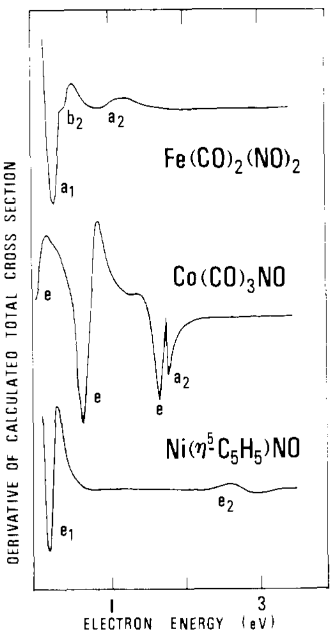

Figure 4. Derivative of the calculated total electron-scattering cross section in iron dicarbonyl dinitrosyl, cobalt tricarbonyl nitrosyl, and nickel cyclopentadienyl nitrosyl, as a function of electron energy.

only serious discrepancy relates to the two resonances in nickel cyclopentadienyl nitrosyl. However, the small intensity of the first resonance in the ET spectrum could, at least in part, be due to its overlap with the intense electron beam signal. On the other hand, the exceptional correspondence of these theoretical results with experiment is counterbalanced by the nearly total absence of signal in the b_1 channel for the iron complex and in the a_1 channel for the cobalt complex, so that the calculations do not reproduce the second and third resonances, respectively, in these two complexes. These two resonances were not found by the calculations even using the corresponding transition-state potentials. The results could probably improve by using higher angular momentum basis functions in the atomic and outer-sphere regions.

Conclusions

The present MS-Xα calculations, including the correction of the overlap between atomic spheres, closely reproduce the AE values measured in the ET spectra of the nitrosyl transition-metal complexes under investigation. Iron dicarbonyl dinitrosyl and cobalt tricarbonyl nitrosyl are predicted to have a positive EA of 1.2 and 0.5 eV, respectively. According to the calculated localization properties, in all three complexes the ground anion state possesses mainly nitrosyl character, but with a large contribution from the metal atom.

The calculated electron–molecule total scattering cross sections display features with energies and relative intensities in good agreement with experiment and reproduce the assignment given by the transition-state calculations. This approach, however, did not detect one resonance in the iron and cobalt complexes.

The experimentally observed stabilization of the anion states with mainly ligand character, with respect to the free ligands, is consistent with the sizeable net transfer of negative charge (about 0.7*e*) from the ligands to the metal predicted by the charge densities calculated for the neutral ground states of the complexes. These results are in line with those previously obtained in ETS and MS-Xα studies of transition-metal complexes and in contrast with the charge densities calculated with LCAO methods.

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^{27}Al Cross Polarization of Aluminas. The NMR Spectroscopy of Surface Aluminum Atoms

H. Douglas Morris and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.

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Abstract: The selective cross polarization of surface aluminum atoms is demonstrated and applied to γ- and α-aluminas. The relatively high hydration levels of the γ-alumina surface (out of the bottle) allow the observance of two surface species. Upon dehydration only one, somewhat broader resonance, with lower signal-to-noise ratio, can be resolved. Upon extensive dehydration this signal disappears. By comparison to Boehmite and α-alumina, these resonances are assigned to surface octahedral sites (3.0 ppm) and tetrahedral sites ($\sim$62.0 ppm). All chemical shifts are reported relative to $Al(NO_3)_3 \cdot xH_2O$. It is demonstrated that these resonances represent surface Brønsted sites, and that they are not contaminated by Lewis acid sites or subsurface species. The Lewis acid sites can be selectively observed by replacing the surface hydroxyl protons with deuterons and adsoring a Lewis base probe, pyridine, on the surface. In this case the ^{1}H's on the pyridine provide the polarization for the ^{27}Al resonance. The α-alumina used in this study appears to have a low number of surface hydroxyls concomitant with its low surface area (5.5 m^2/g). This is reflected in the low (relative to γ-alumina) ^{27}Al signal-to-noise ratio obtained with this sample. Overall, this approach appears to be an excellent way to nondestructively characterize these surfaces. More importantly, the success of surface selective cross polarization methodology illustrates that other nuclides are equally amenable to such experiments, and that this approach could be very useful as a general surface chemistry method for characterization of surfaces.

