Characterization of zeolites and amorphous silica–aluminas by means of aluminum-27 nuclear magnetic resonance spectroscopy: A multifield, multiparameter investigation

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We have obtained the aluminum-27 nuclear magnetic resonance (n.m.r.) spectra of a large number of ZSM-5 (MFI) zeolites and amorphous silica aluminas by using static, spin-echo, and "magic-angle" sample-spinning (*MAS*) techniques, at various magnetic field strengths in the 2.35–11.7 Tesla range. Our results give the mean nuclear quadrupole coupling constants (QCC), the static and *MAS* line widths, the chemical shifts and shift distributions, the spin-spin relaxation times (T_{2H}), as well as the effects of hydration on T_{2H} . We show that such a multiparameter analysis permits an unambiguous differentiation between framework and nonframework (ZSM-5 and amorphous silica-alumina) aluminum sites, which is of use in characterizing the structures of complex commercial zeolite catalysts. We present a theoretical approach to the determination of the QCC values in zeolites and silica-aluminas based upon the field dependence of the *MAS* or static line widths, which also yields an approximate bond-angle distribution that is found to be in accord with that deduced from X-ray diffraction and ²⁹Si n.m.r.

Keywords: N.m.r.; zeolites; aluminum; silica-alumina

INTRODUCTION

Nuclear magnetic resonance (n.m.r.) spectroscopy has been used extensively during the past 10 years to investigate the structures of zeolites, with much emphasis being placed on the aluminum-27 nucleus.¹ In most of these studies, pure zeolites have been used. As we show elsewhere,²⁻⁴ it is now generally a straightforward matter to "electronically edit" away the vast majority of the ²⁷Al signals from typical alumina or silica–alumina binders, based on differential spin-echo decay behavior (T_{2H}) between most (hydrated) zeolites and amorphous aluminas or silica–aluminas. In this paper, we investigate this topic in more detail and answer the general question: What does it take to characterize a ²⁷Al resonance in a complex system as being due to either a zeolite (in this instance, ZSM-5) or an amorphous (nonframework) silica-alumina?

We will show that determination of the spectral appearance, chemical shift, static and magic-angle sample-spinning (MAS) line widths, quadrupole coupling constants, and T_{2H} values and their response to hydration are required in order to confidently assign a resonance to one or other of these materials, and we show by using "soft-pulse" selective-excitation spin-echo techniques that it is possible to quantitatively determine MFI and FAU zeolites, even in the presence of large amounts of nonframework aluminum-rich binder materials. Such determinations are generally not possible by using conventional one-pulse MAS techniques, since small amounts of zeolite are usually totally obscured by binder ²⁷Al resonances.

EXPERIMENTAL

N.m.r. aspects

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²⁷Al nuclear magnetic resonance spectra were

obtained on seven different instruments: At Princeton, we used a 100 MHz (¹H)-200 MHz spectrometer based upon a JEOL FX-200 console, used in conjunction with Chemagnetics (Ft. Collins, CO) 2.35 Tesla 2.8 in.-bore and Oxford Instruments (Osney Mead, UK) 4.7 Tesla 3.5 in.-bore superconducting solenoid magnets, together with Chemagnetics (Fort Collins, CO) probes. In Urbana-Champaign, we used 270, 360, and two 500 MHz instruments, which basically consist of Oxford Instruments 6.35 Tesla 2 in., 8.45 Tesla 3.5 in. and 11.7 Tesla-2.0 in.-bore superconducting solenoids, Nicolet Instruments (Madison, WI), Model 1280 computers and Model 2090-3C transient recorders, Amplifier Research (Souderton, PA), Model 150LA, or 200L radiofrequency amplifiers, and assorted digital and radio-frequency circuitries, together with "home-built" magic-angle sample-spinning and static, solenoidal coil probes. For spin-echo measurements, we typically used a $\pi/2_{(x)}$ - τ - $\pi_{(x)}$ spin-echo sequence, with selective (solid) 90° pulse widths of ~ 20-40 μ s duration. Pulse lengths were set using a sample of ZSM-5. The ²⁷Al signal was set on resonance and the power level adjusted to obtain a null signal at a pulse length twice the desired solid 90-degree pulse length. Nonselective excitation was used for the MAS experiments, with solid 90° pulse widths of 1.5 µs. Chemical shifts are reported in ppm from a 1 M solution of Al(NO₃)₃ containing a small amount of HNO₃, using the convention that low-field, high-frequency, paramagnetic or deshielded values are denoted as positive (IUPAC δ -scale). A limited number of ²⁹Si (MAS) experiments were also performed, with chemical shifts being referenced to an external sample of tetramethylsilane (TMS), at 0 ppm.

Chemical aspects

All the ZSM-5 samples, and most amorphous silica-aluminas, were research samples produced at Mobil using conventional synthetic methods (see e.g., Refs. 4 and 5). In addition, a number of amorphous silica-aluminas (Ketjen Catalysts) were purchased from Akzo Chemie (Amersfoont, The Netherlands). Samples were investigated at 52% relative humidity, unless otherwise noted in the text.

