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Quinuclidine derivates as structure directing agents for the synthesis of boron containing zeolites

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n-Alkylquinuclidinium ions with alkyl groups in the range from C_1 to C_6 were synthesized with the purpose of studying their influence as structure directing agents (SDAs) in zeolite synthesis, in particular on the structure type formed. Syntheses were performed in the system SiO_2–B_2O_3–SDA–H_2O–CH_3OH under hydrothermal conditions at 160, 180, and 200 °C. B_2O_3 was added in order to allow for charge balance through partial replacement of silicon atoms by the trivalent atom as established by ^{11}B MAS NMR spectroscopy. The synthesis experiments led to the formation of seven different structure types: dodecasil 1H (DOH); decadodecasil 3R (DDR), sigma-2 (SGT), RUB-1 (LEV), ZSM-5 (MFI), EU-1 (EUO) and ZSM-12 (MTW) all containing *n*-alkylquinuclidinium ions as templates. In one case (SGT-type material) the active templating ion, methylquinuclidinium, was formed *in situ* from quinuclidine and methanol present in the reaction mixture. In order to identify the templating molecules (SDA) in the zeolite host framework solid-state ^1H–^{13}C CP MAS NMR was used. A single crystal structure refinement of quinuclidinium–DDR clearly shows the host–guest arrangement inside the zeolite pores.

Introduction

The use of structure directing agents (SDAs) is a successful method used to synthesize high-silica zeolites[1–4] although the actual role of the SDAs is not completely understood. Zeolites are metastable phases and are produced *via* kinetic pathways.[5] The organic molecules which are used as SDAs become enclathrated in cage or channel-like voids during the crystallization of the zeolite material. Although it is possible to deliberately synthesize a certain zeolite structure type by using appropriately sized molecules as SDAs, the relation between the structure of the inorganic host framework and the shape of the occluded organic molecule are not close enough to speak of a true templating effect.[4] Indeed most of the SDAs usually lead to the formation of different zeolite structure types depending on the synthesis temperature, concentration of the precursor compounds, *etc.* On the other hand, most zeolite structure types can be obtained with several SDAs. Nevertheless, it has been shown for high-silica zeolites that molecules of sphere-like shape preferentially form zeolite structure types with cage-like voids while chain-like molecules lead to zeolites with channel-like pores.[3]

Among organic compounds, amines and alkylammonium ions are very effective SDAs. To further investigate the effect of the structure directing agents, a series of different alkylquinuclidinium ions were synthesized which comprise sphere-like templates (the quinuclidinium ion), chain-like ions (*e.g.* hexylquinuclidinium ion) and intermediate members.

Quinuclidine and its protonated form, the quinuclidinium ion, have proved to be very effective templates in forming aluminophosphates such as $AlPO_4$-16,[6] gallophosphates (*e.g.* cloverite[7]), porous silica (octadecasil[8]) and borosilicates (dodecasil 1H and others[9]) among others.

This study deals with the effect of the alkyl chain lengths of alkylquinuclidinium ions used as the structure directing agents on the crystal structure of the reaction product. In the as-synthesized zeolite the positive charge of the template has to be compensated by the silicate framework. Since pure SiO_2 frameworks are electrically neutral it is necessary to replace some of the Si^{4+} ions by T^{3+} or T^{2+} ions to form a negatively charged framework. For this purpose, boric acid was added to our reaction mixtures. As has been shown in many zeolite syntheses, the addition of boron improves the crystallinity of the microporous material compared to boron-free reaction mixtures.

Experimental

Synthesis of *n*-alkylquinuclidinium hydroxide SDAs

The new templates were synthesized using ethanol as solvent. A given alkyl iodide ($C_nH_{2n+1}I$, $n = 1$–6) (4 g) and quinuclidine (Aldrich, 97%) (2 g) were dissolved in ethanol (5 ml). This solution was stirred at room temperature for *ca.* 1 h during which an exothermal reaction of the two reagents took place. Evaporation of the solvent at room temperature led to crystallization of the alkylquinuclidinium iodide which was carefully washed with acetone and then dried at room temperature. The iodide was then ion exchanged to the hydroxide form by treating a 1 M aqueous solution of the salt with an anionic ion exchanger (AG1-X8, Bio Rad). The 1 M solutions of the six different alkylquinuclidinium hydroxides were subsequently used for the zeolite syntheses. Table 1 summarizes the different alkylquinuclidinium cations including quinuclidine which was also used as an SDA in this study.

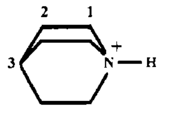
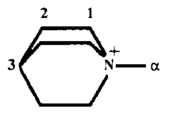
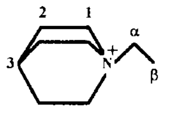
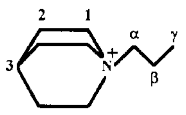
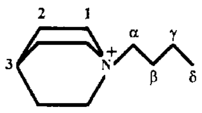
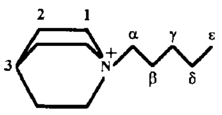
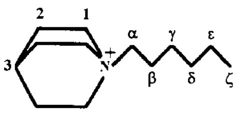
Solution NMR spectroscopy

The new templates were characterized using ^{13}C solution NMR on a Bruker DRX 400 spectrometer and D_2O as the solvent.