NMR spectroscopy has proven to be a powerful tool for the elucidation of molecular structures in a wide variety of conditions and phases. An area which has not received the attention it should is the application of solid-state NMR methods to the selective observation of the surface of systems of catalytic interest. The essential goals of such research would be the characterization of surfaces, structural identification, quantifying molecular motion, and following surface chemistry, while not being hampered by resonances associated with the bulk material. In a series of seminal papers,[1-7] Sindorf and Maciel have directly addressed some of these

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points. They observed the ^{29}Si resonances of silica surfaces by cross polarization[8] (CP) and magic-angle spinning[9] (MAS) methods. They recognized that surface groups were the only residues which contained protons, and hence they observed only surface silicon atoms which were dipole-coupled to the ^{1}H bath. Armed with this methodology, Maciel and Sindorf were able to characterize the surface and follow several important surface chemical reactions which relate to the derivatization of silica surfaces. Further, by quantitative analysis of their data, they were able to demonstrate that no single previously proposed model of the silica surface could adequately describe the surface structure and behavior that they observed. In another paper, Shatlock and Maciel[10] investigated the surface structure of CdO with solid-state ^{113}Cd NMR by again utilizing the selective nature of the CP experiment to observe only those atoms which are proximal to the ^{1}H spin reservoir. They accomplished this by adsorbing water to the CdO surface.

In a recent paper Majors and Ellis[11] employed ^{15}N-labeled pyridine as a probe molecule to examine the surface distribution of tetrahedral and octahedral anion vacancies (Lewis acid sites) on γ-alumina. From such indirect measurements they concluded that, rather than considering the surface of γ-alumina to be composed of just (110) and (100) low-index crystallographic planes,[12] the surface could be described in terms of the (110) and (111) planes as well. In view of these results, one can ask the question; can more fundamental information concerning the nature of the surface and its adsorbates be garnered from experiments utilizing direct observation of the surface aluminum atom? In analogy with Maciel and co-workers, this experiment will take advantage of the surface hydroxyl residues being the sole source of ^{1}H's in the sample. However, this experiment differs significantly in one respect: we are proposing to cross polarize to the $\pm^{1}/_{2}$ transition of a quadrupolar nuclide with a nuclear spin of $^{5}/_{2}$.

The feasibility of this experiment has been demonstrated indirectly by Oldfield and co-workers.[13] In that work they observed the quadrupolar nucleus ^{17}O by CP methods, and demonstrated that the potential problems concerning the associated spin dynamics of the ^{17}O, i.e., T_{1S} and $T_{1\rho}$ of the oxygen and protons, were not critical enough to prevent the experiment from working. Also, they stressed the selective nature of the CP experiment, namely, that one could easily differentiate protonated from nonprotonated oxygens by this experiment. Similar results and conclusions have recently been reported by Woessner[14] concerning CP/MAS experiments with ^{11}B. We report here the coupling of these two ideas: the cross polarization of a quadrupolar nucleus, namely, aluminum, and the characterization of the catalytic surface sites of γ- and α-aluminas.

Experimental Section

Samples. The γ-alumina samples were prepared from carefully ground high-purity pellets (Norton catalyst support No. SA 6573, Lot No. 08145; surface area = 220 m^2/g). Samples (1.0 g) were added to glass break-seal tubes (Pyrex or quartz), dried under vacuum, and flame sealed under vacuum. Three individual methods of vacuum drying the γ-alumina samples were employed. A partially dehydroxylated alumina (PDA) was prepared by evacuating the sample for 8 h at 350 °C to a final pressure of 10 μTorr. An intermediate dehydroxylated alumina (IDA) was evacuated at 510–550 °C, calcined under O_2 for 30 min (3–10-min intervals with intermediate evacuation), and evacuated for 3 h at 610 °C to a final pressure of 5 μTorr. Finally, an extremely dehydroxylated alumina (EDA) sample was obtained by calcining the starting material under O_2 for 1 h at 815 °C and evacuating for 5 h at the same temperature to a final pressure of 5 μTorr. Deuterium-exchanged surfaces were prepared by repeatedly boiling in 99.8% D_2O (Aldrich Chemical) and then freeze-drying the surfaces to a 50-mTorr vacuum. The surface area for all γ-alumina samples remained at approximately 220 ± 3 m^2/g after heat treatment and (in the case of the deuterated sample) the addition of D_2O.

