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Solid-State Magic-Angle Spinning ^{27}Al NMR Used to Study Alumina Support and Surface Compound Structure of Catalysts[1]

High-resolution NMR spectroscopy of solids is now a well-recognized structural tool (*2, 3*) and there have been several recent applications to catalysts per se. Slichter and his co-workers have applied ^{195}Pt NMR to Pt/Al_2O_3 catalysts (*4–6*) and several groups have investigated ^{29}Si in zeolites (*7–14*). The NMR of ^{27}Al in zeolites has also been examined (*13, 15, 16*). For zeolites, it was noted that ^{27}Al NMR is much more structure sensitive than ^{29}Si NMR which is first nearest-neighbor dependent (*15*). Specifically, Al can exist in both octahedral and tetrahedral coordination and, when the ligands are oxygen, the chemical shift of ^{27}Al differs by 55–80 ppm for these different coordinations (*17, 18*). Thus, ^{27}Al NMR can, in principle, be very useful for following the tetrahedral/octahedral ratio in alumina supports as a function of thermal treatment as has been demonstrated by John *et al.* (*19*).

Even with magic-angle spinning of highly crystalline α-alumina (corundum), the NMR linewidth of ^{27}Al is quite broad. This would lead one to surmise that it would not be feasible to observe the formation of surface compounds of the alumina support or active catalytic phases since the NMR signal of the surface phase would be masked by the bulk if the two phases were of comparable linewidth and chemical shift. What we wish to demonstrate in this communication is that the surface and bulk phases of alumina need not have the same linewidth and, depending on the surface compounds formed, may have substantial chemical shifts relative to bulk Al^{3+}. In the case of a NiMoP/Al_2O_3 hydrodesulfurization catalyst, at least, Al^{3+}-containing surface phases are formed during calcination which can easily be distinguished from the bulk γ-Al_2O_3 support.

Our spectra were obtained on a Bruker WM 500 (500 MHz for protons) spectrometer using a probe supplied by Doty Scientific, Inc., which could be tuned to the ^{27}Al frequency at 130.3 MHz. The response of the samples under a single-pulse excitation combined with magic-angle spinning at 3–3.5 kHz, was used to obtain time domain data which was Fourier transformed for frequency domain information. The rotors were cylindrical and constructed from Vespel (a du Pont polyimide) and the stator was constructed from a high-temperature recrystallized α-Al_2O_3 (99.8% pure). Pulses of approximately 0.3 μs ($\pi/2 \sim 4$ μs) were applied to excite the transition, and 1000 free induction decays were accumulated with a repetition time of 1.0 s. The rf coil of the probe is wound on the alumina stator which gives rise to a broad background signal. This background has been substracted from each spectrum. We were, however, unable to match the phasing of the sample spectra and the background spectrum exactly and this has resulted in a phase distortion of the peaks which falls at about 90 ppm, i.e., in the region of tetrahedral Al^{3+} of the samples.

Figure 1 shows the spectra of θ-, γ-, δ-, and α-aluminas (all except γ were X-ray diffraction standards) (*20*). These have been referenced to $Al_2(MoO_4)_3$ (see Fig. 2d), which is shifted upfield from $Al(H_2O)_6^{3+}$ by 17 ppm (*17*). The α-Al_2O_3 exhibits a single

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[1] A preliminary version of this work has been published (Ref. (*1*)). All of the spectra presented previously were obtained at 52.1 MHz. The spectra presented here are improved by the higher frequency used, but the conclusions are substantially the same.

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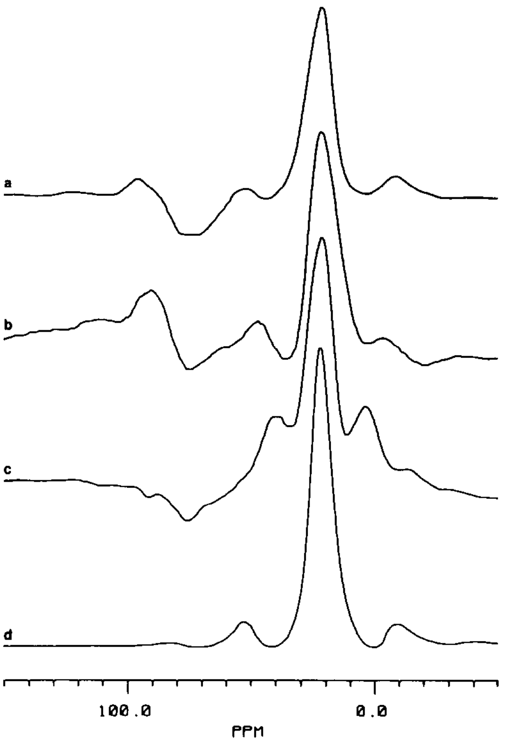