RESULTS AND DISCUSSION

The question this paper seeks to address is: How can a given ²⁷Al resonance in a complex system be assigned to a particular chemical site? For example, how can we differentiate between zeolitic ²⁷Al resonance (in particular, ZSM-5), and an amorphous silica-alumina, which might resonate at approximately the same chemical shift (≈ 55 ppm)? To answer this question, we will consider the following parameters that might be used to characterize a sample: (1) the number of ²⁷Al resonances; (2) the chemical shift; (3) the static line width; (4) the MAS line width; (5) the nuclear quadrupole coupling constant; (6) the spinecho decay rate (T_{2H}); and (7) the effect of hydration on T_{2H} . Using two- and three-dimensional representations of our results, we show that a clear distinction may be made between ZSM-5 and the amorphous silica–aluminas, even in situations where the silica–alumina spectrum is characterized by a single line at the "ZSM-5 chemical shift." We also show that the observed ²⁷Al line widths of hydrated ZSM-5 zeolites can be understood in terms of known bond-angle distributions convoluted with the other line broadening mechanisms that we have determined.

We now consider each of the parameters listed above, in turn:

The number of resonances

The number of resonances in the ²⁷Al spectrum of a calcined ZSM-5 zeolite or amorphous silica-alumina is a strong indicator of the nature of the material under investigation. We have investigated over 60 ZSM-5 zeolites and found only one resonance (at \sim 55 ppm at 11.7 Tesla), unless the material had been calcined at excessively high temperatures ($\geq 500^{\circ}$ C). In this case, some dealumination can occur, with concomittant formation of a resonance at ~ 0 ppm, due to nonframework aluminum. In contrast, 18 of the 20 amorphous silica-aluminas investigated show two, or even three resonances, due in the latter case, presumably, to four-, five-, and six-coordinated aluminum. Typical results are shown in Figure 1, where we show a static ²⁷Al spectrum of ZSM-5 and MAS n.m.r. spectra of two calcined amorphous silicaaluminas. In two other calcined amorphous silicaaluminas, there was only a single, intense peak (centered at ~ 55 ppm). However, as we show below, other n.m.r. parameters can be used to differentiate between the ZSM-5 zeolites and these (very Al-poor) silica-aluminas. Thus, in the vast majority of cases, the ZSM-5 zeolites are characterized by a single ²⁷Al peak, as expected, while the amorphous silicaaluminas exhibit two, and often even three, ²⁷Al resonances.

The chemical shifts

In most cases, the chemical shift of a resonance is a strong indicator of the underlying chemical structure. Unfortunately, however, this powerful parameter is less useful for distinguishing between ZSM-5 zeolites and silica-aluminas since, especially for very dilute Al levels, the major bonding around the Al will be as Al[OSi]₄ in both materials, in which case chemical shifts of ≈ 55 ppm are to be expected (at 11.7 Tesla). For high-Al silica-aluminas, other structures, e.g., Al[OSi]₃[OAl] and Al[OSi]₂[OAl]₂, are to be expected, since the end-member will be essentially a Si-doped Al₂O₃ and the chemical shifts are further deshielded and multiple peaks occur (see, e.g., Figures 1B and C). However, for more dilute Al levels, there is a convergence in the isotropic shift, δ_i , toward that exhibited by the zeolites, in which case an assignment based solely on chemical shift values, or on chemical shift and the number of resonances, would not be completely reliable, since our results show that examples of single ²⁷Al resonances at essentially the



Figure 1 Typical 11.7 Tesla ²⁷Al n.m.r. spectra of ZSM-5 (static) and two amorphous silica–aluminas (with *MAS*). (A) NH₄⁴ ZSM-5, 1800 ppm Al, hydrated, 150.9 mg, 50,000 scans at a 50 ms recycle time, spin echo spectrum using 90°_x (solid) = 20 μ s, τ = 3.5 ms, 500 Hz Gaussian line broadening. (B) 40/60 wt% SiO₂/Al₂O₃ (containing 2 wt% B₂O₃), hydrated, 9.3 kHz *MAS*, 6000 scans at a 100 ms recycle time, 1.5 μ s (nonselective, solid 90°) pulse excitation, 100 Hz Gaussian line broadening. (C) Akzo-Chemie silica–alumina # LA-30-5P (13% Al₂O₃, 0.07% Na₂O, 0.2% sulfate, balance SiO₂, surface area = 140 m²g⁻¹), hyrated, 8.8 kHz *MAS*, 5418 scans at a 100 ms recycle time, other conditions as in (B).

zeolite chemical shift are possible, as shown, e.g., in *Figure 2*. Thus, additional parameters are needed for assignment purposes.