Zeolite syntheses

The zeolites were hydrothermally synthesized in the system SiO_2–B_2O_3–template–H_2O–CH_3OH. For a typical reaction, tetramethoxysilane (Fluke, purity >98%) was hydrolyzed in distilled water and the methanol formed through hydrolysis was not removed. Then quinuclidinium hydroxide or one of the alkylquinuclidinium hydroxides was added as the structure directing agent. Finally boric acid (Merck, p.a., saturated aqueous solution at RT) was added. The final composition of the reaction mixture was: 1.0 SiO_2 : 1.0 template : 0.65 B_2O_3 : 210 H_2O: *ca.* 2 CH_3OH.

Table 1 The seven different SDAs used in the syntheses of boron containing zeolites

Compound	Formula	Structural formula
quinuclidinium	$C_7H_{13}N\text{-}H^+$	
methyl-quinuclidinium	$C_7H_{13}N\text{-}CH_3{}^+$	
ethyl-quinuclidinium	$C_7H_{13}N\text{-}C_2H_5{}^+$	
propyl-quinuclidinium	$C_7H_{13}N\text{-}C_3H_7{}^+$	
butyl-quinuclidinium	$C_7H_{13}N\text{-}C_4H_9{}^+$	
pentyl-quinuclidinium	$C_7H_{13}N\text{-}C_5H_{11}{}^+$	
hexyl-quinuclidinium	$C_7H_{13}N\text{-}C_6H_{13}{}^+$	

The reaction mixture was then sealed in a silica tube and heated at 160, 180 or 200 °C for up to 12 months. The formation of crystals was monitored with an optical microscope over intervals of 14 days. The solid products were separated from the mother-liquor, washed with ethanol and distilled water, and dried at room temperature. The crystalline phases were identified by optical microscopy and X-ray diffraction.

X-Ray diffraction

The Gandolfi method was used to identify the different materials obtained.

To determine the crystallinity and for refinement of the lattice constants, X-ray powder patterns were recorded on a Siemens D5000 powder diffractometer in Debye–Scherrer geometry and the samples were sealed in glass capillaries of 0.3 mm diameter. For the structure analysis of boron containing DDR, a single crystal synthesized with quinuclidine as the template was used. The intensity data were collected on a four circle Syntex R3 diffractometer in ω–2θ scan mode and details of the structure analysis are listed in Table 5. No adsorption correction was applied because of the small crystal size (rhombohedron of dimensions 90 μm) and the small absorption coefficient. The structure refinement was performed with the Siemens SHELXTL program system.[10] The starting model for the refinement was based on the fractional coordinates determined for silica-DDR.[11] Scattering factors for neutral atoms were used as implemented in the program.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/170.

Solid-state NMR spectroscopy

In order to establish the incorporation of the templates into the zeolite pores, solid-state ^1H–^{13}C CP MAS NMR spectra were run for those materials which were obtained in sufficient quantity. In addition ^{11}B MAS NMR spectroscopy was performed on four samples. The solid-state NMR spectra were recorded on a Bruker AXL-400 spectrometer using Bruker standard probes and $SiMe_4$ (^{13}C) or $NaBH_4$ (^{11}B) as external standards.

Chemical analysis

The boron contents of the materials were determined in three different ways: (i) for four different materials the boron content was determined using a KONTRON plasma spectrograph with an ICP Plasmatherm generator: SGT (quinuclidinium), DOH (ethylquinuclidinium), DDR (quinuclidinium) and LEV (quinuclidinium). (ii) For all seven structure types the boron content was calculated from the number of template ions which are included per unit cell. For clathrasils this number is given by the number of large cages (DOH, SGT, LEV, DDR) assuming that all suitable pores are fully occupied. For the zeolite MTW which has a one-dimensional pore system the length of the straight channel ($b_0 = 5.0$ Å, four channels per unit cell) was divided by the size of the template. For MFI the value was taken from the thermogravimetric analysis, and for EUO calculated from the density. (iii) According to Taramasso *et al.*[12] the substitution of Si^{4+} by the smaller B^{3+} ion leads to a reduction of the unit cell volume compared to the corresponding pure silica phases since the B–O bond length is considerably smaller than that of Si–O. Consequently, the boron content can, in a first approximation, be calculated from the corresponding unit cell volumes using eqn. (1) as given by Taramasso *et al.*:[12]

$$B/(B+Si) = [d^3_{Si-O}/d^3_{Si-O} - d^3_{B-O}][1 - V_{Si,B}/V_{Si}] \qquad (1)$$

The calculation was carried out for all seven structure types using the unit cell volume of the boron containing phase $V_{Si,B}$ with $d_{Si-O} = 1.61$ Å and $d_{B-O} = 1.46$ Å. The unit cell volumes of the pure silica phases V_{Si} were taken from the literature (see Table 3). It has, however, to be considered that the size of the occluded template also has an influence on the size of the unit cell. Moreover, the type of interaction between host framework and template, whether ionic (if B^{3+} is part of the framework) or based on van der Waals type interactions (in the case of a neutral silica framework) might affect the unit cell dimensions. Therefore, eqn. (1) will give only approximate values concerning the boron content.

Thermal analysis

The thermal properties of the MFI material synthesized with butylquinuclidinium ions (weight loss of the material and heat flow) were investigated with a Linseis (Type 2045) thermal analyzer from room temperature up to 800 °C with a heating rate of 10 °C min^{-1}.

Determination of densities

Density measurements were performed in sink-and-swim experiments with tribromomethane and butylacetate as standard density liquids.