FIG. 1. Magic-angle spinning ^{27}Al NMR spectra of aluminas at 130.3 MHz: (a) θ, (b) γ, (c) δ, and (d) α. The chemical shift is set to zero for the reference compound $Al_2(MoO_4)_3$; see Fig. 2d.

relatively sharp peak plus spinning side bands with no evidence of distortion by the background subtraction because the sample and background have Al^{3+} in the same kind of environment. The γ-Al_2O_3 in Fig. 1b exhibits tetrahedral and octahedral Al^{3+} at about 85 and 22 ppm, respectively, plus spinning side bands most predominant on either side of the octahedral peak. This result is the same as has been previously reported (*13, 19, 21*). However, the tetrahedral-to-octahedral ratio which is expected to be about 1 : 3 (*22*) cannot be deduced because of the phase distortion introduced by the background from the probe, but γ- and δ-Al_2O_3 (Figs. 2b and c, respectively) appear to be qualitatively distinguishable and probably quantitatively distinguishable when the stator background does not exist. However, it should be noted that a part of the intensity is probably in transitions other than the $-\frac{1}{2}$ to $\frac{1}{2}$, and the amount will depend slightly on pulse width and the distortion from ideal tetrahedral and octahedral symmetry (*23*). Thus, it might not be possible to simply obtain quantitative tetrahedral-to-octahedral ratios without careful consideration of the effects of pulse width on the peak integrals. The agreement between NMR measurements and X-ray structure predictions of the tetrahedral/octahedral ratios of γ- and η-Al_2O_3 (*19*) suggests that this need not always be a serious problem. The ratios reported by John *et al.* (*19*) were probably the result of similar distortions from cubic symmetry for all sites because when the distortion is very different, as in [($Al_{13}O_4$

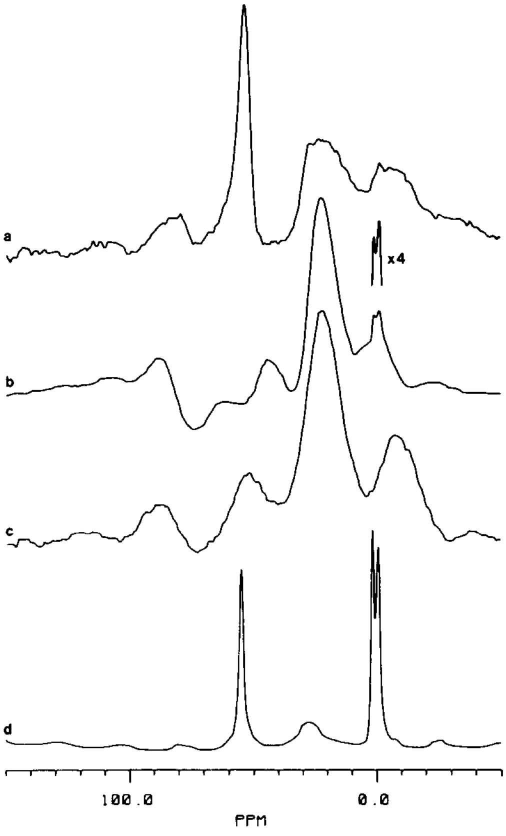

FIG. 2. Magic-angle spinning ^{27}Al NMR spectra at 130.3 MHz of (a) NiMoP/Al_2O_3, (b) Mo/Al_2O_3, (c) Ni/Al_2O_3, and (d) a physical mixture of references compounds $Al_2(MoO_4)_3$ and $AlPO_4$. The three catalysts were calcined in air at 980 K.

$(OH)_{25}(H_2O)_{11}]Cl_6$, only the central Al–O tetrahedron was detected while the *12* distorted octahedra were not (*17*). In another example of effects of severe distortion on ^{27}Al signals, the tetramer of aluminum isopropoxide which has a central nondistorted octahedral AlO_6 unit and three distorted tetrahedral AlO_4 units, the correct integrated intensity ratio was observed but the linewidth of the tetrahedral Al peak was 10 times that of the octahedral Al peak (*24*).