Certain noted γ-alumina samples were loaded with a Lewis base adsorbate, pyridine. The sample preparation was accomplished with a two-chamber break-seal apparatus. In one chamber the alumina was prepared in one of the several ways described above. The other break-seal chamber was loaded with purified pyridine (dried over calcium hydride and then vacuum distilled). An amount of 370 μmol (corresponding to approximately 25% of a monolayer per gram of γ-alumina surface, where one monolayer is defined as four molecules per 100 Å^2 of surface) is added via a microliter syringe under an inert atmosphere and flame sealed under vacuum. The adsorbent and adsorbate were combined and equilibrated by shattering the break-seal and heating the sample at 120 °C for 1 h before cooling to room temperature.

Samples of α-alumina (Norton catalyst support SA 5551; surface area = 1 m^2/g) were prepared in a manner similar to that of the γ-alumina. Samples of Boehmite (Norton, Lot No. 08061) were used as received. A sample of α-alumina (surface area = 5.5 m^2/g) was prepared from Boehmite (Norton, Lot No. 08061) by heating the precursor at 1100 °C in the presence of air for 20 h.

All surface area measurements were made with a Monosorb Surface Area Analyzer from Quantachrome Corp. (5 Aerial Way, Syosset, NY 11791) using the method of nitrogen gas desorption. The desorption rate measured by the analyzer is interpreted by the Brunauer–Emmett–Teller (BET) description of multilayer gas adsorption.[15,16] All measurements are the average of three separate adsorption–desorption cycles to minimize operator error. The single-point method (i.e., assume BET intercept is zero) is used and results in an value with less than 4% error.

All atmosphere-sensitive NMR samples were prepared just prior to the CP/MAS experiments by opening the break-seal tubes in a Vacuum Atmospheres drybox (N_2 atmosphere) and packing the treated surface into zirconia or silicon nitride ceramic high-speed MAS NMR rotors. These samples are stable to O_2 and H_2O for several days when spinning with dry N_2 gas.

Spectra. ^{27}Al NMR spectra of the aluminas were obtained with a Bruker WH-400 spectrometer (equipped with a home-built transceiver modification as described in Claiborne et al.[17]) at a resonance frequency of 104.25 MHz utilizing a 5-mm high-speed magic-angle spinning probe from Doty Scientific, Inc. (600 Clemson Rd., Columbia SC 29223). The techniques of cross polarization,[8] with magic-angle spinning,[9] and high-power decoupling were employed. The recycle delay and cross polarization contact times were optimized for accurate representation of present resonances.

The recycle delay was 1.0 s, which is greater than five times the T_1 for the ^{1}H's for γ-alumina (T_1 = 180 ms), while the contact time was 0.5 ms. Also, dipolar dephasing experiments were performed to check for the presence of ^{27}Al–^{1}H dipolar coupling[18] in aluminum species with no directly bonded OH groups.

The pulse sequence phase-cycle employed spin-temperature alternation on the cross-polarizing ^{1}H reservoir and CYCLOPS phasing on all pulses.[19,20] A rigorous phase cycle of this nature is necessary in cross-polarizing from a rare spin to an abundant spin to avoid significant amounts of spin-locked-non-CP magnetization in the observed signal. Such signals can arise from a nonrigorous phase cycle simply because the cross polarization sequence is no longer being used as a signal enhancement technique, but as a signal filter.

