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Control the position of framework defects in zeolites by changing the symmetry of organic structure directing agents

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Abstract

Double quantum-single quantum (DQ/SQ) ^1H NMR spectroscopy has been used to localize the siloxy/silanol defects in two pure silica MFI zeolite samples synthesized by the symmetric tetrapropylammonium hydroxide (TPAOH) and non-symmetric methyltributylammonium hydroxide (MeTrBA) templates. Using the ^1H DQ/SQ NMR, we provide important information on the positions of the structural defects in the MFI zeolite framework that have been tuned during the hydrothermal synthesis by changing the symmetry of the templates. The preferential location of the defects is found to be near the terminal methyl groups of the longer alkyl chains and far from the nitrogen atoms: in the case of the non-symmetric MeTrBA template, the defects are located in the sinusoidal channels, while for the symmetric TPA template they are randomly distributed among the two types of channels. It is foreseen that control the position of framework defects in zeolites might be the way to control the position of the active sites in acid zeolite catalysts.

Keywords: NMR spectroscopy, silanols defects, template modification, silicalite-1.

1. Introduction

Organic molecules have been used in zeolite synthesis since the sixties¹. Bulky and positively charged organic molecules, i.e. tetraalkylammonium, play a similar role as the alkali or alkaline earth cations. Their positive charge compensates the negatively charged alumino-silicate framework of zeolites. However they also permit the synthesis of a great variety of zeolites with much higher Si/Al ratio than using inorganic cations solely, or even pure siliceous materials. In addition, these molecules also play the role of organic structure directing agents (OSDA) and as such they have shown a strong ability to direct the formation of zeolite structures². A large number of OSDA was explored in the past decades in order to stimulate selectivity toward specific zeolite structures and/or to modify their chemical nature^{3,4}. The ability of organic molecules to direct the synthesis of very different zeolite structures is due inter alia to their high versatility (size and shape) and flexibility⁵. In addition, it has been shown that the phase selectivity of an OSDA molecule frequently depends on the nature and concentration of defects in a given zeolite structure⁶.

Moreover, while a given OSDA molecule can lead to the synthesis of several different zeolite structures, a specific structure may be obtained using different molecules. A cornerstone factor that explains the structure directing ability of OSDA is the occurrence of Van der Waals interactions between the molecule and the inner surface of the pores⁷. Therefore, the study of the OSDA/framework interactions is of paramount importance to understand the

selectivity for a given zeolite and defects positioning during synthesis, considering the complexity of hydrothermal processes.

Hydrogen (proton) solid-state nuclear magnetic resonance (NMR) is a powerful technique permitting access to new information on OSDA–framework interactions in as-synthesized zeolites. Indeed, protons are the only shared nuclei between the organic and the inorganic parts of the final crystalline material (zeolite). The occurrence of strong magnetic through-space dipole-dipole couplings between protons, inversely proportional to the cube of the inter-nuclear distances, is then an advantage to probe the OSDA–framework interface. It has been largely shown in the NMR literature that a valuable way to identify and measure dipolar couplings between various protons, while preserving the high spectral resolution necessarily provided by a rapid magic-angle axis spinning (MAS), is the use of the two-dimensional (2D) double-quantum/single-quantum (DQ/SQ) correlation NMR spectroscopy⁸.

It has been previously observed that pure-silica zeolites in their as-synthesized form, thus containing the OSDA molecule, with very different topologies (MFI, AFI, MTW, NON, DDR, and TUN), all exhibit a typical proton NMR resonance at a chemical shift of 10.2 ppm. Such resonance has been attributed to the protons involved in the siloxy/silanol (SiO–...HOSi) defects⁹. Using the 2D-DQ/SQ ¹H MAS NMR experiments and modeling the data obtained on the as-synthesized silicalite-1 with the classical TPA template, we have shown that these protons are unambiguously located in the close vicinity of the methyl groups belonging to the Tetrapropylammonium cation (TPA), at a distance of approximately 3.0 Å¹⁰. In agreement with these observations, a recent study showed similar results in the case of other as-synthesized zeolites such as ZSM-12, ZSM-5, SSZ-74 and SSZ-24¹¹.

