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Two-dimensional heteronuclear ^{1}H ↔ ^{27}Al-correlated MAS NMR spectra of layered silicates

María D. Alba,* Ana I. Becerro, Miguel A. Castro and Ana C. Perdigón

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales, Universidad de Sevilla, Consejo Superior de Investigaciones Científicas, Avda. Américo Vespucio s/n, 41092-Sevilla, Spain. E-mail: alba@cica.es

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The structural locations of aluminium in layered silicates, with different chemical environments but similar co-ordination polyhedra, can be established unequivocally from the correlation between the chemical shifts of protons and ^{27}Al nuclei, *via* their heteronuclear dipole–dipole couplings.

Among the quadrupolar nuclei studied by nuclear magnetic resonance (NMR), the ^{27}Al nucleus has received a great deal of interest for two reasons: on the one hand, aluminium is a main constituent of many interesting basic or applied solid systems; on the other hand, it is a very favourable nucleus for NMR investigations because it is a 100% naturally abundant isotope. However, even when conventional single pulse ^{27}Al MAS NMR spectra are recorded under the best conditions, *i.e.* very high magnetic fields, fast magic angle spinning speeds, and strong radiofrequency pulses with small flip angles,[1] only limited information is obtained. Those ^{27}Al MAS NMR spectra allow the determination of the coordination number of aluminium but they are much less sensitive to the nature of second neighbour species. Thus, very different structural aluminium sites with similar coordination environments can not clearly be differentiated on the basis of those ^{27}Al MAS NMR spectra.

In order to obtain this information, two-dimensional ^{1}H ↔ ^{27}Al cross-polarisation experiments, which are selective to the existence of dipole–dipole interactions between both nuclei, are very useful in distinguishing similar aluminium coordination environments. The proposed experiments, very recently employed for mesoporous solids,[2] provide spectra with a simple and straightforward interpretation: the identification of the proton species correlated with the aluminium nuclei allows one to obtain precise structural information. However, two difficulties need to be overcome to perform these experiments. First, special care needs to be taken to perform cross-polarisation experiments of quadrupolar nuclei,[3] even though the optimum experimental conditions have already been explored for the case of ^{27}Al nuclei.[4] Second, available and unequivocally assigned high resolution ^{1}H MAS NMR spectra of the studied solid systems are required in order to correlate adequately the 2D signals that appear in the spectra. This second requirement has been recently fulfilled by our group for the solid systems here analysed.[5]

In this report, the advantages of applying this new solid-state NMR method to the family of phyllosilicates are reported for the first time. We describe both the method and the new available information from 2D spectra of aluminosilicates. From these spectra it is demonstrated that the method allows one not only to distinguish between different coordination environments for aluminium, but also to assign to these nuclei a precise structural location. Likewise, useful applications for such measurements are proposed.

The proposed technique is a two-dimensional heteronuclear ^{1}H ↔ ^{27}Al chemical shift-correlation experiment, HETCOR. It is similar to conventional cross-polarisation, CPMAS NMR, experiments[6] except that the ^{1}H magnetisation is allowed to evolve for a period of time before the magnetisation transfer to the investigated nuclei, *i.e.* the ^{27}Al nuclei.

In order to illustrate the advantages of using this methodology, two well-characterised samples, available from the Source Clay Repository of the Clay Mineral Society, were selected. These samples include the possible structural positions of aluminium in layered silicates. Aluminium ions may occupy

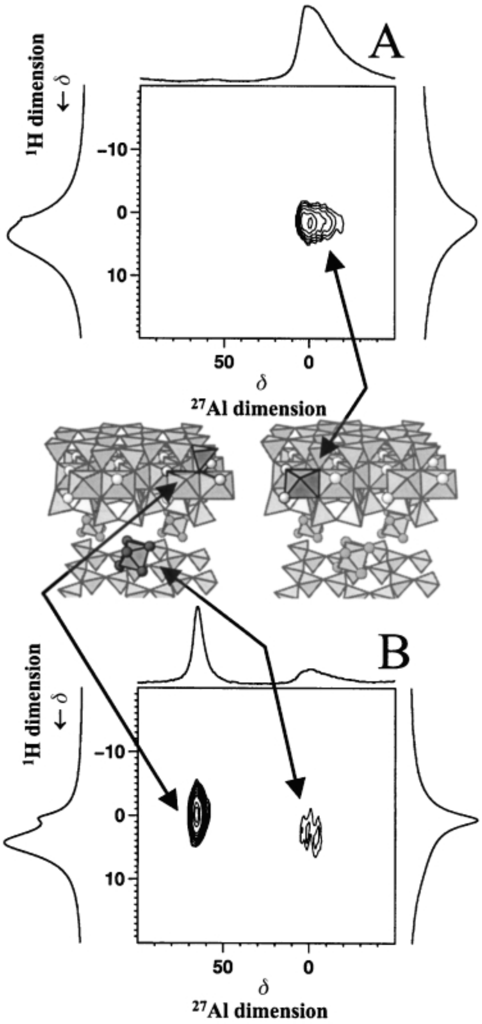

Fig. 1 (A) Contour plot of the 2D ^{1}H ↔ ^{27}Al correlation experiment on hydrated sodium-saturated SAz-montmorillonite obtained with a ^{1}H π/2 pulse of 4.8 μs, a 0.3 ms contact time, a 250 ms recycle delay, and a 12.0 kHz spinning rate. A set of 84 FIDs was obtained with a t_1 increment of 5 μs and a dwell time of 5 μs. Separate ^{27}Al and ^{1}H MAS NMR spectra are plotted along their corresponding axes in accordance with the text. A silicate structure drawing is included to emphasize the dipole–dipole coupling found. (B) Contour plot of the 2D ^{1}H ↔ ^{27}Al correlation experiment on hydrated aluminium-saturated SapCa-saponite. The conditions for this experiment were identical to those presented in (A), with the exception that a set of 96 FIDs was collected. Separate ^{27}Al and ^{1}H MAS NMR spectra and an appropriate silicate structure drawing are also included.