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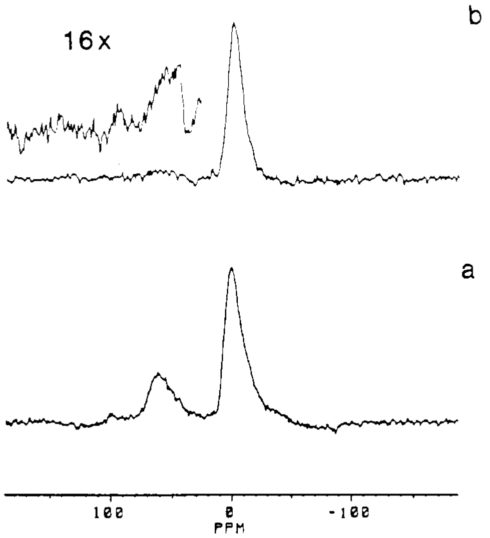

Figure 1. (a) ^{27}Al MAS Bloch decay NMR spectrum of γ-alumina as received from supplier. All chemical shifts are with respect to Al(N$O_3)_3\cdot xH_2O$. The resonance at ~0 ppm is the octahedral site and the resonance at ~68 ppm is the tetrahedral sites of bulk γ-alumina. The number of transients is 256 and the amount of Lorentzian line-broadening is 50 Hz. The line width at half-maximum peak intensity (lwhm) is 22.0 ppm for the T_d site and 17.0 ppm for the O_h site. (b) ^{27}Al CP/MAS spectrum of the same γ-alumina sample as in (a). The large peak at 6.0 ppm is the surface O_h site. The insert is the T_d site at ~55 ppm and is enlarged by a factor of 16. The number of transients to obtain the spectrum is 7477. The FID is multiplied by a 100-Hz Lorentzian line-broadening function. The lwhm is 21.5 ppm for the T_d site and 12.7 ppm for the O_h site.

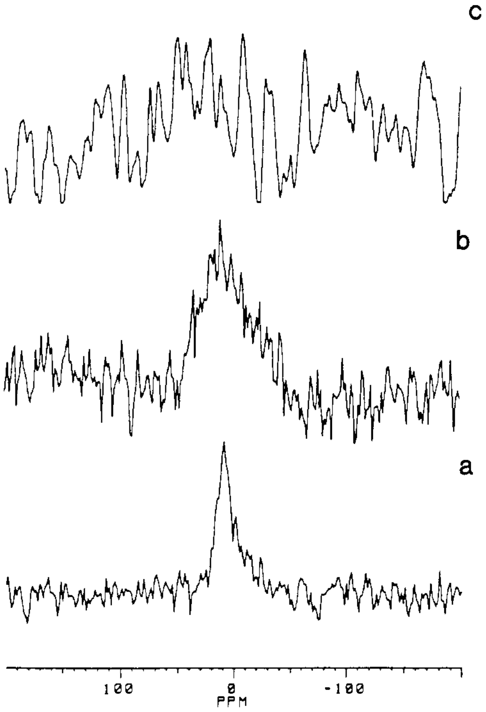

Figure 2. ^{27}Al CP/MAS spectra of (a) PDA γ-alumina, (b) IDA γ-alumina, and (c) EDA γ-alumina. The heat treatment procedures for each sample are described in the Experimental Section. The number of transients accumulated in each spectrum was 31 168, 40 192, and 80 000, respectively. The FIDs are multiplied by a Lorentzian line-broadening function with the values of 100, 500, and 500 Hz, respectively. The lwhm's for (a) and (b), in that order, are 13.5 and 33.2 ppm.

Discussion

By examining the ±$^1/_2$ transition we are performing a selective pulse experiment, and, as a result, the effective gyromagnetic ratio of the observed nucleus increases by a factor of $(S + {}^1/_2)$.[21] Here, S is the nuclear spin quantum number of the nucleus of interest. As a result of this, the Hartmann–Hahn[22] condition becomes