Based on these results and other recent works^{12,13,14}, it can be suggested that the OSDA molecule, through both its charge distribution and geometry, is driving the silanol/siloxy defect location in the all-silica zeolite framework. The objective of the present work is to understand the role of the OSDA in the positioning and orientation of the siloxy/silanol defects in pure silica zeolite. Indeed, understanding the interactions between the OSDA and defects in zeolites is a necessary step toward a rational control of their distribution, and to subsequently use this knowledge for positioning catalytic sites using heteroatom substitutions.

2. Experimental

2.1. Materials

Tetra-n-propyl-ammonium hydroxide (TPAOH, 20 wt.% in water solution, Alfa Aesar); methyltri-n-butyl-ammonium hydroxide (MeTrBAOH, 20 wt.% in water solution, Alfa Aesar) and tetra-ethyl orthosilicate (TEOS, 98%, Aldrich) were used without further purification. Doubly deionized water was used throughout the synthesis and post-synthesis treatments. Syntheses were carried out in 100 cm³ polypropylene bottle (PP bottle) at autogenous pressure without agitation.

2.2. Synthesis

The following molar composition of the precursor suspensions were used for the synthesis of silicalite-1 samples with MFI type framework structure: 1.0 SiO₂ : 0.24 SDA : 20 H₂O. In a typical synthesis, 5.0 g of TEOS was added to the corresponding weight of structural directing agents (SDA: MeTrBAOH and TPAOH) and 3.95 g of water under stirring at room temperature (pH =12). The obtained water-clear suspensions were stirred for 3 h at room temperature and further hydrolyzed for 4 h on an orbital shaker. The final suspensions were subjected to hydrothermal treatment at 363 K for 8 h. After crystallization, the suspensions were purified and the nanometer-sized silicalite-1 crystals were purified by high-speed centrifugation (20000 rpm, 20 min). The obtained solid product was washed with hot doubly deionized water (heated at 343 K for 30 min) till the pH reaches 7.5. The nanometer-sized silicalite-1 crystals were subjected to freeze drying in order to prevent irreversible agglomeration. The freeze-dried samples were calcined at 823 K (heating rate 2 K/min) in air for 6 h. The samples synthesized with TPA and MeTrBA are abbreviated as TPA-silicalite-1 and MeTrBA-silicalite-1, respectively.

2.3. Characterization

X-ray diffraction: The crystallinity of the nanometer-sized zeolites (TPA-silicalite-1 and MeTrBA-silicalite-1) were revealed by powder X-ray diffraction (XRD), obtained with a PANalytical XPert Pro diffractometer using Cu K α radiation (α = 1.5418 Å, 45 kV, 40 mA).

Electron microscopy: The crystal size and homogeneity of the sample were determined by scanning electron microscope (SEM) using a MIRA-LMH (TESCAN) equipped with a field emission gun using an accelerating voltage of 30.0 kV.

Thermal analysis: The thermogravimetric analysis (TGA/DTA) were carried out on a SETSYS 1750 CS evolution instrument (SETARAM). The samples were heated from 298 to 1173 K with a heating ramp of 5 K/min (air flow rate: 40 mL/min).

Nuclear Magnetic Resonance: One and two dimensional ¹H magic-angle spinning (MAS) NMR spectra were acquired at 500.07 MHz on a Bruker Avance III-HD (11.7 T), using 1.9-mm outer diameter probes zirconia rotors spun at 40 kHz, a radiofrequency power of 100 kHz and a recycle delay of 2s. The recoupling of the DQ coherence was performed following the BaBa pulse sequence. The incremented delay in the indirect dimension (dt1) is equal to 50 ms (i.e., two times the rotor spinning period).

3. Results and discussions

A pure silica silicalite-1 (MFI structure) zeolite was synthesized using methyltributylammonium hydroxide (MeTrBA) molecule instead of the classical tetrapropylammonium hydroxide OSDA (TPA). In this way, the symmetry of the OSDA (MeTrBA) is changed keeping the mass of the molecule as close as possible to the TPA, as well as the total number of carbon atoms. In parallel, pure silicate-1 (MFI) using TPA as OSDA was prepared as a reference sample. MFI was chosen as it presents two different types of channels, in which previous works have shown that alkyl chains may have preferential

orientation and therefore, it is a good candidate to evidence possible change in the defect locations depending on the OSDA structure and symmetry¹⁵.

