Two-dimensional *J*-scaled ^{29}Si NMR COSY of Highly Siliceous Mordenite

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The two dimensional solid-state *J*-scaled COSY NMR spectrum of highly siliceous mordenite reveals the tetrahedral site connectivities, permitting the unambiguous assignment of the ^{29}Si spectrum.

Applications of two-dimensional (2D) NMR techniques to the study of solids are still in their infancy. There have been, however, several successful investigations into the connectivities of tetrahedral sites in highly siliceous zeolites[1-7] using either COSY or INADEQUATE pulse sequences. However, use of conventional COSY is limited by the need to resolve weak cross-peaks which are very close to the intense signals on the main diagonal of the 2D spectrum. This is not possible except for extremely narrow signals. By contrast, the INADEQUATE experiment gives no diagonal peaks, but suffers from low sensitivity. We report here the application of the *J*-scaled COSY pulse sequence,[8] for the first time in the solid state, to the study of highly siliceous mordenite. The technique scales up the scalar couplings involved in the COSY experiment, thereby enhancing cross-peak intensities and consequently improving spectral resolution between adjacent diagonal and cross-peaks.

Mordenite is a zeolite of considerable commercial interest.[9] Our highly siliceous sample was prepared from a synthetic mordenite (Toyo Soda Manufacturing Co. Ltd) with natural ^{29}Si isotopic abundance. It was calcined at 600 °C for 12 h and then ion-exchanged twice in NH_4Cl (1 mol dm^{-3}) aqueous solution at 80 °C using a 1 : 10 w/w solid-to-liquid ratio. The NH_4^+–mordenite was then hydrothermally dealuminated at 600 °C for 12 h, exchanged with NH_4^+ again, and then dealuminated at 800 °C. The hydrothermal dealuminations were carried out using a vertical tube-furnace with a water injection rate of about 1 ml min^{-1}. The final product was highly crystalline (by XRD) and had a Si/Al ratio of several hundred.[10]

The *J*-scaled COSY experiment (Fig. 1) was performed using a scaling factor of 5. The 2D ^{29}Si NMR spectrum (Fig. 2) was recorded at 79.5 MHz on a Bruker MSL-400 spectrometer with magic-angle spinning (MAS) of the sample at 4.2 kHz using the following parameters: ^{29}Si $\pi/2$ pulse of 4.8 μs, 33 ms acquisition time, 6 s recycle delay, 256 real data points in the F_2 dimension, 96 experiments for the second spectral dimension with 16 dummy and 288 real scans in each. Zero-filling to 2K and to 1K was used in F_2 and F_1 dimensions, respectively, and sine bell squared apodization with power calculation followed by symmetrization was applied for data processing.

The conventional ^{29}Si MAS NMR spectrum of highly siliceous mordenite consists of three peaks in the intensity ratio of 2 : 1 : 3.[10-12] This may be explained on the basis of the known structure of mordenite[13,14] which contains four distinct tetrahedral crystallographic sites in the intensity ratio T1 : T2 : T3 : T4 = 2 : 2 : 1 : 1 (Fig. 3) with two of the peaks overlapping. Assignment of the signals has, in the past, relied on the correlation between ^{29}Si chemical shifts and mean Si–O–Si bond angle, α. This is theoretically a $<\cos\alpha/(\cos\alpha - 1)>$ dependence, but follows an approximately linear relationship in the regime under investigation.[15,16] The published structure solutions for various forms of mordenite[13,17,18] show that the mean T–O–T bond angles vary slightly with the degree of dealumination, cation type and water content, but the relative values remain approximately constant. The values for a siliceous mordenite prepared by acid leaching[17] given in Table 1 permit the immediate assignment of the

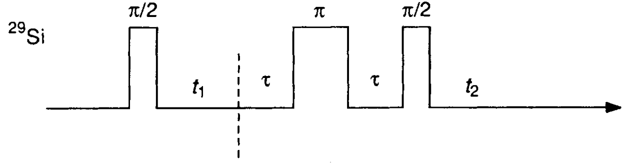

Fig. 1 *J*-scaled COSY ^{29}Si MAS NMR pulse sequence. The relationship between τ and t_1 is chosen so that *J*-couplings are scaled up by, in our case, a factor of five.