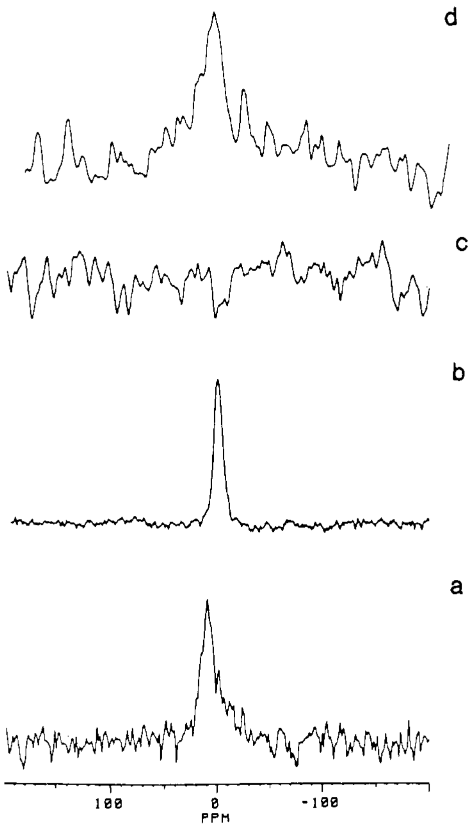

Figure 3. ^{27}Al CP/MAS spectra of (a) PDA γ-alumina, (b) Boehmite, (c) α-alumina (surface area = 1 m^2/g), and (d) α-alumina (surface area = 5.5 m^2/g). The preparative procedures for each are described in the Experimental Section. The number of transients were 31 168, 256, 80 000, and 266 560, respectively. The FIDs of the above spectra were multiplied by a Lorentzian line-broadening function of 100, 50, 500, and 1000 Hz, respectively. The lwhm for PDA γ-alumina, Boehmite, and α-alumina (SA = 5.5 m^2/g) are 13.5, 10.0, and 19.0 ppm.

$$(S + \tfrac{1}{2})\gamma_{\mathrm{Al}}B_{\mathrm{Al}} = \gamma_{\mathrm{H}}B_{\mathrm{H}}$$

Utilizing this equation we have performed ^{27}Al CP/MAS experiments on γ-alumina and several pretreated γ-aluminas, the results of which are depicted in Figures 1–4. In Figure 1a we have the normal MAS Bloch decay spectrum of γ-alumina as it comes out of the bottle. Here, the chemical shifts are reported with respect to solid $Al(NO_3)_3\cdot xH_2O$. The smaller resonance at ~65 ppm corresponds to the bulk tetrahedral (T_d) sites, while the larger resonance at 3 ppm corresponds to the bulk octahedral (O_h) sites. The ^{27}Al CP/MAS experiment performed on the same sample is illustrated in Figure 1b. The two resonances in Figure 1b arise for aluminum atoms which are associated with hydroxyl groups on the surface, i.e., the Brønsted sites. From IR measurements there are typically five different hydroxyl environments on the surface.[12] Three are associated with the surface octahedral sites, and two with the surface tetrahedral sites. Heating the surface should change the relative amounts of those sites. This is illustrated in Figures 2a–c. If the heating process simply removed water from the surface without changing the surface structure, one would expect the spectra in Figure 1b and Figure 3a–c, to show only a reduction in intensity. That appears to be the case in going from γ-alumina out of the bottle to the PDA heat treatment in Figure 2a. However, extending the heat treatment beyond the conditions associated with Figure 2a appears to alter the surface structure as well. This is reflected in the

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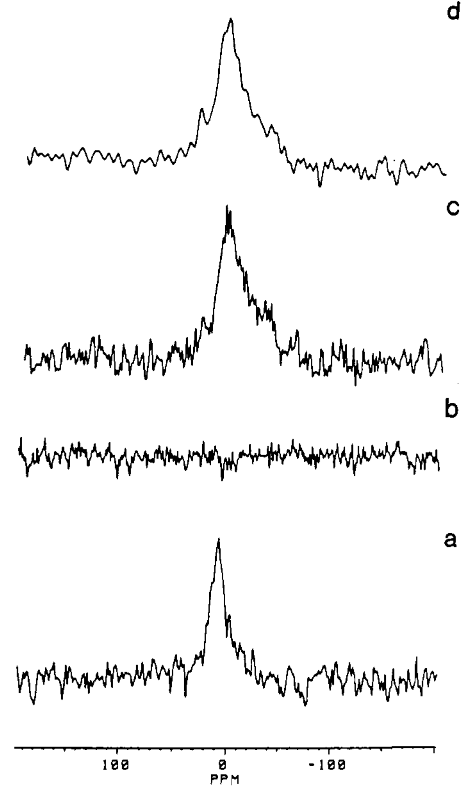

