

Location of Organic Bases and Identification of Brønsted Acid Sites in Zeolites by ^{14}N Solid State NMR

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Solid state ^{14}N NMR spectra of R_4N^+ ions in zeolites, like ZK-4 and ZSM-20, are easily detected due to high tetrahedral symmetry at the ^{14}N site; spectral perturbations due to ^{14}N quadrupolar interactions distinguish TMA^+ (TMA^+ = tetramethylammonium) ion environments in α - and β -cages of ZK-4 and a lone TEA^+ (TEA^+ = tetraethylammonium) environment in ZSM-20 and it is further shown that solid state ^{14}N NMR spectroscopy offers a convenient method to detect the presence of Brønsted acidic sites in zeolites.

In the structural characterization of zeolites by nitrogen NMR spectroscopy, only ^{15}N has emerged as a useful probe.¹ The dilute spin ^{15}N offers very good spectral selectivity, but not sensitivity. Without isotopic enrichment it is not possible to observe ^{15}N NMR with sufficient signal to noise ratio (S:N). The potential for using naturally abundant ^{14}N (99.63%), however, has not been explored. This neglect is likely due to the widely held notion that ^{14}N quadrupole couplings are large² and the resulting ^{14}N NMR spectra are broadened beyond detection.

The problem of excessive spectral line broadening (LB) due to ^{14}N quadrupole interactions is alleviated to a great extent when the symmetry of the ^{14}N environment is nearly perfectly tetrahedral. In such circumstances, the electric field gradients are small and the quadrupole couplings fall in the tens of kHz range.³ This offers considerable scope to observe ^{14}N NMR spectroscopy directly without having to resort to elaborate indirect methods.⁴

Two potentially useful cases for the application of solid state ^{14}N NMR to zeolites can be identified. (i) A non-framework environment can be probed when alkylammonium organic bases (R_4N^+) are used as templates. (ii) Tetrahedrally symmetric and stable ammonium ions are likely to be created

by protonation of ammonia gas at the Brønsted acid sites, thus offering an opportunity to probe the acidic environment. The latter is especially important since zeolites are mostly used in acid type catalytic reactions. In this communication, we address these aspects and show for the first time the practical utility of ^{14}N NMR spectroscopy for zeolite catalysts.

The zeolites ZK-4 (Si:Al = 3.1) and ZSM-20 (Si:Al = 7.8) were freshly prepared according to reported procedures^{5,6} and were well characterised by XRD, IR, TG-DTA, MAS-NMR (^{27}Al , ^{29}Si and ^{13}C), SEM,[†] and sorption measurements, prior to the recording of ^{14}N NMR spectra. ^{14}N NMR spectra were recorded at 21.67 MHz on a Bruker MSL-300 FT-NMR[†] spectrometer at ambient probe temperature (293 K). A quadrupolar echo pulse sequence⁷ was used to give distortionless ^{14}N line shape.

We show in Fig. 1, the static ^{14}N spectra of TMABr (Me_4NBr) as a neat solid (a) and the same ion in ZK-4 (b). The axially symmetric quadrupolar pattern with $e^2Qq/h = 25.2$ kHz, simulated for TMABr (d), appears in the spectrum for ZK-4. A 'best fit' between the observed and computed ^{14}N powder pattern is obtained when three distinct TMA ion environments are considered (e). Considering that ZK-4 is isostructural with zeolite A,⁵ motionally restricted TMA ions in the smaller sodalite (β) cage and mobile TMA ions in the larger super (α) cage are readily located. Inspection of the observed ^{14}N powder pattern further shows that the TMA ion [I in (e)] is intact in the sodalite cage and acts merely as a charge balancing cation. Further, not all the TMA ions in the α -cage are freely mobile, and some of them are restricted in their mobility [II in (e)] owing to possible interactions with the framework. A comparison of the ^{14}N spectrum taken on dehydrated ZK-4 (in vacuum at 323 K, figure not shown), helps us to identify the narrowest component [III in (e)] to be associated with the hydration sites in the super cage. The