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three different positions in these solids. If aluminium is a main constituent of the silicate lattice, *i.e.* the silicate sheet, it can occupy either an octahedral or a tetrahedral location. When aluminium enters in the silicate structure as an exchange cation, *i.e.* in the interlayer space, it exhibits octahedral coordination.[2]

The first location, octahedral aluminium in the silicate sheet, is represented by a sodium-saturated montmorillonite from Arizona, which has been described in detail elsewhere.[7] The 1D ^{27}Al MAS NMR spectrum for this sample, horizontal projection in Fig. 1A, consists of a single peak centred at around 0 ppm that is assigned to these aluminium environments.[8] For the other two locations, tetrahedral aluminium in the silicate sheet and octahedral aluminium in the interlayer space, an aluminium-saturated saponite was selected.[9] In the corresponding 1D ^{27}Al MAS NMR spectrum, horizontal projection in Fig. 1B, two aluminium signals centred at 0 ppm (the octahedral aluminium) and 67 ppm (the tetrahedral aluminium) are observed. A comparison between the 1D NMR peaks obtained for the two different octahedral aluminium environments reveals the difficulties encountered to elucidate the structural location of octahedral aluminium in silicates. Conventional ^{27}Al MAS NMR spectroscopy fails for this purpose.

Fig. 1 also shows the application of the proposed technique to layered silicates for the first time, the 2D spectra for both samples being included. The 2D ^{1}H ↔ ^{27}Al HETCOR spectra are displayed as contour plots along with the following: ^{27}Al MAS NMR (top) and ^{1}H MAS NMR (left) spectra from the hydrated sample, and ^{1}H MAS NMR (right) spectra from the samples after dehydration at 110 °C which were separately acquired for each. Drawings of the silicate structure are also included in which the coupled aluminium and proton species are outlined in bold to aid in the analysis of the 2D ^{1}H ↔ ^{27}Al HETCOR spectra obtained.

On the one hand, the 2D spectrum for the sodium-saturated montmorillonite sample (Fig. 1A) consists of a single cross-peak which correlates the unique ^{27}Al signal, corresponding to an indistinguishable octahedral aluminium in the 1D spectrum, with the hydroxyl proton peak from the silicate lattice. Thus, the intensity profile in the contour plot clearly indicates that the aluminium ions are only occupying octahedral positions of the silicate sheet. On the other hand, the 2D spectrum for the aluminium-saturated saponite (Fig. 1B) consists of two cross-peaks, related to the two 1D-aluminium signals. The tetrahedral aluminium, 1D signal at around 67 ppm, is correlated with the hydroxyl proton signal from the silicate lattice in a similar manner as the former case. The octahedral aluminium, 1D signal at around 0 ppm, is correlated with the water proton peak from the interlayer space. This latter correlation reveals the new position of the aluminium species in the silicate mineral, octahedral positions in the interlayer space, in addition to demonstrating the advantages of using this technique. The indistinguishable 1D octahedral aluminium chemical shifts (horizontal projections of each 2D spectrum) are separated from dipole–dipole coupled species into two frequency dimensions, which allow adjacent nuclear species to be readily determined.

In summary, this paper describes a technique that enables, for the first time, the determination of the coordination number of a particular aluminium species from the ^{27}Al chemical shift, in addition to allowing the identification of the location of this polyhedron within the structure, from the dipole–dipole coupling with adjacent protons. Thus, the technique presented here offers a new approach to the improvement of the NMR information extractable from quadrupolar nuclei.

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Notes and references

1 A. Samoson and E. Lippmaa, *Chem. Phys. Lett.*, 1983, **100**, 205.

2 M. T. Janicke, C. C. Landry, S. C. Cristiansen, D. Kumar, G. D. Stucky and B. F. Chmelka, *J. Am. Chem. Soc.*, 1998, **120**, 6940.

3 R. K. Harris and G. J. Nesbitt, *J. Magn. Reson.*, 1988, **78**, 245.

4 (*a*) H. D. Morris and P. D. Ellis, *J. Am. Chem. Soc.*, 1989, **111**, 6045; (*b*) H. D. Morris, S. Bank and P. D. Ellis, *J. Phys. Chem.*, 1990, **94**, 3121; (*c*) J. Rocha and J. Klinowski, *J. Chem. Soc., Chem. Commun.*, 1991, 1121; (*d*) L. Kellberg, M. Linsten and H. J. Jakobsen, *Chem. Phys. Lett.*, 1991, **182**, 120.

5 M. D. Alba, A. I. Becerro, M. A. Castro and A. C. Perdigón, *Chem. Commun.*, 2000, 37.

6 P. Caravatti, G. Bodenhausen and R. R. Ernst, *Chem. Phys. Lett.*, 1982, **89**, 363.

7 R. E. Grim and G. Kulbicki, *Am. Mineral.*, 1961, **46**, 1329.

8 M. D. Alba, R. Alvero, A. I. Becerro, M. A. Castro and J. M. Trillo, *J. Phys. Chem. B*, 1998, **102**, 2207.

9 A. I. Becerro, Ph. D. Thesis, University of Seville, 1997.