X-ray powder diffraction (XRD) patterns of the as-synthesized silicalite-1 samples with TPA (sample TPA-silicalite-1) and MeTrBA (sample silicalite-1- MeTrBA) are shown in Figure 1. Both samples are highly crystalline with high purity, as they both exhibit XRD Bragg peaks matching well with the standard MFI-phase and only those peaks corresponding to this structure are present in their diffraction pattern¹⁶. In addition, SEM pictures of both zeolites show comparable sizes with an average hydrodynamic diameter slightly lower than 100 nm (Figure 1).

Both samples show similar thermal behavior (Figure 2). The first weight loss (around 2 wt. %) which occurs below 473 K is due to the release of physically adsorbed water. The weight loss in the range 473-1173 K is attributed to the thermal decomposition of the OSDA. It is observed that the weight loss for TPA-silicalite-1 (13.8 wt%) is slightly lower than for MeTrBA-silicalite-1 (15.0 wt.%), which is easily explained by comparing the mass of the MeTrBA and TPA molecule. Indeed, the ratio of MeTrBA/TPA molecular mass equals to 1.09, which is comparable to the ratio calculated from the weight loss (1.08). This indicates that the same number of OSDA molecules is present in the channels of both samples, and the measured weight losses correspond to the presence of one OSDA molecule per channel intersection in the MFI structure.

The conventional ¹H MAS NMR spectra of both the as-synthesised TPA-silicalite-1 and MeTrBA-silicalite-1 zeolites are shown in Figure 3. They both display a group of resonances between 1.0 and 4 ppm assigned to the protons of the TPA and MeTrBA cations. The isolated peak at 10.2 ppm present in two cases is attributed to the SiO– . . . HOSi defects. An additional peak appears around 6.5 ppm, which corresponds to physically adsorbed water and water associated with some weakly hydrogen bonded defects as pointed out in earlier studies.

The 2D DQ/SQ ¹H NMR correlation experiment performed on both TPA-silicalite-1 and MeTrBA-silicalite-1 samples are shown in Figure 4. In both cases, the principal information given by this experiment is the presence of the correlation (shown by the dashed lines) observed between the siloxy/silanol defects at 10.2 ppm and the protons from the terminal methyl groups in the propyl and butyl chains of the TPA and MeTrBA cations, respectively. In the particular case of MeTrBA-silicalite-1, it is interesting to note that no cross-peak resulting from the interaction between the methyl protons of the isolated methyl group (3 ppm) and the ones present in the butyl chains (1 ppm) is observed, nor between the isolated methyl group and the defects.

These observations can be interpreted as follows: the defects are definitely in the close vicinity of the terminal methyl groups of the longer chains (propyl or butyl) in both samples. Such a conclusion was already delivered in the case of the TPA cation¹⁰. However the present observations for the MeTrBA-silicalite-1 show clearly the general tendency of the siloxy/silanol defects to be always located near the end of the longer chains. Considering that the positive charge of the alkyammonium is mainly carried by the nitrogen atom, the present

results show that the negative charge of the defects are situated as far as possible from the nitrogen atoms. This can be understood by considering that this arrangement is optimal to minimize the whole crystal electrostatic energy.

However, it has been shown for non-symmetric alky ammonium, there is a preferential orientation of the alkyl chains in the channels¹⁵. For instance, the butyl chains have a preferential orientation toward the sinusoidal channels. Therefore, for TPA, with one molecule per intersection, all channels must contain a propyl chain. The fact that the silanol groups are close to the terminal methyl of these propyl chains show that the defects are mostly located in the middle of the channels. There is no evidence that these defects may occupy preferentially either the straight or sinusoidal channels, and therefore the defects are most likely randomly parted between the two possible positions.

The arrangement is different in the case of silicalite-1 synthesized with MeTrBA (sample MeTrBA-silicalite-1) because the butyl chains should be preferentially oriented in the sinusoidal channels, and hence the methyl is expected to point toward the linear channels. Moreover, the steric constraints must favor the location of two butyl chains in the longer sinusoidal channel, instead of the linear channels. Considering these arguments, we expect that the MeTrBA cations are ordered in the channels, with two butyl groups in the sinusoidal and one butyl and one methyl group in the linear channels (Figure 5). Consequently, as the defects are located close to the terminal methyl of the butyl groups, they are most probably located in the sinusoidal channels.