Figure 4. ^{27}Al CP/MAS spectra of (a) protonated PDA γ-alumina, (b) deuterated PDA γ-alumina, (c) 25% of a monolayer coverage of pyridine (natural abundance) on PDA γ-alumina, and (d) 25% of a monolayer coverage of [^{15}N]pyridine on PDA γ-alumina. Note the factor of 3 increase in signal-to-noise between (c) and (d). The number of transients was 31 168, 32 000, and 127 104, respectively. The line-broadening by which the FIDs were multiplied is 100, 100, 500, and 500 Hz, respectively. The lwhm's for (c) and (d) are 23.8 and 25.6 ppm.

broadening of the resonance in Figure 2b. The line broadening may represent a localized distortion associated with surface O_h sites due to removal of adjacent hydroxyl groups and an increase in the local quadrupole moment as site symmetry is reduced. Upon extensive heat treatment and calcination associated with Figure 2c, no CP/MAS signal is observable. The loss of signal is presumed to be caused by the rarity of hydroxyl groups.

In Figure 3 we have summarized ^{27}Al CP/MAS experiments on the PDA γ-alumina (Figure 3a), Boehmite (Figure 3b), α-alumina (1 m^2/g SA, Figure 3c), and α-alumina (5.5 m^2/g SA, Figure 3d). Boehmite and α-alumina are composed exclusively of octahedral aluminum sites within the bulk and surface.[23] Hence, from these experiments we assign the resonances at or near 0 ppm to be those surface aluminum atoms associated with octahedral Brønsted sites, and the small resonance at 62 ppm with the tetrahedral Brønsted sites. Thus, we are left asking why the T_d Brønsted sites are so diminished in intensity. Extensive searching of cross polarization conditions has not yielded any greater enhancement in the intensity of the T_d Brønsted sites. The current explanations for this reduction in intensity of T_d site relative to those for O_h sites is unfavorable CP parameters associated with the T_d sites. This could possibly stem from the geometry of the Al-O-H groups and that of the T_d site itself. This proposal is derived from results of trying to observe spectra on lithium aluminum hydride and sodium magnesium aluminosilicate via a CP/MAS experiment. Both compounds possess only T_d aluminum coordination, and yet neither compound could be cross polarized. This is especially odd since both compounds contain either directly or closely coordinated ^{1}H's. Thus it appears that some factor associated with the ^{27}Al quadrupole in a T_d geometry affects the $T_{1\rho}$ for this site, making it too short for effective cross polarization.

It is of interest to inquire if one can also observe the Lewis sites by this approach. To address this question, we ask how much of the intensity associated with the ^{27}Al resonances arises from aluminum atoms which are not "strongly" coupled to hydroxyl ^{1}H's. The results (not shown) of such experiments indicate that both aluminums are strongly coupled to ^{1}H's. That is, with a 200-μs blanking delay on the ^{1}H channel before acquisition, all of the transverse magnetization disappears.[24] Therefore, it appears the CP resonances reflect only surface aluminums associated with Brønsted sites and not Lewis acid sites. However, we can examine the Lewis acid sites by removing the ^{1}H reservoir accessible to the Brønsted sites and adding a probe which will allow only access to Lewis acid sites.