Results and discussion

Zeolite synthesis

Before synthesis all templates were checked for purity: ^1H–^{13}C NMR spectra of the templates showed that the syntheses of the alkylquinuclidinium ions had been successful. All signals were unambiguously assigned to the corresponding carbon atoms.

In all synthesis runs the new templates were active and led to the formation of porous materials (Table 2). These materials belong to seven different zeolite structure types: dodecasil 1H (DOH), decadodecasil 3R (DDR), sigma-2 (SGT), RUB-1 (LEV), ZSM-5 (MFI), EU-1 (EUO) and ZSM-12 (MTW) (Table 2). For details of the crystal structures the reader is referred to the *Atlas of Zeolite Structure Types*.[13]

The synthesized silicate frameworks can be arranged in two groups, one with cage-like voids: DOH, DDR, SGT, LEV and the other with channel like pores: MFI, EUO, MTW. The frameworks MTW and EUO possess non-intersecting one-dimensional pore systems with straight tubular channels (MTW) or channels possessing large side pockets (EUO). The MFI structure type has a two-dimensional pore system with intersecting channels. The different pore geometries clearly reflect the geometry of the template molecules and their influence as SDAs on the type of framework formed.

The templates quinuclidinium, methylquinuclidinium and ethylquinuclidinium are almost isometric and predominantly form structures with cage like voids. The size of the template has an influence on the pore volume: the largest of the nearly isometric templates (ethylquinuclidinium) forms DOH with the largest cage ($V_{cage} = 430$ Å^3) while the smaller ions form smaller cages as in DDR ($V_{cage} = 350$ Å^3), LEV ($V_{cage} = 370$ Å^3) or SGT ($V_{cage} = 390$ Å^3). The (free) cage volumes were taken from Grünewald-Lüke and Gies[9] and correspond to the largest ellipsoid that can be placed in the cage (taking into account the van der Waals radii, 1.40 Å, of the framework oxygen atoms). However, there is also an influence from the synthesis temperature on the structure type formed. Similarly to what has been observed previously[3,9] different synthesis temperatures led to formation of different structure types. This is obvious for the smallest templates quinuclidinium and methylquinuclidinium.

MFI is stabilized by templates with side chains longer then an ethyl group, and is observed when the SDA contains propyl to hexyl substituents. It is interesting that among these SDAs only hexylquinuclidinium leads to the formation of a second phase (EUO). It appears that the particular chain length of hexyl perfectly fits the channel geometry of the EUO framework. A similar influence of the SDA chain length on the structure type of the stabilized zeolite had been observed by Moini *et al.*[14] and Casci[15] who used a series of different diquaternary cations $[(CH_3)_3N(CH_2)_nN(CH_3)_3$, $n = 3$–$16]$ as structure directing agents. Only for a particular chain length of the SDA ($n = 5$ and 6) was the EUO material formed. Molecular modelling studies suggested that a specific chain length provides an ideal fit for the formation of the EUO framework structure.[14]

Table 2 Zeolite phases obtained in the synthesis system 1.0 SiO_2 : 1.0 template : 0.65 B_2O_3 : 210 H_2O : *ca.* 2 CH_3OH

	Template $C_7H_{13}N$–R^+						
T/°C	R = H	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}	C_6H_{13}
160	LEV MTW	LEV SGT	DOH	MFI	MFI	MFI	MFI EUO
180	LEV SGT	LEV SGT	DOH	MFI	MFI	MFI	MFI EUO
200	DDR	DOH LEV	DOH	MFI	MFI	MFI	MFI

For templates with long side chains the synthesis temperature had little influence on the zeolite type being formed.

Analysis of the silicate framework of the zeolite structures

All porous materials were obtained as colorless crystals with crystal sizes in the range of 10 μm (MTW) to 200 μm (DOH). In X-ray powder diffraction patterns all phases show a high crystallinity with line widths of *ca.* 0.09° 2*θ*. Fig. 1 shows typical powder patterns of the boron containing DOH, MFI, MTW, SGT, LEV, EUO and DDR materials which were obtained with the quinuclidine derivates.

The boron content of the different materials is given in Table 3.

The wet chemical analysis technique gave a low but significant boron content for the four samples analyzed. These experimentally determined values are almost equal to those calculated from the number of template ions per unit cell. The boron content of DOH, DDR, LEV, SGT and MTW was calculated assuming that all pores are fully occupied by guest ions and the necessary charge compensation for each guest ion is provided by a boron atom in the host framework. The resulting B/(B + Si) values (fifth column of Table 3) are the highest values possible for the given framework and template. By contrast, the boron content of the MFI and EUO materials was calculated from the experimentally determined number of guest ions.

Thermogravimetry of MFI synthesized with butylquinuclidinium gave a total weight loss of 15.0% occurring in one step at *ca.* 550 °C accompanied by an exothermic DTA signal. Since no loss of water was detected all the weight loss is due to the expulsion of the template. This leads to a unit cell content of $[C_{11}H_{22}N]_{6.0}[B_{6.0}Si_{90.0}O_{192}]$ assuming a mutual charge compensation of SDA cations and boron atoms in the framework. The as-synthesized EUO material has a density of 2.01(2) g cm^{-3} while the calculated density of the pure framework of EUO is 1.82 g cm^{-3}. This leads to an estimate of 3.32(4) template molecules as well as boron atoms per unit cell.

