



TRAPDOR double-resonance and high-resolution MAS NMR for structural and template studies in zeolite ZSM-5

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ABSTRACT

A combination of ²⁷Al magic-angle spinning (MAS)/multiple-quantum (MQ) MAS, and ²⁷Al–¹⁴N TRAnsfer of Population in DOuble-Resonance (TRAPDOR) nuclear magnetic resonance (NMR) was used to study aluminium environments in zeolite ZSM-5. ²⁷Al–¹⁴N TRAPDOR experiments, in combination with ¹⁴N NMR were employed to show that the two tetrahedral peaks observed in the ²⁷Al MAS/3Q-MAS spectra of as-synthesized ZSM-5 are due to aluminium atoms occupying crystallographically inequivalent *T*-sites. A ¹³C–²⁷Al TRAPDOR experiment was used to study the template, tetrapropyl ammonium bromide (TPABr), in the three-dimensional pore system of ZSM-5. The inequivalency of the methyl groups of TPA was observed in the ¹³C–²⁷Al TRAPDOR spectra of as-synthesized ZSM-5 and the motion of the methyl end of the propyl chain appeared to be more restricted in the sinusoidal channel than in the straight channel.

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1. Introduction

Zeolite ZSM-5 (Zeolite Secony Mobil-Five) has 12 crystallographically inequivalent *T*-sites and typically crystallizes in the orthorhombic space group *Pnma* [1,2]. The three-dimensional (3-D) structure contains two intersecting pores, a straight channel and a sinusoidal (zig-zag) channel [1–4]. Tetrapropyl ammonium bromide (TPABr) is the organic structure-directing agent (SDA) for the formation of this 3-D structure. TPA is positioned at the channel intersections of the zeolite with two arms projecting into the straight channels and two into the sinusoidal channels [3,4]. The excess charge on the zeolite originating from the framework aluminium is compensated by TPA⁺ cations for high Si/Al ratios. For low Si/Al ratios, the excess charge is compensated by TPA⁺ and NH₄⁺ or Na⁺ cations [4]. Hence, the synthesis of ZSM-5 with low Si/Al ratios requires extra cations like NH₄⁺ and Na⁺. A calcination of the templated-material burns away the organic TPA, giving a template-free ZSM-5.

There are several issues in the structural analysis of zeolite ZSM-5, which have contradicting interpretations in the literature.

One of these issues is the interpretation of the two narrow tetrahedral peaks observed in ²⁷Al MAS solid-state NMR spectra of the as-synthesized zeolite ZSM-5: do these peaks stem from different *T*-sites or are they the same *T*-sites, but associated with different cations? A second issue with as-synthesized ZSM-5 is the origin of the two methyl resonances in the ¹³C CPMAS NMR of TPA. These issues have been studied by several groups using various spectroscopic [4–10] and computational [11] approaches. The reason for the change in the chemical shifts and quadrupolar coupling constant of aluminium resonances in ²⁷Al MAS NMR with and without template is yet another issue [12].

The present study tries to clarify the above-mentioned issues using a combination of high-resolution and double-resonance NMR spectroscopic techniques. The origin of the two narrow tetrahedral peaks observed in the ²⁷Al MAS solid-state NMR spectra of as-synthesized and calcined ZSM-5 [5–7] is studied using high-resolution ²⁷Al MAS/3Q-MAS [13–15] NMR as well as with ²⁷Al–¹⁴N TRAnsfer of Population in DOuble-Resonance (TRAPDOR) [16–18] and ¹⁴N NMR spectroscopy. The two methyl resonances of TPA⁺ as observed in the ¹³C cross polarization (CP) MAS NMR of TPA⁺ in templated ZSM-5 [8], is investigated using ¹³C–²⁷Al TRAPDOR NMR.

