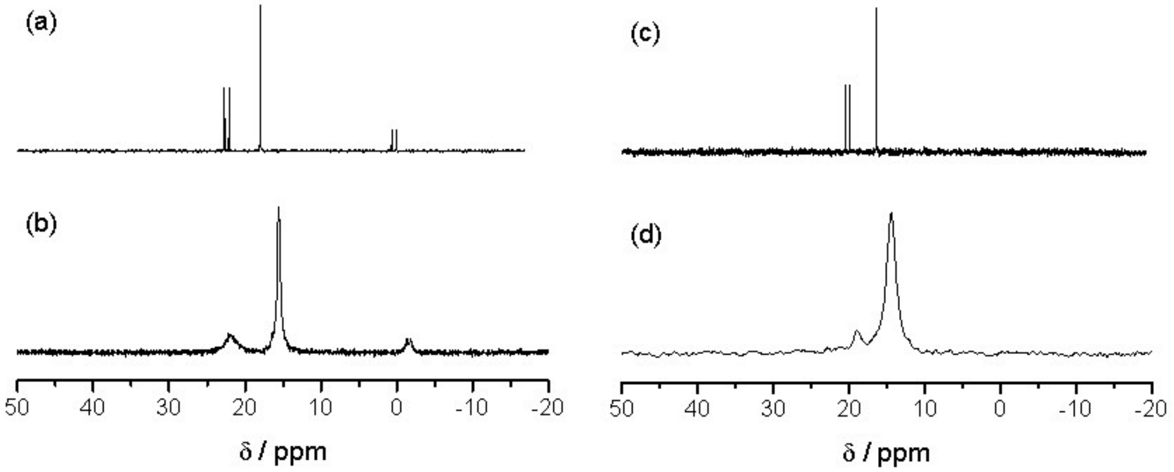

Figure S5. ^{13}C NMR of the employed materials: free SDA TriIPMP (a), zeolite RTH obtained with TriIPMP SDA (b), free SDA TetIPP (c), and zeolite RTH obtained with the TetIPP SDA (d).

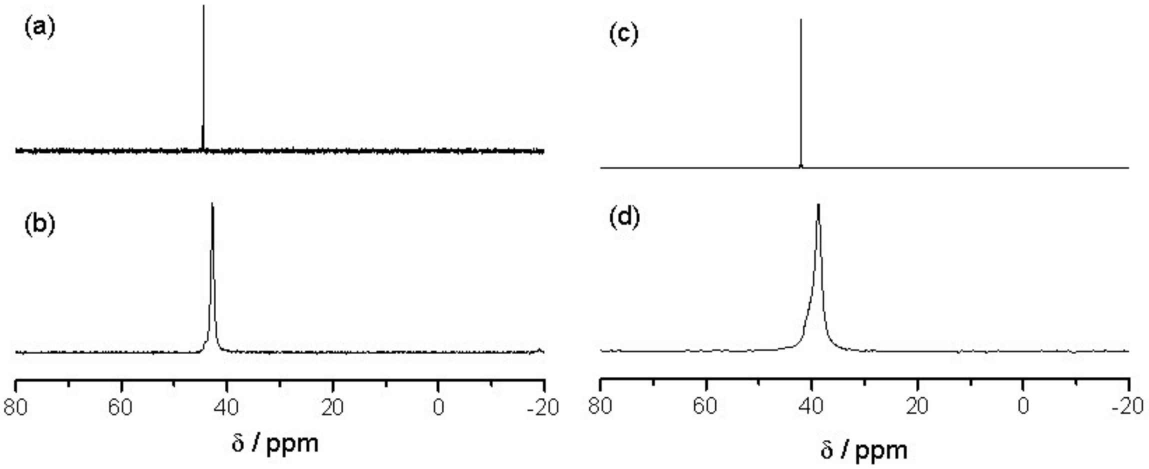

Figure S6. ^{31}P NMR of the employed materials: free SDA TriIPMP (a), zeolite RTH obtained with TriIPMP SDA (b), free SDA TetIPP (c), and zeolite RTH obtained with TetIPP SDA (d).