The boron contents derived from the size of the unit cells are also listed in Table 3. Comparing the calculated boron contents of the different phases (calculation based on Taramasso's equation, see Experimental section) a similar variation is observed as for the boron contents determined by the two other methods. The calculated values, however, are always about twice as high as the values determined by chemical analysis and theoretical considerations based on charge compensation.

The coordination and location of the boron atoms in the as synthesized materials

Four ^{11}B MAS NMR spectra have been recorded from DOH, SGT, LEV and MTW showing sharp signals with chemical shifts in the range δ −3.0 to −4.6. This indicates that boron is exclusively tetrahedrally coordinated and is in the silicate framework replacing silicon atoms at T-positions. However, it was not possible to obtain a pure sample for every zeolite structure type. In all spectra, two to three lines are resolved which either belong to different T-sites in one material or to T-sites of materials of different structure types. Nevertheless, it is clear that all the boron is located in the silicate framework of the as-synthesized crystals.

In general, the different chemical environments of boron atoms at T-positions in the silicate frameworks have only a minor influence on the isotropic chemical shift values of the signals in the ^{11}B spectra (*ca.* ±1 ppm).[22] Therefore in most cases only one sharp resonance is observed in the ^{11}B spectra of the boron containing zeolites, regardless of whether one or several T-positions are partly occupied by boron atoms. The spectra can be interpreted as follows: Spectrum 1 [Fig. 2(a)] of

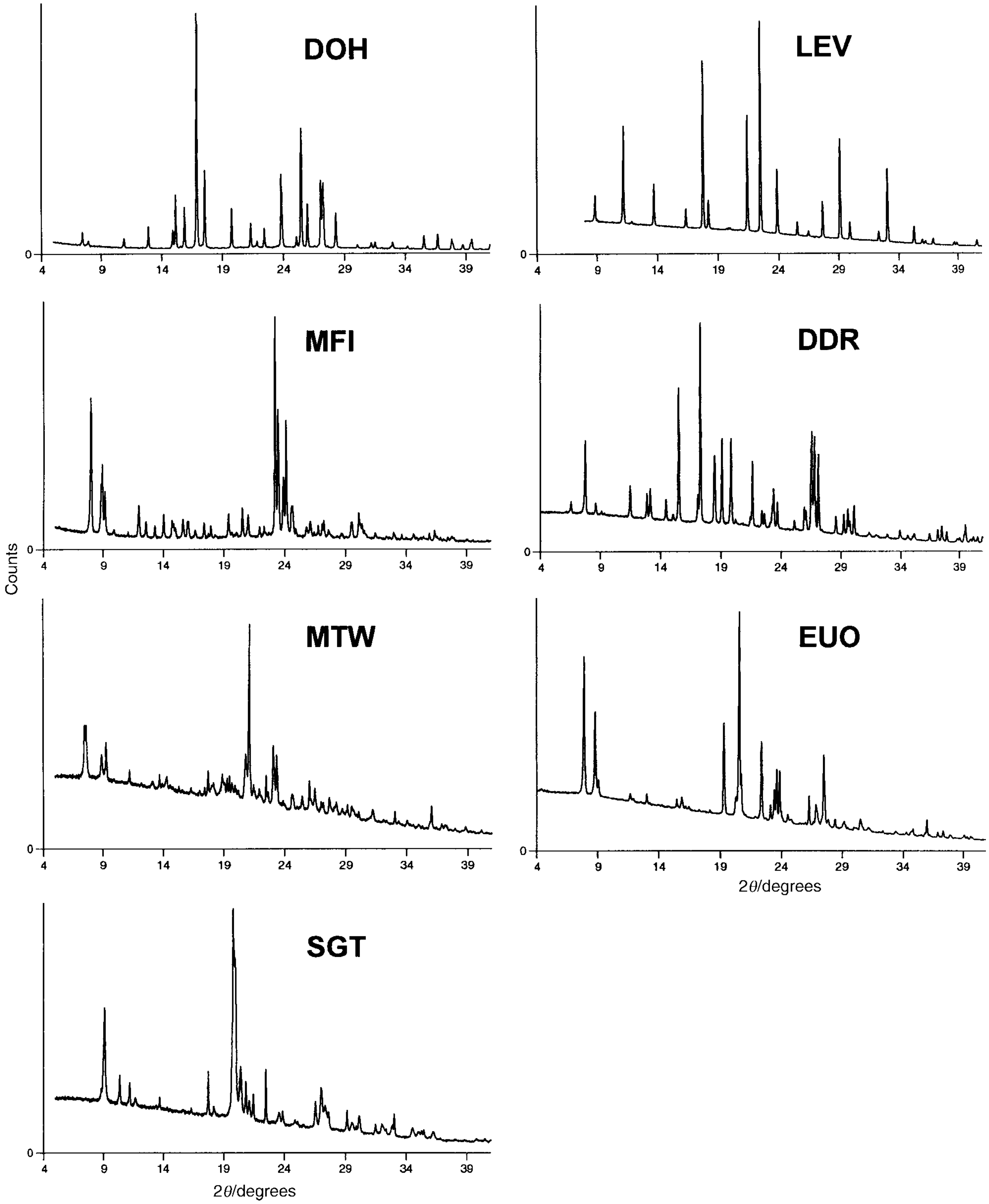


Fig. 1 X-Ray powder diffraction patterns of typical DOH, MFI, MTW, SGT and LEV samples.

the pure DOH material shows one sharp ^{11}B signal at δ -3.65 [this DOH sample was synthesized with quinuclidine as the template at 200 °C with a low B/(B+Si) ratio of 0.2].