With the TRAPDOR experiment one can probe proximities between different nuclei via their dipolar interaction. In this experiment the intensity of a rotor-synchronous echo on spin *I* is

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compared with an experiment in which the other nucleus, spin S , is irradiated during the echo period. The S -spin should be a quadrupolar nucleus so that the radiofrequency (RF) irradiation in combination with the spinning will induce rotor-synchronous level crossings on the S spins. This diminishes the echo intensity, in a way similar to that of a Rotation Echo Double Resonance (REDOR) experiment [19]. The difference intensity, called the TRAPDOR fraction, depends on various factors. First of all on the effectiveness of the level transitions, described by the adiabaticity parameter α , which is a function of the spinning speed, the strength of the RF-field and the strength of the quadrupole interaction ($\alpha = v_{rf}^2/v_Q \cdot v_{MAS}$). Secondly, the stronger the dipolar interaction, the more the echo dephases and hence the larger the TRAPDOR fraction. Naturally, the longer the echo, the larger the effect, though signal to noise will also reduce due to T_2 relaxation. One should bear in mind though that the dipolar interaction experienced during the echo not only depends on the proximity of the nuclei (it is proportional to $1/r^3$) but that motions can partially average the dipolar coupling and therefore reduce the effectiveness of the dipolar dephasing. Finally, one should note that there is also a dependency on the orientation between the quadrupolar tensor and the dipolar interaction [20]. The TRAPDOR experiment is effective over a wide range of conditions and, although it is not straightforward to quantify this effect, it can readily give important clues to structural issues. For the ^{27}Al - $\{^{14}\text{N}\}$ TRAPDOR a standard triple resonance probe can be used but because the Larmor frequencies of ^{13}C and ^{27}Al are so close, special adjustments to the NMR probe have to be made [21].

2. Materials and methods

2.1. Preparation

As-synthesized ZSM-5 with a Si/Al ratio of 23 was synthesized using equal molar amounts of NH_4F (+98%, Aldrich) and TPABr (98%, Aldrich) in NH_4F media to minimize the influence of defects in the ZSM-5 framework [5]. Amorphous silica (Aerosil 200, Degussa) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99% Wako) were used as silicon and aluminium source, respectively. Hydrothermal crystallization was done at 473 K in a Teflon-lined autoclave for 5 days. The final solution was filtered and dried at 393 K. The H-form of ZSM-5 was prepared by open-air calcination at 823 K for 6 h. Part of this sample was treated with a flow of ammonia at 423 K for 3 h to obtain $\text{NH}_3(\text{H})$ -ZSM-5. All samples were fully hydrated.

2.2. Experimental

X-ray diffraction patterns showed that the samples were phase-pure and of good crystallinity. The Si/Al ratio was obtained from ^{29}Si MAS NMR by deconvolution of the spectra (79.46 MHz, 10 kHz MAS, 30 s recycle delay) and was determined to be 23. The Si/Al ratio from elemental analysis was 27.

^{27}Al MAS and 3Q-MAS experiments were done on a Bruker Avance 700 NMR spectrometer using a 2.5 mm double-resonance probe-head. The resonance frequency for ^{27}Al was 182.4 MHz. The z-filter pulse sequence [15] was used with an excitation ($0\text{Q} \rightarrow \pm 3\text{Q}$) and conversion pulse ($\pm 3\text{Q} \rightarrow 0\text{Q}$) of 4.2 and 2.4 μs , respectively. The central transition selective soft $\pi/2$ pulse was 6 μs . A 2D Fourier transformation followed by a shearing transformation gave a pure absorption mode 2D contour plot where the 1D projection of the 2D contour plot on to the F1 axis gives the isotropic spectra. All spectra were obtained at a spinning speed of 20 kHz and had a recycle delay of 1.0 s. The ^{27}Al chemical shifts were referenced to Alum, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

