High-resolution ¹H MAS NMR spectra of 2:1 phyllosilicates

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Solid-state ¹H MAS NMR at high magnetic fields and high spinning speeds provides a powerful means of identifying the different proton sites in smectites and affects information on the octahedral nature, the octahedral layer charge deficit and the charges on the cations residing in the interlayer space of the silicate.

Solid-state magic angle spinning nuclear magnetic resonance, MAS NMR, spectroscopy has long been recognised as a powerful tool for the study of the structural and physico-chemical properties of inorganic silicates, aluminosilicates and zeolites, as well as for the study of the structure of adsorbed molecules and the sorbate–sorbent interactions between molecules and such solids. In consequence, MAS NMR is an experimental technique widely used in solid state chemistry research, both from basic and applied points of view.[1]

In particular, solid-state proton NMR offers an extremely useful tool in the characterization of both the proton-containing parts of the solids, *i.e.* structural hydroxyls and water, and the adsorbed molecules in these materials.[2] Moreover, it provides several advantages over other experimental techniques, such as X-ray diffraction and IR spectroscopy: (i) it is an intrinsically quantitative measurement, the area of the spectrum being directly proportional to the amount of hydrogen present;[3] (ii) the chemical shifts are characteristic of the hydrogen environment, different bands being associated with different structural sites;[4] (iii) both the inter-hydrogen distances, d_{H-H},[5] and the hydrogen bonding distances[6] can be determined; and (iv) the strength and concentration of Brönsted acid sites can be quantitatively studied.[7]

However, conventional proton MAS NMR spectra in the solid state are usually very broad due to homo- and hetero-nuclear dipolar interactions and, to a lesser extent, chemical shift anisotropy. The main problem generally encountered in ¹H MAS NMR is the strength of the homogeneous dipolar interactions among protons, which produce significant line-broadening. Experimental techniques that make use of combined rotation and multiple-pulse spectroscopy, such as CRAMPS and WAHUHA, improve the quality of these spectra but imply the acquisition of more complicated experimental systems.[8] Partial deuteration of the samples reduces the spectral broadening but, again, a more complicated manipulation of the samples and a much more expensive preparation is involved.[9]

In contrast with these disadvantages, the advent of higher field magnets and the technical possibility of achieving very high spinning speeds has allowed the acquisition of high-resolution proton spectra through conventional single-pulse MAS NMR experiments on solids samples, provided that either the hydrogen density in the sample is less than about 15 atoms nm⁻³ or the motions of the molecules containing protons are fast enough, which is in accordance with classical works on the subject.[10] This technique has been successfully used to characterise many hydrous species in minerals, including pyrophyllite and talc, the two end-members of the smectite family.[11] However, the application of the solid-state ¹H MAS NMR technique to the study of clay minerals and their reactions has been largely unexplored, even when the information which could be obtained might be extremely useful for those numerous researchers who employ these samples in various areas of the chemistry.

This report details the study of proton spectra of samples representative of the smectite group and analyses the relationship between the spectra and the mineralogical composition of the samples. Likewise, useful applications for such measurements are proposed.

Samples of representative species among smectites with mineralogical compositions close to ideal were selected and homoionised in sodium. The set of samples was supplied by the Source Clay Minerals Repository of Missouri University (Columbia), and includes members of the dioctahedral and trioctahedral series as well as others with different tetrahedral Si/Al ratios. Additionally, the samples were also homoionised with different interlayer cations. The structural formulae of the samples studied in this report are included in Table 1 and characterised in more detail elsewhere.[12]

High-resolution ¹H MAS NMR spectra were recorded at room temperature for the smectites equilibrated in air (hydrated samples) and after heating at 150 °C, to ensure the complete removal of interlayer water (dehydrated samples), in order to separate both contributions. A more detailed description of the experimental procedure is given elsewhere.[12] Spectra were acquired in a magnetic field of 9.39 T and rotors were spun at 12 kHz. Pulse spaces of 5 s were used and the radiofrequency field for protons was 60 kHz.

¹H MAS NMR spectra of the different sodium-saturated smectites described in Table 1, after dehydration at 150 °C, are given in Fig. 1 (dotted lines in the right-hand column). The spectra of talc and pyrophyllite have also been included. All of the spectra show a single component, assigned to structural hydroxyl groups, which have been fitted with a Lorentzian curve (solid lines in the right-hand column of Fig. 1). The chemical shift (δ) and the full-width at half-height (fwhh) values are displayed in the upper-right-hand graph of Fig. 1.