The static line widths

As we have indicated above, neither the chemical shift nor the number of lines, alone or in combination, permit an unambiguous assignment of a given ²⁷Al resonance to zeolite ZSM-5 vs. a nonframework, amorphous silica-alumina. Fortunately, however, other measurements do permit such an identification, and we have found that one of the simplest measurements to carry out, which is readily amenable to spin-echo spectral-editing, is a determination of the static line width, *W. Figure 2* shows typical results for a ZSM-5 sample and an amorphous silica-alumina (samples that exhibit essentially only a single resonance, at ≈ 55 ppm, have been chosen, since multiple resonances are not characteristic of the zeolite). *Table 1* contains a compilation of the static widths for a

series of zeolites (hydrated, H^+ or NH_4^+ forms) and amorphous silica-aluminas.

The results of Figure 2 and Table 1 (together with additional results on ~ 50 other zeolites and silicaaluminas — data not shown) clearly show that an excellent differentiation between ZSM-5 zeolites and amorphous silica-aluminas can be made on the basis of static line widths. The origins of this differentiation are very easy to understand: The zeolite has a very regular structure with a restricted range of T-O-T angles (where T represents an individual SiO₄ [typically] or AlO₄ tetrahedron). Since it has been shown by Lippmaa et al.⁶ that the following relation between the T-O-T angle (θ') and ²⁷Al isotropic chemical shift (δ_{CS}^{Al}) holds for framework aluminosilicates:

$$\delta_{\rm CS}({\rm Al}) = -0.50 \,\theta' + 132 \,(\rm ppm) \tag{1}$$

this means that a relatively narrow spread in θ' values leads to a relatively narrow spread in δ_{CS} .

On the other hand, the amorphous silica-aluminas, almost by definition, do not have this crystallographically imposed restriction on θ' . Thus, if a large range of θ' values exist, then there will be a large range in δ_{CS} and a broad line will result for the amorphous materials, as can be seen from the results presented in *Table 1* and *Figure 2*.

In addition, we have found that there are two other effects that cause additional line broadening for the amorphous silica–aluminas: large quadrupole coupling constants, due presumably to distorted tetrahedra, and short T_{2H} values, due possibly to restricted H₂O/counterion motion, as we discuss below. However, we will consider next the line widths observed under *MAS* conditions, since this not only permits an accurate determination of the quadrupole coupling constants, but also permits an estimate of the widths of the chemical shift distribution, Δ^{CS} .



Figure 2 Static 11.7 Tesla ²⁷Al n.m.r. spectra of NH₄⁺ ZSM-5 and an amorphous silica–alumina, showing large line-width differences. (A) 1:1 wt ratio NH₄⁺-ZSM-5 (1800 ppm Al): γ -Al₂O₃, hydrated, 10,000 scans at a 50 ms recycle time, spin-echo spectrum using 90°_x (solid) = 20 µs, τ = 5 ms, 500 Hz Gaussian line broadening. (B) Amorphous silica–alumina 10,000 ppm Al, hydrated, 10,000 scans at a 50 ms recycle time, spin-echo spectrum using 90°_x (solid) = 20 µs, τ = 200 µs, 500 Hz Gaussian line broadening.

System	[AI] (ppm)*	W (ppm) ^{<i>b</i>}	∆∞ (ppm)°	QCC (MHz) ^d	T _{2H} (ms) ^e
ZSM-5 zeolites	19,900	9.9		1.1	4.6
	11,300	9.1	5.3	1.5	3.7
	6,100	9.1	5.5	1.4	3.4
	1,350	9.6	5.4	1.6	4.7
	660	9.6	6.2	1.7	2.8
	44	NM ^f	6.0	1.6	NM
		9.5 ± 0.4^{g}	5.7 ± 0.4 ⁹	1.5 ± 0.2^{g}	3.8 ± 0.8 ^g
Silica–Aluminas	20,000	25.5	15.0	2.3	1.0
	10,000	23.5	12.0	2.7	1.2
	5,000	22.9	12.5	2.7	1.6
	2,500	36.0	15.0	3.1	1.2
	1,250	36.0	13.4	2.2	1.4
	625	23.0	11.1	2.1	1.1
		27.8 ± 6.4 ^g	13.2 ± 1.6 ^g	2.5 ± 0.4^{g}	1.3 ± 0.2^{g}

Table 1 Aluminum-27 n.m.r. static line widths, infinite-field line widths, quadrupole coupling constants, and spin-echo decay time constants for ZSM-5 zeolites and amorphous silica-aluminas

*Al concentrations are nominal and are typically ±20%

^b Static line width, in ppm, at 11.7 Tesla, measured on a partially relaxed spectrum; error is \pm 1–2 ppm, depending on the width

Infinite-field half-height line width of the Gaussian distribution from measurements of MAS line widths at 2.35, 4.7, 8.45, and 11.7