4. Conclusions

In conclusion, the location of the siloxy/silanol ($\text{SiO} \dots \text{HOSi}$) may be tuned during hydrothermal synthesis by changing the symmetry of the OSDA. It was shown that preferential location of these defects is near the terminal methyl groups of the longer alkyl chains, and thus far from the nitrogen atoms. We postulate based on the preferential orientation of the alkyl groups in the various channels of the MFI structure, that in the case of the non-symmetric MeTrBA template, they are located in the sinusoidal channels, while for the symmetric TPA template they can be randomly distributed among the two types of channels. This work shows that a careful choice of the OSDA agent may be a means to induce a preferential location of the defects in the structure, which can be evidenced by 2D DQ/SQ correlation ^1H NMR spectroscopy. Finally, it can be anticipated that such approach might be the way to control the position of the active sites, for example, in acid zeolite catalysts¹⁷.

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Figures and captions

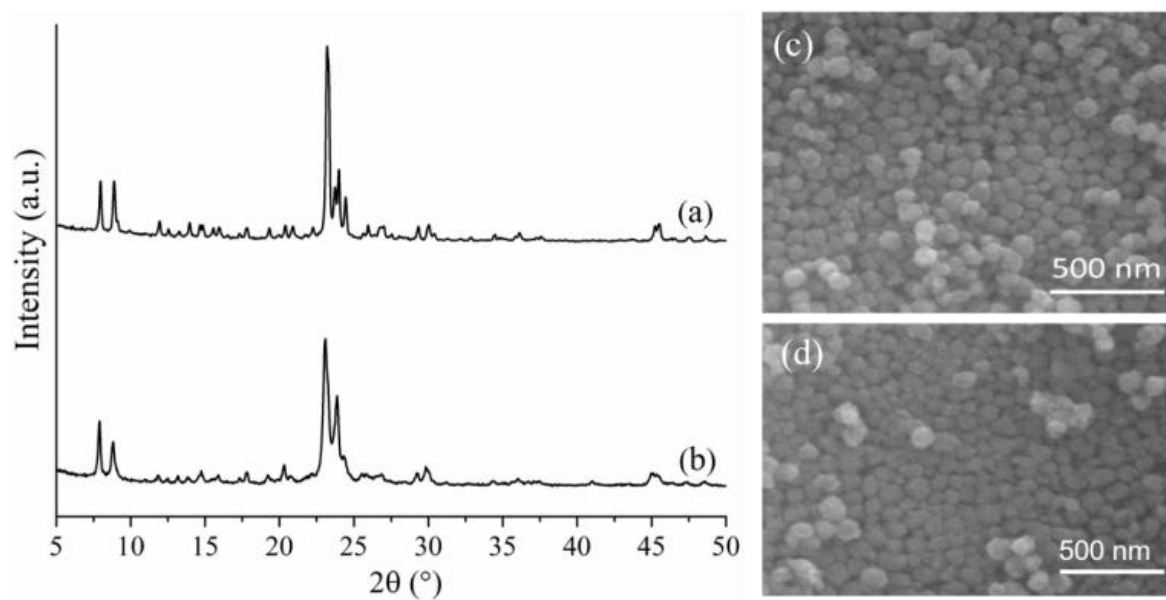


Fig. 1 Powder XRD patterns of as synthesised silicalite-1 zeolite samples with (a) TPAOH (TPA-silicalite-1) and (b) MeTrBAOH (MeTrBA-silicalite-1). FE-SEM pictures of (c) TPA-silicalite-1 and (d) MeTrBA-silicalite-1.