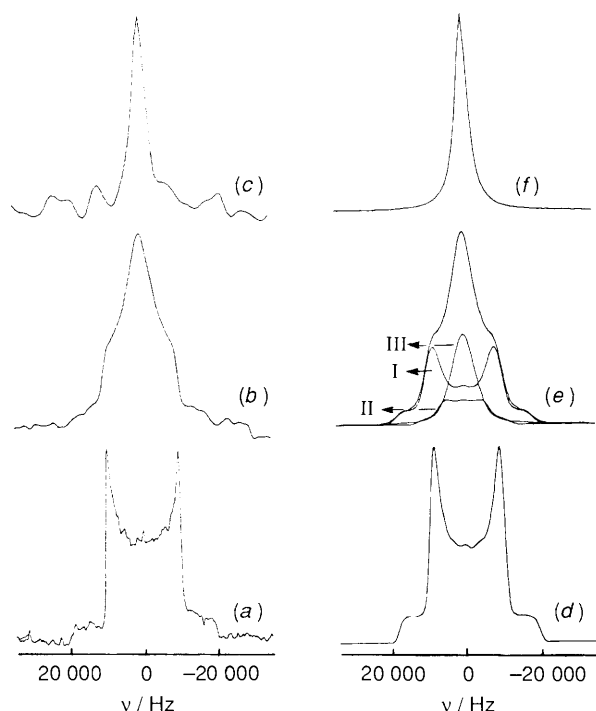


Fig. 1 21.67 MHz ^{14}N NMR spectra of (a) TMABr , (b) TMA-ZSM-20 and (c) TEA-ZSM-20 and the corresponding computer simulated spectra in (d), (e) and (f), respectively. The following quadrupolar parameters were used in the simulation (d) $e^2Qq/h = 25.2$ kHz, $\eta = 0.0$, LB = 2800 Hz; (e) I, 40%, $e^2Qq/h = 25$ kHz, $\eta = 0$, LB = 3600 Hz; II, 15%, $e^2Qq/h = 16$ kHz, $\eta = 0.0$, LB = 3600 Hz; III, 45%, isotropic line with Gaussian broadening (GB) = 7500 Hz; (f) isotropic line with GB = 4500 Hz.

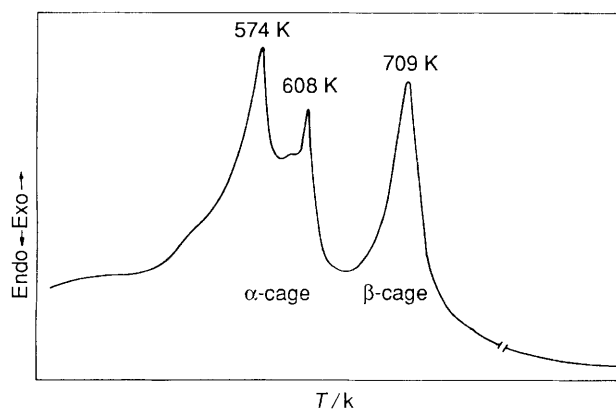


Fig. 2 DTA of TMA-ZK-4 . TG analysis gives molecules per unit cell as β -cage = 1.07 (44.7%); α -cage = 1.79 (40.3 and 15%).

[†] Abbreviations used: XRD = X-ray diffraction; TG = thermal gravimetric; DTA = differential thermal analysis; MAS = magic angle spinning; SEM = scanning electron microscope; FT = Fourier transform.