Tesla; error is =0.4–2.0 ppm, depending on the width ^d Nuclear quadrupole coupling constant in MHz (η assumed = 1.0) as determined from field-dependent MAS line widths (see ^c above);

error is ±0.2–0.4 MHz ^o Spin-echo decay time constant ($\pi/2_{(x)}$ – τ – $\pi_{(x)}$ pulse sequence using "soft-pulse" or selective excitation), in ms. The samples were equilibrated at ~ 52% relative humidity

^fNot measured due to a small nonframework peak overlap in the static spectrum

⁹ Mean value $(\pm 1 \sigma)$ of the data set

MAS line widths

Recently, Meinhold and Bibby⁷ and Challoner and Harris⁸ made estimates of the nuclear quadrupole coupling constants (QCC) of ZSM-5 samples, from the field dependence of the MAS line widths. Meinhold and Bibby⁷ estimated the QCC from the dependence of line width on field strength, but used a linear relationship that is expected to be less accurate at very high magnetic field strengths. Challoner and Harris⁸ determined both the QCC and a "shielding anisotropy" from the solution of two simultaneous equations, but did not interpret their "shielding anisotropies" in structural terms. We outline below in detail our method of extracting the QCC and the width of the chemical shift distribution, which we believe is superior to either of the two above methods, since it involves curve fitting of four field-dependent line widths, is applicable to static or MAS spectra, and is capable of handling experimental T-O-T angle distributions (from X-ray diffraction measurements on pure ZSM-5 materials) or any given chemical shift distribution function. We now consider this approach in detail.

The width of the central (1/2, -1/2) transition of a quadrupolar nucleus (e.g., ²⁷Al) in a zeolite or an amorphous silica-alumina powder can be influenced by a number of parameters: First, there may be a distribution of chemical shifts, due to a range of bonding situations (e.g., different T-O-T θ' values) — this effect is independent of magnetic field strength (is constant in ppm) and is applicable equally to both static and MAS experiments. Second, there may be an orientation-dependent shielding — the chemical shielding anisotropy (CSA), which will be

zero under MAS, and, in all probability, very small in static samples, due to the high symmetry of the [AlO₄] tetrahedra. Third, there may be dipolar coupling (both homonuclear and heteronuclear). Fourth, there may be relaxation (T_1 and T_2) contributions. Fifth, there may be second-order quadrupolar interactions, and sixth, there will be instrumental contributions.

For the ZSM-5 zeolites and silica-aluminas, the second-order quadrupolar and chemical shift distributions are expected to make the largest contributions to the experimentally observed line widths.^{7,8} The second-order quadrupolar interaction causes a resonance shift of the central transition, it is field-dependent, and analytical expressions for this resonance shift are known. The second-order quadrupolar shift, $\omega_{qs}^{(i)}$, of a given spin species, *i*, in a powder sample, is the same for static or *MAS* experiments and is given by the following equation:

$$\omega_{qs}^{(i)} = -\frac{1}{5} \frac{\omega_Q^{(i)2}}{\omega_L} \frac{I(I+1) - 3/4}{6} \left[1 + \frac{1}{3} \eta^{(i)2} \right], \quad (2)$$

where $\omega_Q^{(i)}/2\pi$ and $\eta^{(i)}$ are the quadrupole frequency and the asymmetry parameter of the electric field gradient tensor for a single spin species, respectively; $\omega_L/2\pi$ is the Larmor frequency of the spins; and *I* is the nuclear spin quantum number (for ²⁷Al, *I* = 5/2).

For a powder sample, the total frequency shift of the center of gravity of a quadrupolar broadened central transition $\omega_{cg}^{(i)}$, with respect to a reference sample, ω_0 , is given by

$$\omega_{cg}^{(i)} = \delta_{cg}^{(i)} \,\omega_L + \omega_{qs}^{(i)} \tag{3}$$

where $\delta_{cg}^{(i)}$ is the chemical shift (in ppm) of the species under consideration. With N different spin species in a powder, i.e., the central line consists of N different single lines, where each single line may have a different chemical shift or quadrupolar coupling, we have for the total center of gravity (first moment) of the central line the following expression:

$$\Omega_{tot} = \sum_{i=1}^{N} I^{(i)} \,\omega_{cg}^{(i)} \tag{4}$$

where *I*^(*i*) is the intensity (number of nuclei) of species "*i*," normalized such that

$$\sum_{i=1}^{N} I^{(i)} = 1 \tag{5}$$

The static second moment (powder average), $M_{2cg/s}$, due to the second-order quadrupolar shift for a singleline constituent with respect to its center of gravity, $\omega_{cg}^{(i)}$, is

$$M_{2cg/s}^{(i)} = \frac{23}{175} \frac{\omega_Q^{(i)4}}{\omega_L^2} \left[\frac{I(I+1) - 3/4}{6} \right]^2 \left[1 + \frac{1}{3} \eta^{(i)2} \right]^2$$
(6)

which, under the influence of fast "magic-angle" sample-spinning, reduces to

$$M_{2cg/m}^{(i)} = \frac{1}{100} \frac{\omega_Q^{(i)4}}{\omega_L^2} \left[\frac{I(I+1) - 3/4}{6} \right]^2 \left[1 + \frac{1}{3} \eta^{(i)2} \right]^2$$
(7)

To a good approximation, the second moment (powder average) corresponding to a single spin species, *i*, can be written as the sum of the second moments due to dipolar and quadrupolar interactions, but they have to be calculated with respect to the center of gravity of the overall line shape, Ω_{tot} . In the presence of "magic-angle" sample spinning, the influence of the dipolar interactions cancel and the dipolar second moment vanishes.