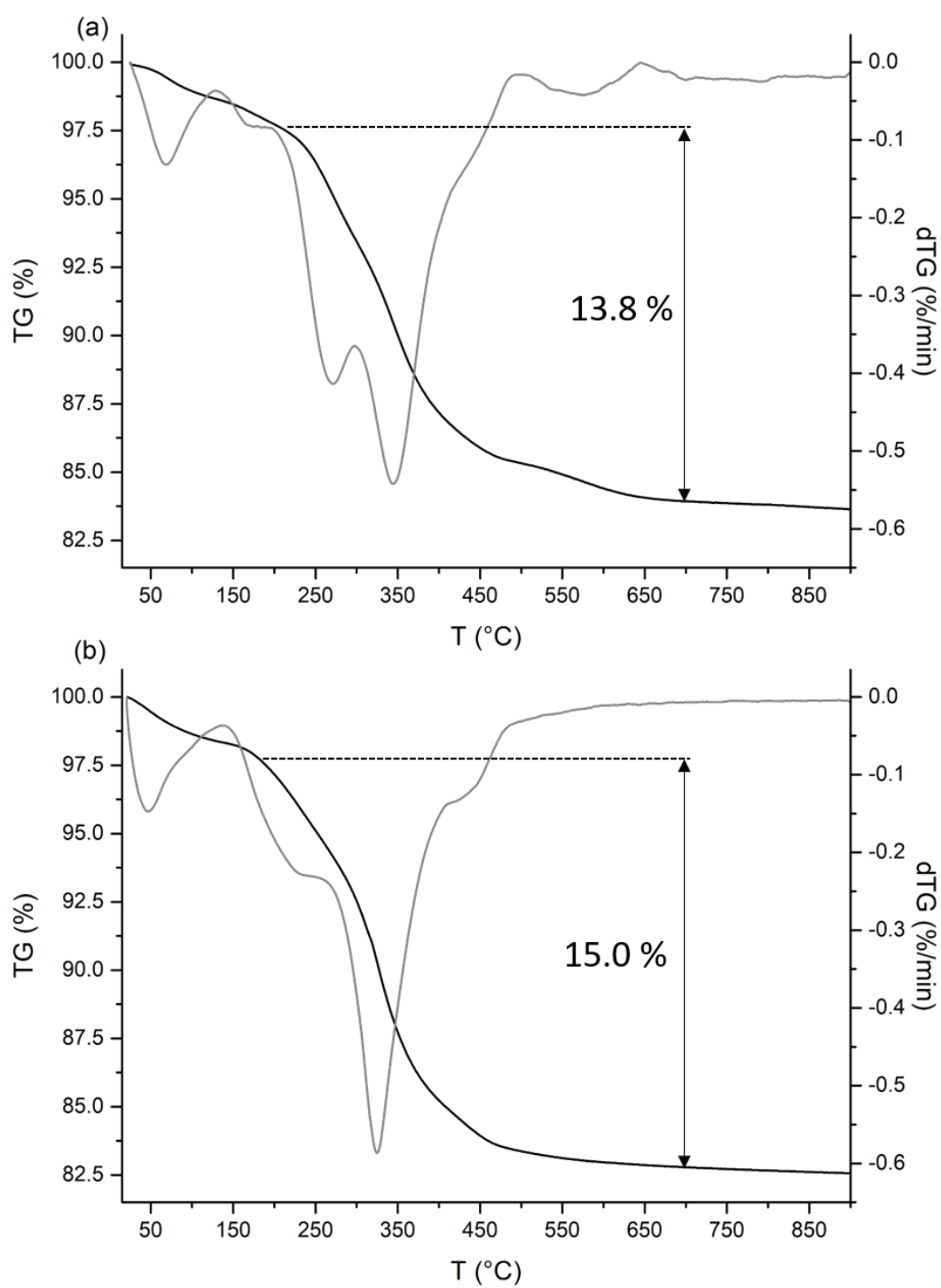


Fig. 2 TG/DTG curves of (a) TPA-silicalite-1 and (b) MeTrBA-silicalite-1 zeolite samples.