The results of such an experiment are shown in Figure 4. As described in the Experimental Section, the γ-alumina surface is ^{2}H exchanged using D_2O and then prepared using the PDA protocol. Figure 4a is a spectrum of the ^{1}H PDA surface and Figure 4b is the same surface that has been deuterium exchanged before heat treatment. Note that all CP signal from the surface Brønsted sites has now been suppressed. The lack of signal in Figure 4b is also indicative of the fact that the CP signal does not come from interstitial (or subsurface) hydrogens. This statement assumes that interstitial hydrogens would not be amenable to simple deuteration procedures. Spectra c and d in Figure 4 have the same deuterated surface in the presence of a 25% monolayer coverage of pyridine. Figure 4c shows the natural abundance pyridine spectrum and Figure 4d depicts the ^{15}N-labeled pyridine ^{27}Al CP/MAS spectrum. Clearly, the spectra depicted in c and d of Figure 4 possess three common features. First, two distinct resonances are apparent at 35 (shoulder) and 7 ppm, and, second, a shoulder on the larger resonance extending to higher shielding from 7 to -27 ppm. The origin of the 7-ppm peak is believed to be that of the O_h Lewis acid site since the chemical shift is appropriate for $Al(O_5N)$ as confirmed via model compounds such as $Al((H_2O)_5MeCN)$.[25] The 35-ppm resonance is believed to be the T_d Lewis acid site with coordinated pyridine. This assignment is based upon the observation that replacement of an O atom by a N atom results in a shift to higher shielding.[26] Clearly, no model has been found for this particular coordination environment. The final feature, the 7-ppm to -27-ppm shoulder, may arise from one of two mechanisms. The first is the effect of the Al quadrupole moment on the line shape in the form of second-order broadening. The second is a distribution of O_h Lewis acid sites with multiple pyridine molecules coordinated to the Al atom. The former explanation can be confirmed by a field-dependent experiment to be presented at a later date. The latter explanation suffers from the necessity of three pyridine molecules coordinating to a surface Al site.

The reduced size of the assigned Lewis acid T_d resonance is clearly not indicative of the amount of surface sites. Previous ^{15}N NMR on this same system confirmed the Lewis acid site T_d/O_h ratio of $^1/_2$ for this level of surface dehydroxylation. Hence, the CP conditions for the Brønsted or Lewis acid surface T_d sites give rise to signals which are not representative of their population, and therefore cannot be considered as quantitative.

Finally, the α-alumina results depicted in c and d of Figure 3 are of considerable interest. Namely, α-alumina is considered to be an inert surface in the absence of surface contamination by transition aluminas. Here, the term inert refers to the "bulk reactivity" and not to the reactivity of any given site. From such a perspective one would expect there should be paucity of Brønsted sites on the surface. Two points are clear from these spectra. First, the relative number of Brønsted sites is considerably lower in the α-alumina compared to the γ-alumina as reflected in the number

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[23] Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; pp 249–260.

[24] The signals decay at different rates, with the tetrahedral sites being the more strongly coupled to the ^{1}H's. Similar behavior is observed in the ^{1}H $T_{1\rho}$ via ^{15}N CP/MAS experiments using pyridine: Morris, H. D.; Ellis, P. D.; Benesi, A., unpublished results.

[25] Delpuech, J. J. *N.M.R. of Newly Accessible Nuclei*; Academic Press; New York, 1983; Vol 2, pp 167–170, 187.

[26] Reference 25, pp 167–170.

of transients (226 560) needed to obtain the signal in Figure 3d compared to the 7477 in Figure 1b. Secondly, the surface area of the α-alumina used in these experiments was 5.5 m^2/g. This surface area has to be considered high for α-alumina. Normal α-alumina has a surface area of less than 3 m^2/g. Hence, one may argue that the surface in the sample used here was contaminated by a transition phase. Using an α-alumina with a surface area of 1 m^2/g did not give rise to a ^{27}Al CP/MAS resonance (Figure 3c). The lack of signal is, in all probability, due to an insufficient number of O_h sites; i.e., a reduction in surface area by a factor of 5 would imply that to obtain the same S/N ratio as depicted in Figure 3d would take 25 times as long or 65.6 days! Therefore, the results depicted in Figure 3d represent a practical lower limit for samples with surface areas in the range from 3 to 5 m^2/g.

In summary, it is clear that there is a great potential to ^{27}Al CP/MAS NMR of alumina surfaces. But the impact of the work goes far beyond the ^{27}Al CP experiment. The success of these experiments supports the notion that surface CP of other nuclides can also be performed with the same relative ease. For example, CP experiments with enriched ^{183}W in HDS catalysts[27] using chemisorbed water as the source of the ^{1}H magnetization, or the CP of enriched ^{95}Mo in the same system using Brønsted sites or chemisorbed water as the source of ^{1}H's, may be envisioned. There are many potential applications, all of which will provide a unique perspective on some complicated and yet very important chemistry.