Summing up all these contributions, we obtain the following expression for the total second moment of the central line, M_{2tot} , in the case of "magic-angle" spinning:

$$M_{2tot/m} = \sum_{i=1}^{N} I^{(i)} \left\{ M_{2cg/m}^{(i)} + \left[\Omega_{tot} - \omega_{cg}^{(i)} \right]^2 \right\}$$
(8)

For static experiments, the second moment, $M_{2tot/s}$, follows from Equation (8) by replacing $M_{2cg/m}^{(i)}$ by the sum of the corresponding static second moment $M_{2cg/s}^{(i)}$, and the dipolar second moment. The second moment of the dipolar broadening is given by Van Vleck's formula. For the homonuclear interaction (for like and semilike spins), Van Vleck's formula changes slightly (see, e.g., Ref. 9, pp. 129–130). The dipolar interactions do not change the position of the center of gravity of the central line, and the second moments do not depend on field strength.

Assuming the final MAS line shape to be Gaussian (which we find to be a very good approximation for the systems studied to date), the line widths, $\Delta\delta$, corresponding to the $M_{2tot/m}$ of Equation (8) become

$$\Delta \delta = \frac{1}{\pi} \sqrt{2 \ln 2} \sqrt{M_{2tot/m}} \cdot \frac{2\pi \ 10^6}{\omega_0} \text{ (in ppm)}$$
(9)

We now need to consider the all-important chemical shift distribution to the line width, since examination of Equation (1) and the known crystallographic coordinates for ZSM-5 (Ref. 10) indicate a major contribution to the observed widths from this source, especially at high magnetic field strengths (as deduced also by Challoner and Harris⁸).

We have thus written a program to handle in a general way any given T–O–T θ' distribution — as might be deduced from, e.g., the X-ray results, or ²⁹Si chemical shifts [and the equations for ²⁹Si chemical shifts as a function of θ' similar to that given in Equation (1)*]. However, since we are unable to input θ' values directly for the amorphous silica–aluminas, we have also used a more general alternative method to describe the chemical shift distribution for the zeolites and silica–aluminas. In particular, we find that a Gaussian distribution of chemical shifts gives indistinguishable results to that obtained by using the crystallographic θ' values for ZSM-5. The Gaussian distribution of lines is described by the following expression:

$$I^{(i)} = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left\{ \frac{(\omega_{cg}^{(i)} - \omega_{cg})^2}{2\sigma^2} \right\}$$
(10)

where ω_{cg} and σ are the center of gravity and the second moment of the Gaussian distribution, respectively. Thus, the line width of the Gaussian distribution, in ppm, which is also the observed line width at an infinitely high magnetic field, Δ^{∞} , is given as

$$\Delta^{\infty} = \frac{1}{\pi} \sqrt{2 \ln 2} \sigma \frac{2\pi \ 10^6}{\omega_0}$$
(11)

The center of gravity for the Gaussian distribution is set to be zero, $\omega_{cg} = 0$.

The final result is that we input the following parameters into our field-dependent line width program: I, ω_L , QCC(MHz), η , Δ^{∞} (ppm), together with a somewhat arbitrary number of lines to compute the Gaussian (n = 23 in all cases shown below). Typical experimental MAS line shapes for ZSM-5 and an amorphous silica-alumina at 11.7 and 4.7 Tesla (¹H resonance frequencies of 500, 200 MHz; ²⁷Al resonance frequencies of 130.2, 52.1 MHz) are shown in Figure 3, and typical MAS line widths as a function of

^{*} There are several relationships, see, e.g., Refs. 6 and 11.



Figure 3 Field-dependence of ²⁷Al MAS n.m.r. spectral line widths of ZSM-5 and an amorphous silica-alumina. (A, B) NH_{4}^{+} -ZSM-5, ~ 6200 ppm Al, ~ 52% relative humidity, nonselective excitation at (A) 11.7 Tesla and (B) 4.7 Tesla. (C, D) Amorphous silica-alumina, 1% $AI_{2}O_{3}$, 52% relative humidity, nonselective excitation, at (C) 11.7 Tesla and (D) 4.7 Tesla.