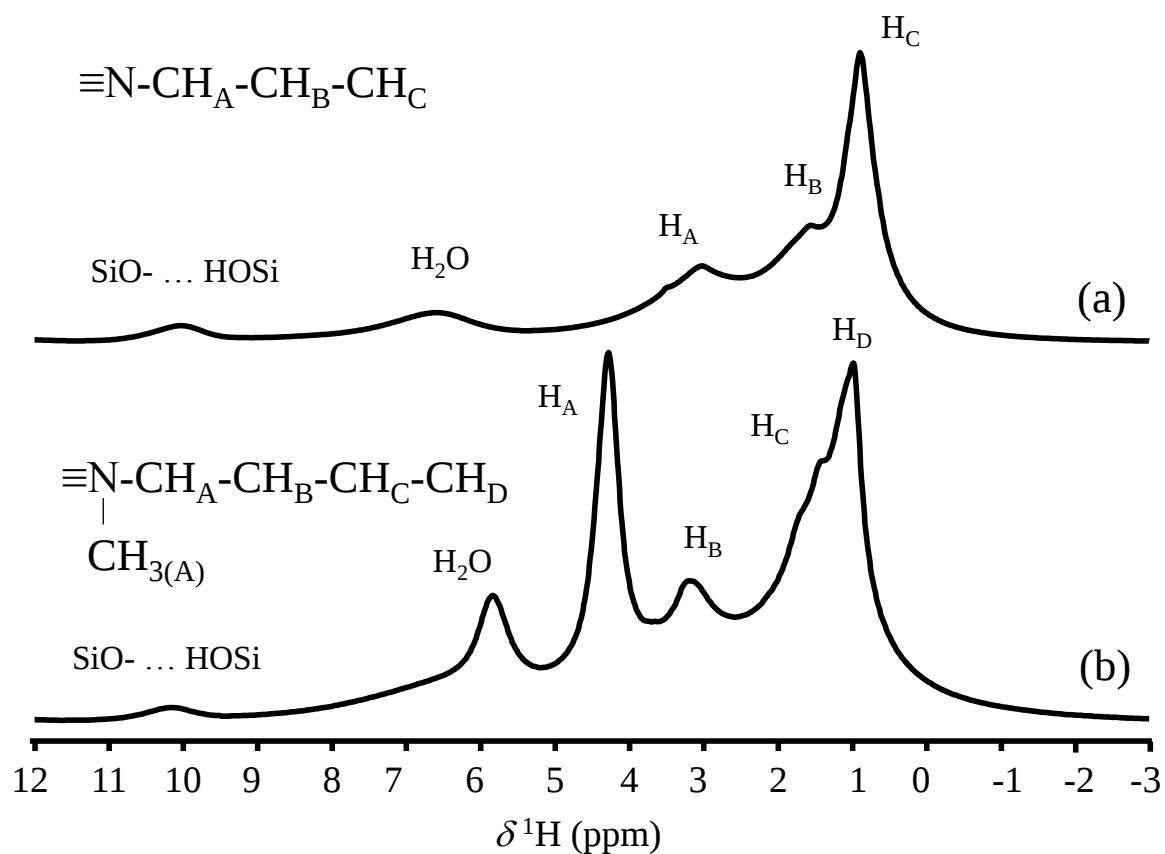


Fig. 3 1D ^1H NMR spectra of as synthesised (a) TPA-silicalite-1 and (b) MeTrBA-silicalite-1 zeolites recorded at 500 MHz.