The ^{14}N MAS experiments and ^{27}Al - $\{^{14}\text{N}\}$ TRAPDOR experiments were performed on a Chemagnetics CMX Infinity 400 NMR spectrometer. A 4 mm HXY APEX probe resonant for ^1H at 399.95 MHz, ^{27}Al at 104.22 MHz and ^{14}N at 28.89 MHz, spinning at 4 kHz was used. The RF field strength (^{14}N NMR and ^{27}Al - $\{^{14}\text{N}\}$ TRAPDOR) on ^{14}N was 73 kHz, with an effective 90° pulse length of 4.3 μs . For the ^{27}Al echo a 2.5 μs 90° pulse and a 5 μs 180° pulse was optimal. For external referencing, NH_4Cl and an aqueous solution of AlCl_3 were used to set 0 ppm for ^{14}N and ^{27}Al , respectively. The spinning speed was stable to within 1 Hz, hence rotor-synchronization could easily be accomplished by setting the timings to their appropriate values. The intensity of the rotor-synchronous ^{27}Al echo was monitored as a function of the number of rotor periods. The effect of the ^{14}N irradiation on the echo intensity was normalized to a full ^{27}Al echo without ^{14}N irradiation for each echo time.

^{13}C - $\{^{27}\text{Al}\}$ TRAPDOR experiments were done on a Chemagnetics CMX Infinity 600 NMR spectrometer using a Chemagnetics 2.5 mm H-X double-resonance APEX probe. Modification of the probe allowed its use for ^{13}C - ^{27}Al - ^1H triple resonance [21] (vide infra). The resonance frequencies were 150.87 MHz for ^{13}C , 156.34 MHz for ^{27}Al , and 599.99 MHz for ^1H . To perform the ^{13}C - $\{^{27}\text{Al}\}$ TRAPDOR experiments, the quality factor (Q) of the X-channel of the double-resonance probe was reduced to about 23 by putting a 3 k Ω resistance in parallel with the tuning insert capacitor. The X channel of the probe was tuned to -8.2 dB at 152.9 MHz, resulting in a reflected power of -5.0 and -3.8 dB at 150.8 and 156.3 MHz, respectively. The unmodified probe has a Q of about 100 and a reflected power of better than -30 dB. The tuning of the proton channel was not affected by these modifications. The spectrometer itself was set up as a standard three-channel machine; however, the carbon and aluminium channels were both fed into the same amplifier using a splitter-combiner and then connected to the X channel. In this way, RF field strengths of 59 kHz were attained for ^{13}C at 175 W RF power, 40 kHz for ^{27}Al at 83 W RF power, and 64 kHz for ^1H at 16 W RF power. Experiments were performed at 10 kHz MAS using variable amplitude CP of 61 kHz (ramping from 1.5 to -1.5 kHz) on ^1H and 51 kHz on ^{13}C in 0.5 ms duration contact time. Proton CW decoupling of 124 kHz was used during the echo and acquisition. Aluminium was irradiated with a 93 kHz strong RF field. As before, stable spinning allowed for the rotor-synchronization to be passive.

3. Results

3.1. ^{27}Al MAS and 3Q-MAS NMR

Fig. 1 shows the ^{27}Al 3Q-MAS NMR spectra of as-synthesized ZSM-5 (a), calcined ZSM-5 (b), and $\text{NH}_3(\text{H})$ -ZSM-5 (c). On top of each 2D spectrum, the corresponding ^{27}Al 1D MAS NMR spectrum is given. The isotropic projections are shown on the right of each spectrum. All the spectra show two peaks in the tetrahedral region. The isotropic chemical shifts and quadrupole parameters P_Q ($= C_Q(1+\eta^2/3)$) were derived from the peak positions in the 3Q-MAS spectra and are listed in Table 1. The isotropic chemical shifts for the two peaks in the spectrum of the as-synthesized ZSM-5 were 52.2 and 54.9 ppm and in the spectrum of the calcined ZSM-5 were 54.5 and 56.6 ppm. The isotropic chemical shifts for the two peaks in $\text{NH}_3(\text{H})$ -ZSM-5 were 53.8 and 56.4 ppm, similar to those of calcined ZSM-5. The quadrupole parameters P_Q are in the range of 1.0–2.0 MHz, which is typical for framework tetrahedral species in a crystalline zeolite framework. In the calcined ZSM-5, a low-intensity peak in the octahedral region around 0 ppm was also present (not shown, less than 5%).

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