10³/ v_L^2 (²⁷Al) at four magnetic field strengths, together with computed curves for given Δ^{∞} and QCC values, are shown in *Figure 4*. A compilation of QCC and Δ^{∞} for six ZSM-5 zeolites and six amorphous silica-aluminas are given in *Table 1*, and it is immediately apparent both that QCC and Δ^{∞} for the amorphous materials are about twice those seen with the zeolites (see below). We also find similar QCC and Δ^{∞} values when using static measurements (e.g., a silica-alumina gave QCC = 3.3 MHz, Δ^{∞} = 13 ppm), and for the single-site zeolite, Linde A, we find a much narrower Δ^{∞} value of \approx 1.8 ppm (data not shown), confirming the idea of a larger chemical shift range in ZSM-5 and the silica-aluminas, due to shielding nonequivalencies.

Nuclear quadrupole coupling constants

The results shown in Table 1 show that the mean nuclear QCC determined for the six ZSM-5 samples is $\sim 1.47 \pm 0.20$ MHz, whereas the mean nuclear QCC for the six amorphous silica–aluminas is 2.51 ± 0.4 MHz (±1 standard deviation of the data). For ZSM-5 samples containing higher than $\sim 1\%$ Al, the QCC values are smaller than those shown, as determined from field-dependent chemical shift and line shape simulations at multiple fields (data not shown). We thus believe that there is no discrepancy with the QCC ~ 0.8 MHz values obtained for a ~ 2.5 Al/unit cell sample of Meinhold and Bibby or the sample (whose composition was not reported) of Challoner and Harris.⁸ The results for both Δ^{∞} and QCC shown in Table 1 clearly indicate that a ready differentiation between the zeolitic and nonframework amorphous silica-aluminas can be made on the basis of either parameter, even when both samples exhibit only a single 27 Al resonance, at about the same chemical shift (at high field). We discuss below in more detail the Δ^{∞} origins.

The much larger QCC values for the amorphous silica-aluminas are also manifest in a number of other ways: For example, the zeolites and amorphous silica-aluminas show different one-pulse nutation behavior (data not shown). In addition, as shown in Figure 5, the spin-echo intensity observed in an in-phase two-pulse spin echo sequence, $\pi/2_{(x)} - \tau - \pi_{(x)}$ (a Knoebel Carr-Purcell Spokas-Slichter "Hahn" echo experiment), using B_1 fields of varying amplitude, show very clear evidence for much stronger quadrupole interactions in the silica-aluminas (Figure 5). For the silica-alumina, we observe a more-or-less selective or soft-pulse response, in which the satellite transitions are minimally perturbed by the r.f. excitation. However, with the ZSM-5 sample, it is clear that for the shorter 90° pulse lengths (increasing B_1 field strengths) that there is a nonselective excitation of the satellite $(\pm 3/2)$ levels, which as we have shown elsewhere causes destructive interference effects with the central (1/2, -1/2) central transition intensities (see, e.g., Refs. 2 and 3 for more discussion of this topic).

The spin-echo decay rate, T_{2H}

We have recently made a detailed study of the spin-echo decay rate, T_{2H} , of a number of inorganic solids, including zeolites and silica-aluminas, and have shown that complex spectra of bound zeolites



Figure 4 Field-dependent ²⁷Al *MAS* n.m.r. line widths of ZSM-5 and an amorphous silica-alumina. (A) The NH₄⁴-ZSM-5 shown in *Figure 3*. (B) The silica-alumina shown in *Figure 3*. Spectra were recorded at magnetic field strengths of 11.7, 8.45, 4.7, and 2.35 Tesla. The *QCC*, Δ^{∞} values used to generate the smooth curves were 1.35 MHz, 5.5 ppm for the ZSM-5, and 2.75 MHz, 12 ppm, for the silica-alumina. The electric field gradient tensor asymmetry parameter was taken to be 1.0.



Figure 5 Radio-frequency field-dependence of the integrated spin-echo intensity of ZSM-5 (6200 ppm AI) and an amorphous silica-alumina (0.5 wt% AI). As the B_1 field increases, the 90°_x pulse width decreases, and there is more nonselective excitation, resulting in smaller echo amplitudes. The effect is much smaller for the silica-alumina, since the satellite levels are farther away.

can be considerably simplified by editing away the background Al_2O_3 or SiO_2/Al_2O_3 ²⁷Al resonances, by use of spin-echo techniques.²⁻⁴ The basis for the success of this technique has been the observation of differential spin-echo decay rates between the (hydrated) zeolites and silica-aluminas, which provides yet another method for characterization of ²⁷Al resonances.

We show in Figure 6A and C typical experimental spin echo decays for a hydrated ZSM-5 and an amorphous silica-alumina, and in Figure 6B and D, we show these decays plotted on a logarithmic scale. As may be seen from Figure 6 and Table 1, the T_{2H} values for the zeolites and silica-aluminas are, in general, quite different, especially for hydrated samples, typical values being ≈ 4 ms for the zeolites and ≈ 1.5 ms for the silica-aluminas. For hydrated samples (at $\geq 52\%$ relative humidity, or preferably fully hydrated), T_{2H} gives another excellent means of differentiating between the two types of material.