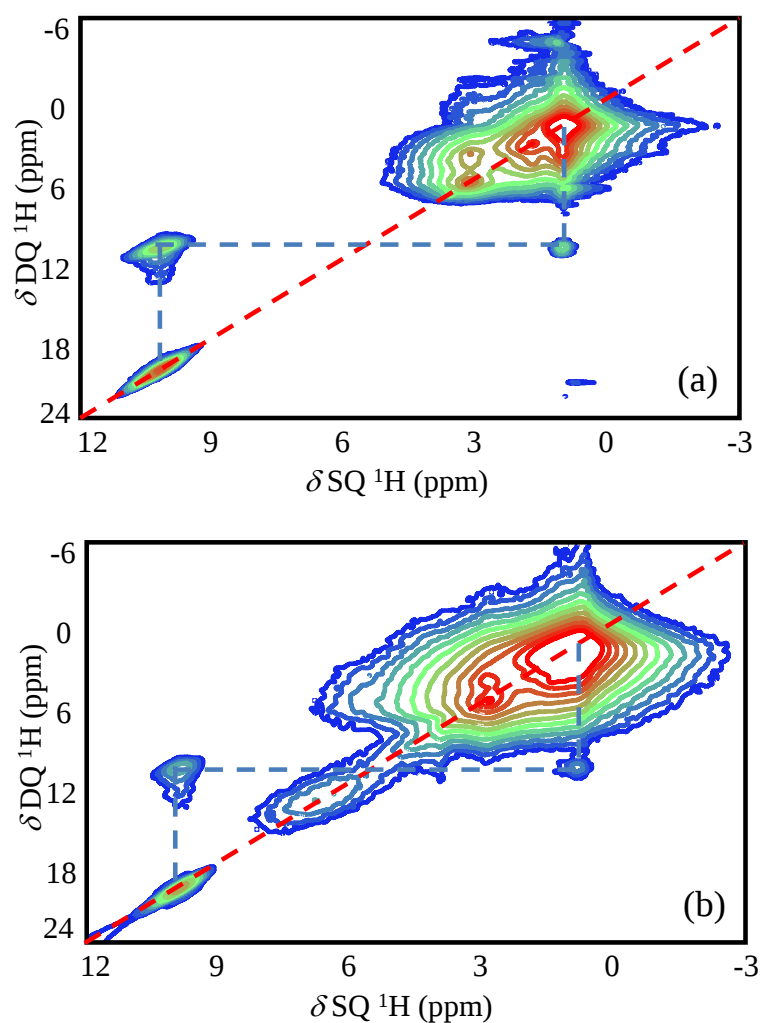


Fig. 4 2D DQ/SQ correlation ^1H NMR spectra of the as synthesised (a) TPA-silicalite-1 and (b) MeTrBA-silicalite-1 recorded at 500 MHz. The DQ coherence were generated under MAS spinning conditions using the so-called back-to-back (BaBa) pulse sequence with a building time equal to four-rotor cycles (100 μs).

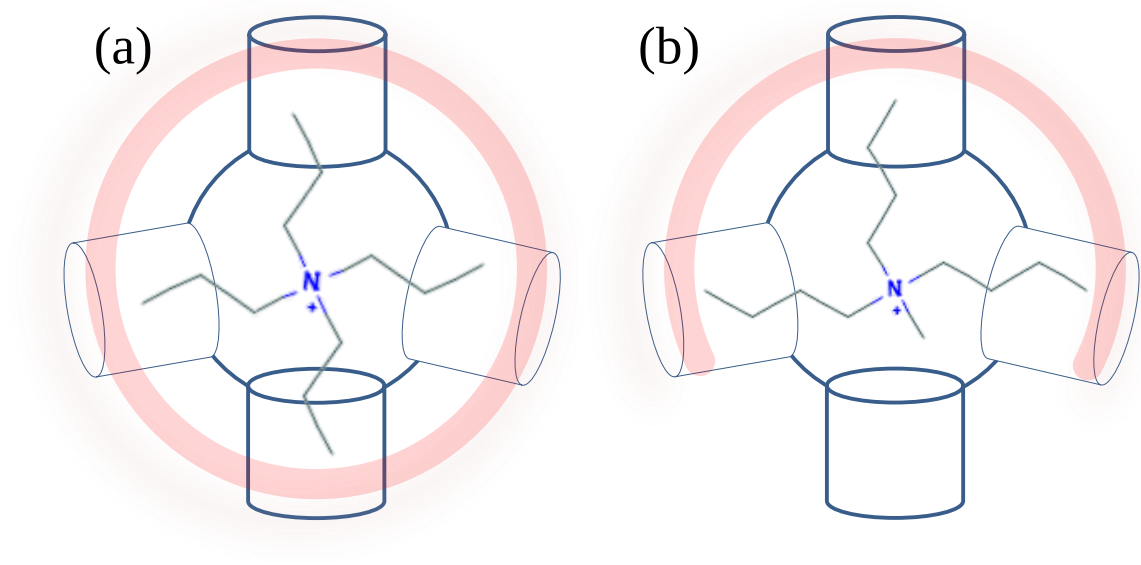


Fig. 5 Schematic representation of the location of OSDA and siloxy/silanol defects in (a) TPA-silicalite-1 and (b) MeTrBA-silicalite-1 samples.