Figure 2 shows the ^{27}Al NMR spectra of three catalysts prepared by impregnation and calcined at 980 K in air. The $NiMoP/Al_2O_3$ (Fig. 2a), was 3.1% NiO, 19.8% MoO_3, and 2.5% P on γ-Al_2O_3. The Mo/Al_2O_3 and Ni/Al_2O_3 catalysts (Figs. 2b and c), were 18% MoO_3 and 3.1% NiO, respectively, on γ-Al_2O_3. We realize that the calcination temperature used exceeds that which is optimum for the precursors to good hydrodesulfurization catalysts. However, it is at this temperature that the sharpest NMR signals were obtained, and these may be related to surface structures which lead to catalyst deactivation. We have used the compound $Al_2(MoO_4)_3$ obtained from Alfa Ventron (Fig. 2d) as a reference because it produces a sharp (although split) NMR resonance, and it may be expected to form when MoO_3 and Al_2O_3 are heated together. The downfield resonance in Fig. 2d is of $AlPO_4$, also obtained from Alpha Ventron. The reference spectrum in Fig. 2d is that of a physical mixture of the two compounds of Al, both of which are formed as surface compounds on the catalysts. We observe a single sharp peak shifted 33.2 ppm with respect to corundum for ^{27}Al in our sample of $AlPO_4$. This is in agreement with results of Blackwell and Patton (*25*) who report a single ^{27}Al peak shifted 33.4 ppm with respect to corundum for $AlPO_4$–tridymite. However, Blackwell and Patton demonstrate that ^{27}Al second-order quadrupole coupling effects can be very pronounced in $AlPO_4$ materials. For example, $AlPO_4$–quartz which, like $AlPO_4$–tridymite, also has one kind of AlO_4 tetrahedra gives rise to what is essentially a powder pattern at low field (4.7 T) and a doublet at 33.2 and 26.3 ppm at high field (9.4 T).

A complete X-ray structure of $Al_2(MoO_4)_3$ does not appear to have been published, but Goldish (*26*) states that it is isostructural with a large class of molybdates and tungstates of the scandium tungstate type and, in particular, with $Al_2(WO_4)_3$ which has been analyzed (*27*). This structure consists of WO_4 tetrahedra and AlO_6 octahedra which extend into an infinite three-dimensional network by corner sharing. By comparing the NMR chemical shift of $Al_2(MoO_4)_3$ (Fig. 2d) with that of α-Al_2O_3 (Fig. 1d), and a large number of aluminates with both tetrahedral and octahedral Al^{3+} coordination, we can unequivocally conclude that Al^{3+} in $Al_2(MoO_4)_3$ is in an octahedral geometry but with two nonequivalent octahedral environments. The possibility that the $Al_2(MoO_4)_3$ doublet is the result of second-order quadrupole coupling effects can be ruled out by the fact that it collapses at lower field (see Ref. (*1*), Fig. 2d).

The formation of $Al_2(MoO_4)_3$ is clearly evident in Mo/Al_2O_3 calcined at 980 K (Fig. 2b), but is not observed in the $NiMoP/Al_2O_3$ catalyst which has been calcined to the same temperature (Fig. 2a). However, we conclude that a surface compound of Al^{3+} had formed in the $NiMoP/Al_2O_3$ catalyst when calcined at 980 K and that the Al^{3+} in this compound is in a tetrahedral environment and gives rise to a narrow peak compared to the γ-Al_2O_3 of the support. We assign this peak to $AlPO_4$ because it is not formed in either Mo/Al_2O_3 or Ni/Al_2O_3; the ^{31}P signal develops in parallel with ^{27}Al, and the chemical shifts of both ^{27}Al and ^{31}P are identical to our $AlPO_4$ reference (see Fig. 2d). The Mo/Al_2O_3 forms the surface structure of $Al_2(MoO_4)_3$ and the NMR of Ni/Al_2O_3 calcined at 980 K is almost that of γ-Al_2O_3.

The ^{27}Al signal of γ-Al_2O_3 underlies that of the surface compounds in Figs. 2a, b, and c. This is most evident in Figs. 2b and c and, by comparison, there appears to be some attenuation of the γ-Al_2O_3 signal in the NiMoP/Al_2O_3. This is very probably real since much of the Al^{3+} may now be in new surface compounds, e.g., $AlPO_4$. Note also the intensity in Fig. 2a around −5 ppm. This cannot be entirely due to spinning side bands and may be due to an amorphous form of $Al_2(MoO_4)_3$ or another unidentified surface compound. Since $Al_2(MoO_4)_3$ forms on Mo/Al_2O_3 but not on NiMoP/Al_2O_3 at 980 K we conclude that the formation of $Al_2(MoO_4)_3$ is probably inhibited by P, even though influence of Ni remains unclear. If the NiMoP/Al_2O_3 catalyst is calcined at temperatures above 1000 K, the surface compound of $AlPO_4$ begins to decompose, and at sufficiently high temperatures, all of the Mo^{6+} is converted to $Al_2(MoO_4)_3$.

In summary, we emphasize that the observation of the NMR of ^{27}Al (and probably ^{29}Si) sufficiently near the surface to be of catalytic interest need not be restricted to the crystalline aluminosilicates (*7–16*). There may be a large class of catalysts where the active phase supported on an oxide may enter into chemical reaction and many of these surface phases may be distinguished from the bulk oxide phase by NMR.

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