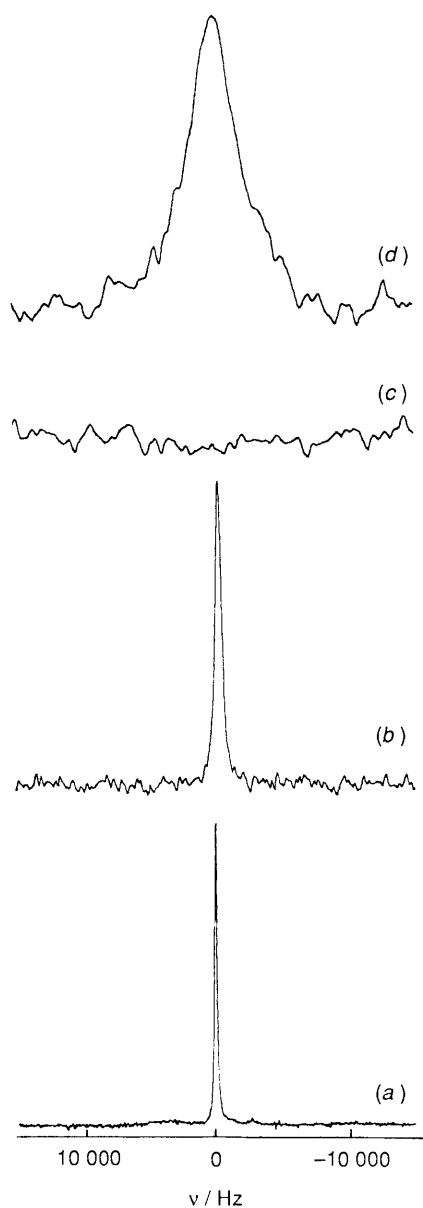


Fig. 3 21.67 MHz ^{14}N NMR spectra of (a) solid NH_4Cl , (b) $\text{NH}_4\text{-Y}$, (c) zeolite H-Y and (d) after saturation of zeolite H-Y with ammonia gas

^{14}N NMR results are further supported by thermal (TG-DTA) analysis data shown in Fig. 2, where three distinct exothermic peaks are detected.

Fig. 1(c) shows the ^{14}N spectra of TEA ion (Et_4N^+) in the ZSM-20 together with the computer simulation (f). The

observation of a narrow ^{14}N line and the absence of quadrupolar powder pattern features indicates that a lone TEA environment is detected and that a greater degree of mobility for the TEA ion in the large super cage of the faujasite structure is envisaged. The absence of the broad ^{14}N spectral component is clearly indicative of the absence of TEA ion within the sodalite cages in ZSM-20. This is not surprising in view of the large molecular size of the TEA ion, compared to the TMA ion, which precludes its occupancy in the sodalite cage during the process of crystallization.

The utility of ^{14}N NMR spectroscopy to detect Brønsted acid sites in zeolites is demonstrated in Fig. 3. We first show the ^{14}N NMR spectrum of $\text{NH}_4\text{-Y}$ (USY; Si:Al = 5.8) zeolite where a narrow resonance due to a highly mobile ammonium ion in a near-cubic environment is observed (b). A complete loss of ^{14}N signal, upon calcination at 773 K for 8 h, is indicated in (c), thus ensuring decomposition of NH_4^+ ions to form H-Y. Upon dehydration and passing of ammonia gas *in vacuo*, a strong but much broader ^{14}N signal reappears (d). Since only NH_4^+ ions are detectable and not NH_3 ($e^2Qq/h = 3.16 \text{ MHz}^8$), the spectrum (d) unambiguously shows the formation of ammonium ions by the protonation of the ammonia gas at Brønsted acid sites. A line broadening of 4.5 kHz in (d) is indicative of perturbations in the ^{14}N quadrupolar interactions at these acidic sites owing to reduced ammonium ion mobility.

Our ^{14}N results therefore clearly demonstrate the potential of using ^{14}N solid state NMR for probing the organic bases and Brønsted acid sites in zeolites. Extensions using ^1H - ^{14}N -CP (cross polarisation) and MASS (magic angle sample spinning) techniques would be useful.

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