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Registry No. α-Alumina, 1344-28-1; pyridine, 110-86-1.

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(27) Reference 21, pp 390–447.

Spin Density Characterizations via Analysis of Variable-Temperature ^{183}W NMR for Paramagnetic (^{4}A and ^{5}E) Heteropoly Complexes. Elucidation of Bonding and Quantitation of Ligand-Centered Dipolar Shifts

Rafael Acerete,*,[†,‡] Nieves Casañ-Pastor,[†] Julia Bas-Serra,[†,‡] and Louis C. W. Baker*,[†]

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057, and the Department of Inorganic Chemistry, School of Pharmacy, University of Valencia, 46010-Valencia, Spain.

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Abstract: Temperature dependences (276–350 K) of ^{183}W NMR isotropic shifts have been measured in solution for paramagnetic heteropoly Keggin structures α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$. The ^{4}A tetrahedral d^7 central Co(II) has three unpaired electrons and the ^{5}E tetrahedral d^6 central Co(III) has four. At room temperature (297 K) the total shift for the Co(II) complex is −887.6 ppm ($\Delta\nu_{1/2}$ = 74 Hz), and it is −1993.7 ppm ($\Delta\nu_{1/2}$ = 26 Hz) for the Co(III) isomorph. This is the first such variable-temperature study of an E system. The results provide strong substantiation for the theoretical approach advanced by Kurland and McGarvey for NMR of nuclei other than ^{1}H or ^{1}D in paramagnetic species. Although in each case the plot of isotropic shifts vs T^{-1} is an excellent straight line, the isotropic shifts are almost entirely *dipolar*, owing to significant unpaired electron spin delocalization from Co to non-s (probably mainly $6p_z$) orbitals of the tungstens. Each of the 12 W's acquires a few hundredths (~0.01–0.06 probably) of an electron's unpaired spin in each complex. This "ligand-centered" (i.e., centered on the observed atoms) dipolar contribution accounts for −780 to −790 ppm of the isotropic shift for the Co(II) complex and −690 to −580 ppm for the Co(III) complex. The Fermi-contact shifts are only −9.9 ± 12.6 and −24 ± 30 ppm, respectively, while the "metal-centered" (Co) dipolar shift is ca. +13 ppm in the Co(II) case and ca. −1300 ppm in the Co(III) species. The smallness of the "metal-centered" dipolar contribution in the Co(II) complex is caused by the absence of **g**-tensor anisotropy for the very regular $Co^{II}O_4$ central tetrahedron. In contrast, the $Co^{III}O_4$ central tetrahedron is significantly Jahn–Teller distorted, and **g**-tensor anisotropy leads to a large "metal-centered" term. Values of the diamagnetic contributions to the total shifts were evaluated from the wavelengths of the lowest energy optical absorptions and the straight-line relationship between such wavelengths and chemical shifts that we have evaluated for diamagnetic Keggin tungstates. The overall results are strongly cautionary, for NMR of nuclei other than ^{1}H or ^{1}D, against the commonplace assumption of a preponderance of Fermi-contact contribution on the basis of apparent straight-line plots of isotropic shifts vs T^{-1}. From the standpoint of the chemistry of heteropoly complexes, the results support (1) a presumed similarity between the MO diagrams for $VO(H_2O)_5^{2+}$ and WO_6 units in polyanions and (2) our previous evidence for extensive delocalization of the heteroatom's unpaired electron spins throughout the structures.

This paper reports the first investigation of temperature dependences (276–350 K) of ^{183}W NMR isotropic shifts for paramagnetic species.[1-3] The complexes studied were two Keggin-structure (Figure 1) heteropolyanions: α-$[Co^{2+}O_4W_{12}O_{36}]^{6-}$ (^{4}A tetrahedral d^7 Co(II) having three unpaired electrons) and α-$[Co^{3+}O_4W_{12}O_{36}]^{5-}$ (^{5}E tetrahedral d^6 Co(III) having four unpaired electrons). This is also the first such study of an E system.

[†] Georgetown University.

[‡] Present address: University of Valencia.

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