An exact analysis of the spin-echo decay behavior of either system requires an exact description of the coordinates of each atom, which is not currently available. Moreover, the exponential nature of the echo decays suggests a motional contribution to T_{2H} , as does the considerable lengthening of T_{2H} in the zeolites upon hydration (data not shown), so there may be important qualitative differences in the nature of the echo decays between these systems and those observed for the generally more well-defined materials that we have discussed elsewhere.^{2,3} Fortunately, this is immaterial for our present purpose, which is to answer the question: How can one be sure that a given peak originates from ZSM-5 or an amorphous silica-alumina? The results of Table 1 show that the spin-echo decay rates of silica-aluminas are faster than those of ZSM-5, and we have found that the latter are lengthened considerably upon addition of H₂O. On average, the amorphous materials have T_{2H} values of ~ 1.3 ms, unchanged upon hydration, whereas the ZSM-5 systems have T_{2H} values that increase from ≈ 1 ms (when dry) to $\approx 5-7$

ms (with excess water). Further work on the temperature dependence of T_1 and T_{2H} of such samples would be of interest, to investigate in more detail the dynamical aspects, but it is not required for our present purpose.

Multiparameter comparisons

The results that we have presented above indicate that some n.m.r. parameters, such as the static and MAS line widths, are useful for differentiating between ZSM-5 zeolites and amorphous silica-aluminas, whereas others, such as the chemical shift, are much less useful. To facilitate comparisons between the two types of aluminosilicate, we have adopted a two- and three-dimensional graphical approach to displaying our results. Although there are many combinations, Figure 7A-C shows three informative "cluster plots," in which we present, respectively, the MAS line widths vs. QCC, the static line width vs. T_{2H} , and T_{2H} vs. the static line width vs. the nuclear QCC (Figure 7A-C, respectively), for five ZSM-5 zeolites and six amorphous silica-aluminas. Quite clearly, when two or more sensitive parameters are compared, the data for the ZSM-5 zeolites and noneframework silicaaluminas become extremely well separated, making identification of an "unknown" resonance in, e.g., a spectrally edited commercial zeolite catalyst, quite



Figure 6 Spin-echo decay spectra and exponential decay curves for the 11.7 Tesla ²⁷Al n.m.r. spectra of static samples of ZSM-5 and an amorphous silica–alumina. (A, B) Spin-echo decay spectra and decay curve for NH₄⁺⁻ZSM-5, 11,300 ppm Al, 52% relative humidity, nonselective excitation with 90°_x (solid) = 42.5 μ s, 1000 scans at a 50 ms recycle time, 500 Hz Gaussian line broadening, with τ -values in the 0.01–3.0 ms range $T_{2H} = (?)$ 3.7 ms. (C, D) Spin-echo decay spectra and decay curve for an amorphous silica–alumina, 2 wt% Al, 52% relative humidity, all other conditions basically as in (A, B) above, $T_{2H} = 1.0$ ms.



Figure 7 Two- and three-dimensional comparisons of various ²⁷Al n.m.r. parameters determined on ZSM-5 zeolites and amorphous silica–aluminas. (A) *MAS* line width vs. quadrupole coupling constant. (B) Static line widths vs. T_{2H} (static sample). (C) T_{2H} (static sample) vs. static line width vs. *QCC*.

unambiguous. Note here that, e.g., the mere presence of a single ²⁷Al n.m.r. peak at 55 ppm — which might typically be thought of as being due to a ZSM-5 zeolite, would actually not in and of itself be a reliable indicator of the presence of framework aluminum, since amorphous silica-aluminas may occasionally give single peaks at ~ 55 ppm (Figure 2). However, when static line widths (W), MAS line widths at infinite field (Δ^{∞}), QCC, and spin-echo decay timeconstant — as well as the number of spectral peaks are determined, assignments - including quantitative analysis of framework aluminum in formulated catalysts --- become possible.^{3,4} Moreover, such comparisons do not necessitate use of very high field measurements. For example, a 360 MHz comparison of T_{2H} and W gives an equally good, or possibly even better, differentiation between the two classes of compound, because of the rapidly increasing secondorder quadrupolar contribution to the line width (data not shown), and such intermediate-field instruments are widely available.

Interpretation of the line width

Given that we can now quantitatively analyze framework aluminum in actual catalysts,^{3,4} we wish to

finally discuss the origins of the observed line widths, which can vary considerably for different states of hydration, as well as varying with the magnetic field strength, and the nature of the experiment (static vs. *MAS* n.m.r.).