Table 1 Structural formulae of the selected smectites

Short name	[4]Si⁴⁺	[4]Al³⁺	[6]Al³⁺	[6]Fe³⁺	[6]Mg³⁺	[6]Li⁺	[6]Ti⁴⁺	M⁺
Talc	8.00	—	—	—	6.00	—	—	—
SHCa-1[a]	7.96	0.04	0.04	—	5.30	0.66	—	0.66
SapCa-1[b]	7.20	0.80	—	0.14	5.79	—	—	0.80
Pyrophyllite	8.00	—	4.00	—	—	—	—	—
Trancos[c]	7.64	0.36	3.09	0.28	0.69	—	—	0.87
SAz-1[c]	7.97	0.03	2.71	0.14	1.13	—	0.02	1.14

[a] Hectorite. [b] Saponite. [c] Montmorillonite.

The hydroxyl NMR bands show a value of *ca.* 0.5 ppm for the trioctahedral samples and of *ca.* 2.0 ppm for the dioctahedral ones. The difference in chemical shift between these samples is a consequence of differences in the composition of the octahedral sheet and is in agreement with the ^{29}Si MAS NMR data reported for these materials.[13] In trioctahedral minerals, OH bond axes are perpendicular to the layers and point toward the hexagonal cavities, while they are almost parallel to the layers in dioctahedral minerals.[14] In consequence, the proton position in the dioctahedral smectites allows an interaction between these OH groups and the apical oxygen atoms of the tetrahedral sheets, a hydrogen bond, which causes a deshielding of the protons and, hence, a displacement of their resonances to lower fields.

Within each series, the chemical shift value is related to the octahedral layer charge: the higher the octahedral layer charge, the higher the field. This fact is explained on the basis of the localisation of charge deficits created by isomorphous substitutions in the smectites.[15] If the deficit originates in the octahedral sheet, the excess negative charge tends to be delocalised around the whole sheet and the proton shielding of the structural hydroxyls increases as the octahedral charge is elevated. However, if the deficit occurs in the tetrahedral sheet, the excess negative charge tends to be localised on single oxygen atoms and the effect on the hydroxyl proton shielding is negligible.

As regards the band widths, these are influenced by both structural and compositional parameters. Firstly, trioctahedral structures provide a more symmetrical environment for the hydroxyl protons than dioctahedral minerals. In the latter structures, the hydroxyls are tilted and pointing toward one of the tetrahedra of the hexagonal array, a librational motion being allowed. In consequence, the trioctahedral minerals show a unique hydroxyl chemical environment and narrower ^1H NMR signals, whilst dioctahedral minerals show an average of different hydroxyl orientations and wider bands.

Secondly, the mineralogical composition affects the band width in a two-fold manner: those samples without isomorphic substitutions show the narrowest bands in each series and the incorporation of paramagnetic impurities and NMR-active nuclei causes a broadening of the signals.

In order to evaluate the influence of the interlayer cation, ^1H MAS NMR spectra of saponite exchanged with different cations are included in the left-hand column of Fig. 1, similar results being obtained for the other smectites. Dehydrated and

exchanged saponites display similar ^1H NMR hydroxyl signals regardless of the identity of the interlayer cations, indicating that these species have no influence on the OH protons.

As regards the ^1H NMR water signal, the centre column of Fig. 1 exhibits, as dotted lines, the experimental spectra shown in the left-hand column, after subtraction of the corresponding spectra of the dehydrated samples. These spectra are composed of a single component, associated with the interlayer water of these materials. A clear relationship between the chemical shift value and the interlayer cation charge is observed. As the charge of the cation increases, the proton acidity increases and the band is shifted to lower fields: chemical shifts for the water protons of samples exchanged with trivalent cations are found to lie within the narrow range 4.60–4.55 ppm; those of samples exchanged with divalent cations lie close to 4.36 ppm; and those of samples exchanged with monovalent cations lie around 4.10 ppm. Identical chemical shifts were found for the other smectites exchanged with the same cations. Therefore, the position of the water band is uniquely affected by the charge of the interlayer cation.[16,17]

However, the fwhh is less influenced by both the charge and the size of the cation, the response being much more complicated. The variations in the linewidths of proton spectra in similar systems are affected by the mobility of water and, in consequence, complicated diffusion processes are involved, more sophisticated models being necessary for a discussion of these effects.