Spectrum 2 [Fig. 2(b)] corresponds to a sample which is a mixture of *ca.* 70% LEV [B/(B+Si)=0.11] and 30% MTW [B/(B/Si)=0.05]. The spectrum shows two well resolved ^{11}B signals of LEV at δ -3.60 and -4.55. The ^{11}B signal of MTW at δ -3.69 overlaps with the signal of LEV and is therefore not resolved.

Spectrum 3 [Fig. 2(c)] corresponds to a sample containing *ca.* 90% MTW and 10% LEV. The strong signal with a maximum at δ -3.69 is related to the MTW material. The main signal of the LEV impurity (at δ *ca.* -3.60) overlaps with this line leading to a slight asymmetry while the weaker signal of LEV is present as a shoulder at δ -4.60.

Spectrum 4 [Fig. 2(d)] corresponds to a sample containing *ca.* 50% SGT [B/(B+Si)=0.06] and 50% LEV [B/(B+Si)=0.11]. Two (δ -3.60 and -4.55) of the three signals can be assigned to LEV. The resonance at δ -3.03 corresponds to the presence of the SGT material.

The assignments of the chemical shifts for the different materials are listed in Table 4.

Table 3 Comparison of the boron contents of the studied materials determined by different methods

	Unit cell volume/Å^3		B/(B+Si) (as determined from)		
Material	Borosilicate (SDA)	Silica phase[a]	ICP spectroscopy	Number of guest ions per unit cell	Unit cell volume
DDR	6595(10) (quinuclidinium)	6803[11]	0.046(2)	0.050	0.12
EUO	6044(4) (hexylquinuclidinium)	6170[16]	—	0.033	0.08
MTW	2853(6) (quinuclidinium)	2923[17]	—	0.054	0.09
SGT	3495(1) (quinuclidinium)	3604[18]	0.049(3)	0.063	0.12
DOH	1818(1) (ethylquinuclidinium)	1852[19]	0.031(2)	0.029	0.07
MFI	5245(2) (butylquinuclidinium)	5383[20]	—	0.060	0.10
LEV	3204(1) (quinuclidinium)	3377[21]	0.082(2)	0.111	0.20

[a]Reference source as indicated.

Analysis of the SDA within the zeolite structure

Solid state ^{1}H–^{13}C MAS NMR spectra of six materials in their as-synthesized forms were recorded: SGT/quinuclidinium, DOH/methylquinuclidinium, DOH/ethylquinuclidinium, MFI/propylquinuclidinium, MFI/butylquinuclidinium and MFI/hexylquiniclidinium.

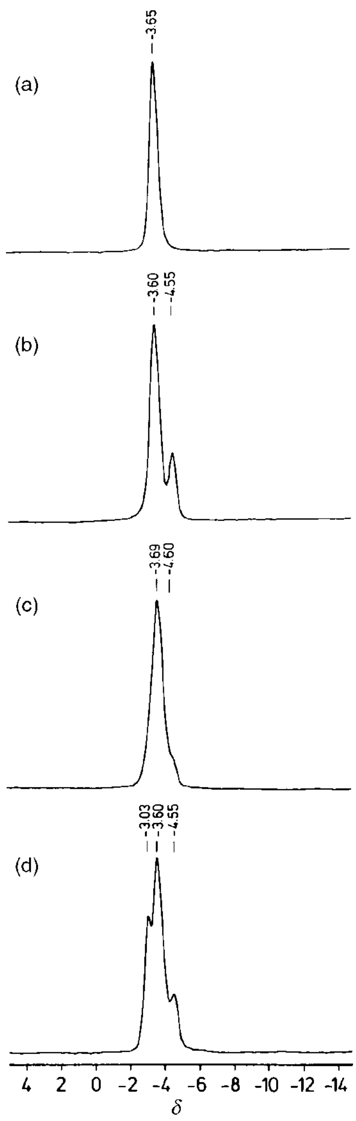


Fig. 2 ^{11}B NMR spectra of boron containing zeolites synthesized with quinuclidine as template: (a) 100% DOH, (b) 70% LEV+30% MTW, (c) 90% MTW+10% LEV, (d) 50% SGT+50% LEV.

With the exception of SGT the spectra established that the structure directing agents used in the synthesis mixture were occluded in the pore system of the zeolites during the crystallization. In two cases minor impurities were also present in the pore systems in addition to the templating ion. According to the chemical shifts of the signals these impurities are most likely methanol, ethanol and the neutral quinuclidine molecule. To illustrate the NMR analysis the spectrum of MFI synthesized with butylquinuclidinium is detailed below. Five signals are seen in the solution ^{13}C NMR spectrum of butylquinuclidinium hydroxide as well as in the solid state ^{1}H–^{13}C MAS NMR spectrum of the MFI material, with very similar chemical shift values and relative intensities of the signals (Fig. 3). It is, therefore concluded that butylquinuclidinium acts as template for MFI.