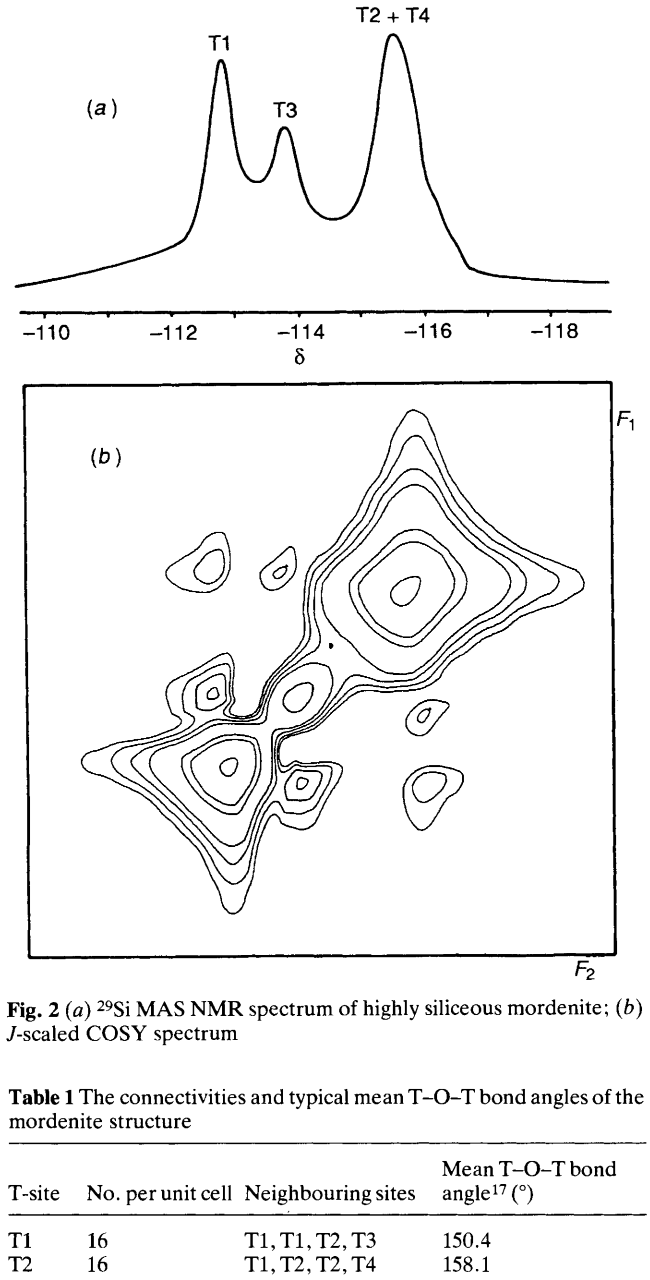

Fig. 2 (*a*) ^{29}Si MAS NMR spectrum of highly siliceous mordenite; (*b*) *J*-scaled COSY spectrum

Table 1 The connectivities and typical mean T–O–T bond angles of the mordenite structure

T-site	No. per unit cell	Neighbouring sites	Mean T–O–T bond angle[17] (°)
T1	16	T1, T1, T2, T3	150.4
T2	16	T1, T2, T2, T4	158.1
T3	8	T1, T1, T3, T4	153.9
T4	8	T2, T2, T3, T4	152.3

downfield peak to the T1 site and shows that the T2 site is a component of the strongest peak. However, the ⟨T3–O–T⟩ and ⟨T4–O–T⟩ bond angles are fairly similar, and so it is not possible to assign confidently the spectrum completely on the basis of bond angles alone. The two possible assignments of the three peaks in the spectrum are to T1 : T4 : T2 + T3 (as in refs. 10 and 12), or to T1 : T3 : T2 + T4 crystallographic sites.

The 2D *J*-scaled COSY spectrum of highly siliceous mordenite (Fig. 2) reveals three cross-peaks. We were unable to resolve these by the COSY experiment with two extra delays, as described by Fyfe *et al.*[1,2] Attempts to do so yielded a spectrum with the cross-peaks obscured by the intense peaks on the main diagonal. The couplings between the tetrahedral sites are expected to be in the range of 10–15 Hz,[4] too small to give rise to prominent cross-peaks for this sample, unless they are scaled up by the particular pulse sequence used as is the case in *J*-scaled COSY. On the basis of the known connectivities of the mordenite structure (Table 1) ony two cross-peaks are expected for the T1 : T4 : T2 + T3 assignment, while the T1 : T3 : T2 + T4 assignment implies that three cross-peaks should be observed. Thus the presence of three cross-peaks in the two dimensional *J*-scaled COSY experiment shows that the correct interpretation is T1 : T3 : T2 + T4. Such unambiguous assignment is not possible by one-dimensional NMR or conventional COSY techniques.

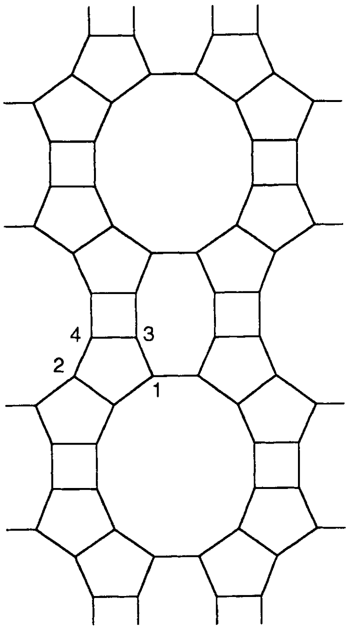

Fig. 3 The structure of mordenite viewed along [001].[13,14] The four kinds of crystallographic sites are indicated. Their relative populations (16 : 16 : 8 : 8 per unit cell) are not reflected in this projection.

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