In summary, this report shows that the combined use of high magnetic fields and spinning speeds affords single-pulse ^1H MAS NMR spectra of smectites of similar quality to those currently obtained by using multiple-pulse sequences. Moreover, these spectra require only very short acquisition times and a simple instrumental set up. The spectra directly provide information on the octahedral nature, the octahedral layer charge, and the charge of the interlayer cation of the mineral, structural aspects of elevated importance in the study of these materials. In particular, they can be used as initial characterization measurements and can be valuable for monitoring structural changes in the course of many treatments in which smectites can change their layer charge, suffer leaching processes, or modify their interlayer compositions. Finally, such spectra afford the opportunity to develop two-dimensional cross-polarisation experiments with other nuclei, such as ^{27}Si, ^{29}Al and ^7Li, which would improve the information currently obtained from MAS NMR spectroscopy.

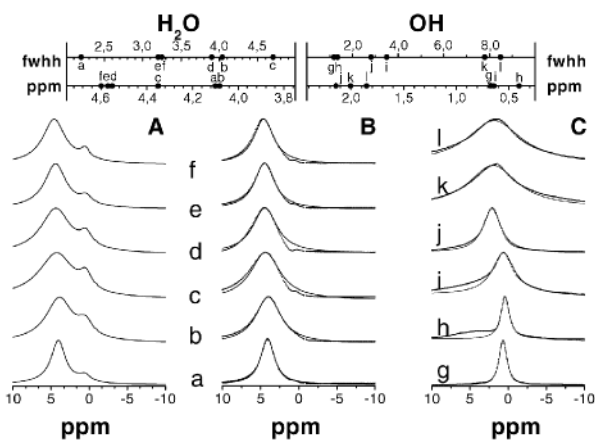**Fig. 1 A**: ^1H MAS NMR spectra of saponite saturated with Na+ (a), Li+ (b), Mg²⁺ (c), Al³⁺ (d), La³⁺ (e), and Lu³⁺ (f) ions. **B**: Subtraction from ^1H MAS NMR spectra shown in the left column of the ^1H MAS NMR spectra obtained from the samples after dehydrating at 150 °C (dotted lines) and Lorentzian fitting curves (solid lines). Chemical shifts and full-widths at half-height are shown in the upper-left diagram for each fitting curve. **C**: ^1H MAS NMR spectra of (g) talc, (h) Na-hectorite, (i) Na-saponite, (j) pyrophyllite, (k) Na-Trancos montmorillonite, and (l) Na-SAz-1 montmorillonite after dehydrating at 150 °C (dotted lines). Lorentzian fitting curves have been included for each experimental curve (solid lines). Chemical shfts and full-widths at half-height are shown in the upper-right diagram for each fitting curve.

Notes and references

1 J. M. Trillo, M. D. Alba, R. Alvero and M. A. Castro, *J. Chem. Soc., Chem. Commun.*, 1993, 1809.
2 J. Klinowski, *Chem. Rev.*, 1991, **91**, 1459.
3 S. C. Kohn, *Am. Mineral.*, 1996, **81**, 1523.
4 A. J. Vega and Z. Luz, *J. Phys. Chem.*, 1987, **91**, 365.
5 B. L. Phillips, P. C. Burnley, K. Worminghaus and A. Navrotsky, *Phys. Chem. Miner.*, 1997, **24**, 179.
6 D. Freude and J. Klinowski, *J. Chem. Soc., Chem. Commun.*, 1988, 1411.
7 H. Pfeifer, *Colloids Surf.*, 1990, **45**, 1.
8 D. R. Kinney, I. Chuang and G. E. Maciel, *J. Am. Chem. Soc.*, 1993, **115**, 6786.
9 A. Thursfield and M. W. Anderson, *J. Phys. Chem.*, 1996, **100**, 6698.
10 S. F. Dec, R. A. Wind and G. E. Maciel, *Macromolecules*, 1987, **20**, 2754.
11 J. P. Yesinowski, H. Eckert and G. R. Rossman, *J. .Am. Chem. Soc.*, 1988, **110**, 1367.
12 A. I. Becerro, Ph.D. Thesis, University of Seville, 1997.
13 J. Sanz and J. M. Serratosa, *J. Am. Chem. Soc*, 1984, **106**, 4790.
14 J. M. Serratosa and W. F. Bradley, *J. Phys. Chem.*, 1958, **62**, 1164.
15 G. Sposito and R. Prost, *Chem. Rev.*, 1982, **82**, 553.
16 P. H. Kasai and P. M. Jones, *J. Mol. Catal.*, 1984, **27**, 81.
17 J. N. Shoolery and B. Alder, *J. Chem. Phys.*, 1955, **23**, 805.

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