The SGT material synthesized with quinuclidinium is an interesting example contradicting the general rule that the SDA used for the synthesis is occluded in the pore volume of the crystalline material. The ^{1}H–^{13}C MAS NMR spectrum of the as-synthesized SGT material surprisingly shows the typical spectrum of methylquinuclidinium. Fig. 4(a)–(c) show the ^{1}H–^{13}C MAS NMR signals of (a) quinuclidine dissolved in D_2O, (b) quinuclidinium hydroxide dissolved in D_2O and (c) the as-synthesized SGT material. Comparison of the chemical shift and intensity values observed for the SGT material (δ 59.1, 54.5, 24.8 and 18.9) and for pure methylquinuclidinium hydroxide (δ 57.0, 52.0, 23.5 and 18.7) clearly indicate the presence of methylquinuclidinium in the zeolite. By constrast, quinuclidine as well as the quinuclidinium ion[23] possess ^{13}C NMR spectra with only three resonances at δ 46.1, 25.1, 19.8 and δ 48.5, 23.0 and 19.3, respectively. These species can therefore be ruled out as possible pore fillers of the SGT material investigated.

We conclude that during the zeolite synthesis quinuclidine and methanol reacted to give methylquinuclidinium hydroxide as the active template. It should be noted that methanol had

Table 4 Observed ^{11}B MAS NMR signals for different boron containing zeolites

Structure type	No. of symmetrically inequivalent T-positions	^{11}B MAS NMR (δ)
DOH	4	−3.65
MTW	7	−3.69
LEV	2	−3.60 and −4.55
SGT	4	−3.03

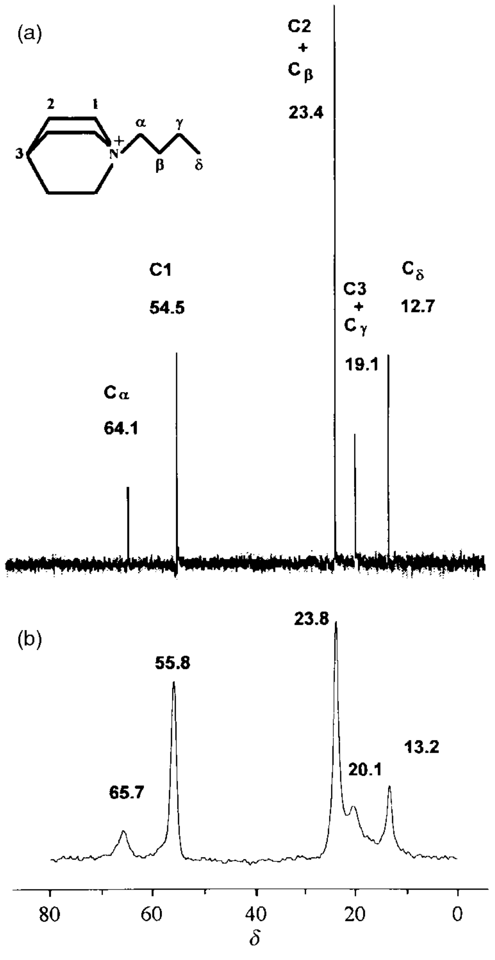


Fig. 3 (a) Solution ^{13}C NMR spectrum of butylquinuclidinium hydroxide and (b) solid-state ^{1}H–^{13}C CP MAS NMR spectrum of MFI with butylquinuclidinium hydroxide as the guest ion.

not been removed from the reaction mixture after hydrolysis of tetramethoxysilane.

A single crystal structure analysis of another zeolite phase was performed in order to identify the guest species occluded in the porosil cages. Since DDR was obtained under similar conditions as SGT and good single crystals were available, a single crystal structure analysis was carried out on this material in order to analyse the active template.

The single crystal structure analysis of the boron containing DDR revealed the well known framework structure of the DDR structure type.[11] The boron containing material had the same space group symmetry $R\bar{3}m$ as the pure silica phase and bond lengths and angles were very similar to values already published for silica–DDR.[11] For the refinement of the framework, population factors of Si on T-sites were reduced to account for the lower scattering power of these sites owing to the partial replacement of silicon by boron. This led to R-values of $R=0.153$ and $R_w=0.126$. Thereafter, difference Fourier maps were calculated to analyze the nature and the location of the guest molecule.

Difference Fourier maps were obtained for the DDR structure and Fig. 5 shows a (001) section through the large cage of DDR at $z=0.38$ with the three-fold axis at the center. The section through $z=0.38$ is where the C2-atoms of the bicyclic molecule are located and it is clearly seen from the smeared out residual electron density that the guest molecule is disordered. Apparently the guest molecule rotates about the three-fold axis of the structure. While the C1 and N2 atoms coincide with the three-fold axis, the C2 and C3 atoms (at

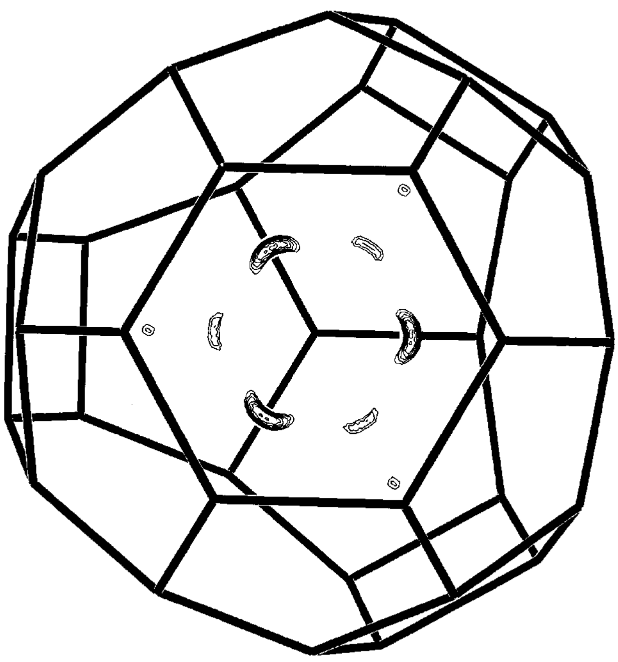


Fig. 5 Difference electron density map in the $[4^{3}5^{12}6^{1}8^{3}]$-cage of DDR synthesized with quinuclidinium as the template: (001) section at $z=0.375$ showing the rotational disorder of the quinuclidinium ion.