For ZSM-5 zeolites, the results of Table 1 show, on average, a Δ^{∞} value of ~ 5.7 ppm vs. ~ 13.2 for the amorphous silica-aluminas, and QCC values of 1.5 and 2.5 MHz, respectively. The Δ^{∞} value is in good accord with that of Challoner and Harris,⁸ who found $\Delta^{\infty} \sim 5$ ppm. The variances in QCC seen between this work and the work of others is attributable, we believe, solely to the use of high Al levels in the previous work. Our own results (data not shown) also clearly indicate that QCC ~ 0.8 MHz components are major contributors at high Al levels. Parenthetically, we note that we obtain essentially the same QCC results when using the slope of the line connecting the two lowest field results (for our 2% Al silicaalumina) as using the Meinhold and Bibby⁷ or Freude et al.¹² method, where

$$W \text{ ppm} = \frac{7064}{v_L^2} \chi^2 \left(1 + \frac{\eta^2}{3} \right)$$
(12)

since at low magnetic field strengths, the observed line width is overwhelmingly dominated by the second-order quadrupolar interaction. However, at low magnetic field strengths, line shape and sensitivity considerations become more important, so we believe that the most accurate method to extract Δ^{∞} and QCC parameters is to use the multi-field curvefitting method described above.

The major contributions to the experimentally observed line widths (at 11.7 T) are thus from the second-order quadrupole interaction, Δ^Q (~ 1 ppm for ZSM-5 MAS, ~ 3.6 ppm static; ~ 3 ppm for silicaalumina MAS, ~ 10.8 ppm static), from magnetic field inhomogeneity and line broadening (~ 0.8 ppm static, ~ 0.2 ppm MAS), T_1 (~ 0.5 ppm), T_{2H} (\approx 0.5– 1 ppm for ZSM-5, ~ 1.3–2.5 ppm for silica-alumina, where the ranges are for MAS and static experiments, respectively). Thus:

$$W_{obs}^{500} = \Delta^{CS} + \Delta^{H_o} + \Delta^{T_1} + \Delta^{T_2} + \Delta^Q$$
(13)

where W_{obs}^{500} is observed width at 11.7 Tesla and Δ_k is the broadening for the k'th interaction. From the observed line widths, we can make estimates for Δ^{CS} , the contribution to the observed widths due to the chemical shift distribution, of $\Delta^{CS} \approx 3.6-4.8$ ppm for ZSM-5 and $\Delta^{CS} \approx 10-13.2$ ppm for the silicaaluminas. These values are close to the Δ^{∞} values of 5.7 and 13.2 ppm given in *Table 1*, which contain all field independent broadening contributions. For ZSM-5, a $\Delta^{CS} \sim 4.2$ ppm value is in quite good

For ZSM-5, a $\Delta^{CS} \sim 4.2$ ppm value is in quite good accord with a ~ 2.8–4.2 ppm width that can be computed by using the known relation between $\delta_{CS}^{(A1)}$ and θ' , the T–O–T bond angle.^{6,10} The $\Delta^{CS} = 2.8$ ppm is the value expected for monoclinic samples, whereas the 4.2 ppm pertains to orthorhombic crystals (both assuming a Gaussian δ_{CS}^{Al} distribution). Clearly, there are uncertainties associated with determining W^{obs} , Δ^{Ho} , Δ^{T_1} , Δ^{T_2} , and Δ^Q , so the final result for Δ^{Cs} is subject to some uncertainty. Nevertheless, the computed Δ^{CS} values for ZSM-5 are in quite good agreement with the results that can be deduced from X-ray diffraction, and they are also clearly very different for ZSM-5 and the amorphous silica-aluminas. The actual Δ^{CS} values determined strongly suggest an approximately two-fold increase in the chemical shift range for the amorphous materials, presumably due to the larger range of T-O-T bond angles permitted in the absence of crystallographic restraints.

CONCLUSIONS

The results that we have presented above are of importance since they enable the unambiguous assignment of a given ²⁷Al resonance to a framework, zeolitic (ZSM-5) site, as opposed to a nonframework, amorphous silica-alumina. Such assignments are much less reliable if based on chemical shifts alone, since both ZSM-5 zeolites and some amorphous silica-aluminas may contain a resonance at ~ 55 ppm, due to Al[OSi]₄ subunits. Although "pure" zeolites and silica-aluminas can naturally be characterized on the basis of their X-ray diffraction patterns, the situation with commercial catalysts is more complex. As we show elsewhere, it is possible to "edit" away alumina, silica-alumina, and clay binder signals from zeolite catalysts on the basis of short binder T_{2H} values,^{3,4} and the residual zeolitic aluminum resonances can then be both qualitatively and quantatively determined, based, e.g., on their static and MAS line widths, T_{2H} and B_1 field-dependent intensities, combined with their absolute intensities in spin-echo n.m.r. experiments.²⁻⁴ Such experiments are not restricted to ZSM-5 catalysts, but are applicable to, e.g., H-Y zeolite cracking catalysts supported on clays and aluminas, as outlined elsewhere,⁴ where, once again, measurements of a number of spectral parameters (chemical shift, static, and MAS line widths, T_{2H} values, hydration effects) permit reliable determinations of zeolitic aluminum levels in complex catalyst materials.

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