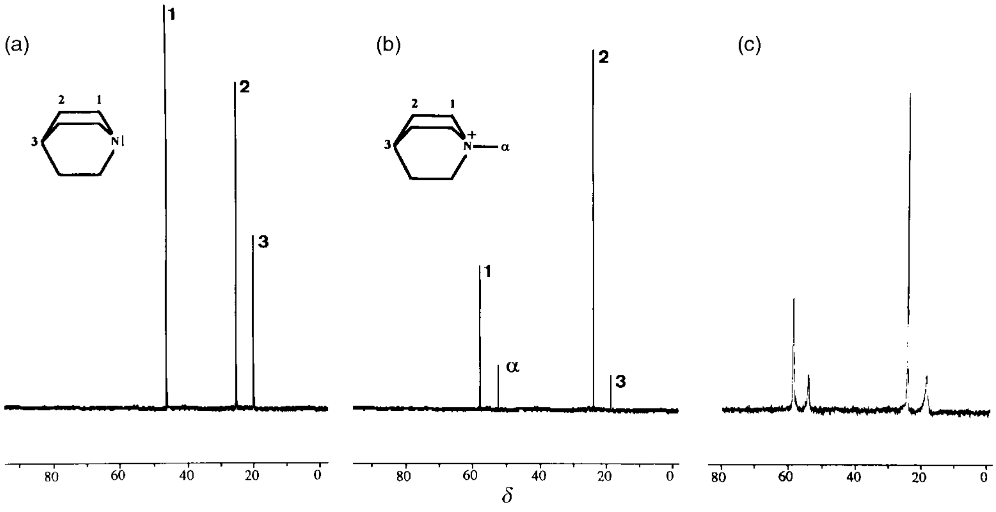


Fig. 4 (a) Solution ^{13}C NMR spectrum of (a) quinuclidine and (b) the methylquinuclidinium ion. (c) Solid-state ^{1}H–^{13}C CP MAS NMR spectrum of SGT synthesized with quinuclidinium as template.

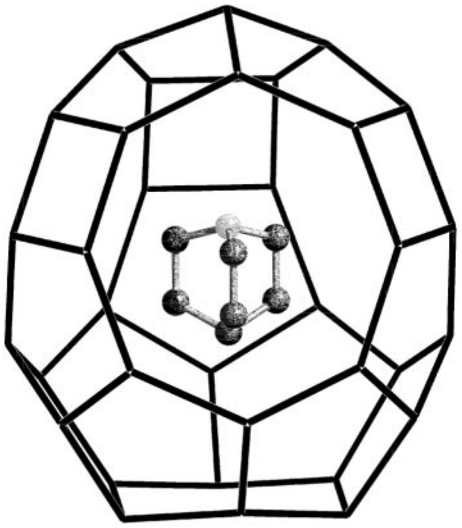


Fig. 6 One possible orientation of the quinuclidinium ion in the $[4^35^{12}6^18^3]$-cage of DDR.

Table 5 Experimental and crystallographic parameters for the structure refinement of as-synthesized DDR

Diffractometer	Syntex R3
λ/Å	0.71073
T/K	293
No. of reflections	5404
No. of reflections used for refinement ($F>4\sigma\|F\|$)	4202
No. geometric restraints	7 (C–C and C–N distances)
μ/mm^{-1}	0.68
R	0.077
R_w	0.060
R_{int}	0.030
Space group	$R\bar{3}m$
a/Å	13.73(1) (hexagonal unit cell)
c/Å	40.37(5) (hexagonal unit cell)
V/Å^3	6595(10)
Unit cell contents	$[Si_{114.5}B_{5.5}O_{240}]\cdot 6C_7H_{13}N$
D_c/g cm^{-3}	1.960

$z=0.3834$ and $z=0.3457$, respectively) both occupy two split positions with a relative occupancy of 2/3 and 1/3.

It is clear from the analysis of the residual electron density distribution in the cavity that only quinuclidinium ions can account for the residual electron density and there is no indication that methylquinuclidinium is occluded in the cage. Fig. 6 shows one possible orientation of the guest molecule in the $[4^35^{12}6^18^3]$-cage of DDR.

In contrast to the synthesis of the SGT-type material, we can conclude that in the case of the DDR synthesis, either the quinuclidine molecules did not react to give methylquinuclidinium ions during the synthesis run or that methylquinuclidinium ions do not act as SDAs for the formation of the DDR structure type.

Upon including the scattering contribution of the quinuclidinium template, the refinement converged to final R-values of $R=0.077$ and $R_w=0.060$. Parameters and results of the diffraction experiment are given in Table 5, atomic coordinates and displacement parameters are listed in Table 6 while selected bond distances and angles of the structure are given in Table 7.

Conclusion

Quinuclidinium as well as the *n*-alkyl substituted templates (alkyl = methyl to hexyl) all led to the formation of microporous materials in the synthesis system SiO_2–B_2O_3–template–H_2O–CH_3OH. Boron is part of the silicate framework in all cases compensating for the charge introduced by the cationic guest molecules. In all materials the pores are completely occupied by the organic SDAs. Where alkylquinuclidinium ions were used as the structure directing agents these species were occluded in the pores. If quinuclidine was added to the synthesis mixture the resulting situation was different. In at least one case, SGT (synthesized with *quinuclidinium* at 180 °C), *methylquinuclidinium* ions (probably generated by reaction with methanol) were found to fill the pores. This shows that reactions of the organic molecules take place during the crystallization leading to new templating species. In order to explain the synthesis results with respect to the templating effect it is necessary to carefully analyze the organic compound occluded in the particular pore system with non-invasive

Table 6 Atomic coordinates, displacement parameters (U_{eq}) and occupation factors p for as-synthesized DDR

Atom	x	y	z	U_{eq}/Å^2	p
Si1	0.7278(2)	0.0528(2)	0.0691(1)	0.021(1)	0.97
Si2	0.1291(1)	0.2582(2)	0.1078(1)	0.015(1)	0.97
Si3	0.2007(1)	0.4014(2)	0.1716(1)	0.013(1)	0.97
Si4	0.1204(1)	0.2407(2)	0.2325(1)	0.014(1)	0.97
Si5	0.2224(2)	0	0	0.025(1)	0.97
Si6	0	0	0.1996(1)	0.011(1)	0.97
Si7	0	0	0.1211(1)	0.012(1)	0.97
O1	0.3633(4)	0.3889(3)	0.6362(1)	0.031(2)	1
O2	0.2749(3)	0.3610(3)	0.5771(1)	0.029(2)	1
O3	0.4236(4)	0.3044(3)	0.5899(1)	0.026(2)	1
O4	0.2289(3)	0.4579(6)	0.6574(1)	0.038(3)	1
O5	0.1842(2)	0.3684(5)	0.7464(1)	0.024(2)	1
O6	0.3203(5)	0.1602(3)	0.5413(1)	0.021(2)	1
O7	0.5395(5)	0.2697(3)	0.5451(2)	0.040(3)	1
O8	0.2707(2)	0.5414(5)	0.5590(1)	0.027(2)	1
O9	0.1821(3)	0.5590(1)	0.5217(1)	0.036(3)	1
O10	0.1888(3)	0.3641(5)	0.5	0.034(2)	1
O11	0	0	0.1603(3)	0.040(4)	1
N1	0.5	0	0.5	0.21(1)	1
N2	0	0	0.3357(4)	0.21(1)	1
C1	0	0	0.3991(4)	0.21(1)	1
C2	0.0589(2)	−0.0589(2)	0.3834(4)	0.21(1)	0.65(2)
C2a	−0.0589(2)	0.0589(2)	0.3834(4)	0.21(1)	0.34(2)
C3	0.0589(2)	−0.0589(2)	0.3457(4)	0.21(1)	0.65(2)
C3a	−0.0589(2)	0.0589(2)	0.3457(4)	0.21(1)	0.34(2)

Table 7 Selected bond lengths (Å) and angles (°)

Si1–O1	1.586(4)	Si1–Si1	3.012(3)
Si1–O2	1.590(5)	Si1–Si2	3.034(4)
Si1–O3	1.589(6)	Si1–Si4	3.084(3)
Si1–O5	1.598(4)	Si1–Si5	3.045(2)
Si2–O2	1.594(5)	Si2–Si3	3.088(3)
Si2–O8	1.581(6)	Si2–Si7	3.116(3)
Si2–O9	1.590(6)		
Si3–O6	1.605(3)	Si3–Si3	3.180(4)
Si3–O9	1.595(6)	Si3–Si4	3.112(3)
Si3–O10	1.596(2)		
Si4–O3	1.601(3)	Si4–Si6	3.156(3)
Si4–O6	1.600(6)		
Si4–O7	1.587(7)		
Si5–O1	1.604(4)	Si5–Si5	3.053(3)
Si5–O4	1.581(5)		
Si6–O7	1.591(7)	Si6–Si7	3.167(5)
Si6–O11	1.587(11)		
Si7–O8	1.584(6)		
Si7–O11	1.580(11)		
<Si–O>	1.592(6)	<Si–Si>	3.095(3)
Si1–O1–Si5	145.4(4)	Si3–O6–Si4	152.3(4)
Si1–O2–Si2	144.6(3)	Si3–O10–Si3	170.0(5)
Si1–O3–Si4	150.5(3)	Si4–O7–Si6	166.4(5)
Si1–O5–Si1	141.0(4)	Si5–O4–Si5	150.0(4)
Si2–O8–Si7	159.8(4)	Si6–O11–Si7	180.0(0)
Si2–O9–Si3	151.9(4)		
<Si–O–Si>	155.6(4)		

analytical techniques, *e.g.* ^{13}C NMR spectroscopy. On the other hand, the *in situ* formation of new templating species can be used deliberately as a new synthesis route for the preparation of zeolite-type materials.

It has been shown that the formation of the particular structure types can be explained by the shape and size of the template ions.[3] The nearly isometric templates quinuclidinium, methylquinuclidinium and ethylquinuclidinium form porous materials with cage like voids whereas templates with long side chains stabilize MFI type materials with channel like pores optimizing the interactions between the template molecule and the appropriately shaped pores.

The templates with long side chains give MFI- or EUO-type materials. While MFI is obtained with four different SDAs EUO only appears with one template (hexylquinuclidinium) which fits perfectly to the given pore geometry.

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