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A Pulsed Electron Nuclear Double Resonance Study of the Lewis Acid Site−Nitric Oxide Complex in Zeolite H-ZSM-5

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One major challenge in the research of microporous materials is the spectroscopic characterization of acid sites such as Brønsted and Lewis centers. In general, Brønsted sites are assigned to OH groups and various spectroscopic tools have successfully been applied to study their structure, concentration, and acidity.[1,2] Lewis sites can be cations or aluminum defect centers, so-called true Lewis sites. Whereas cations in zeolites are likewise well characterized, the structure of true Lewis sites is controversially discussed. Various extraframework species such as Al^{3+}, AlO$_3^{3-}$, AlO^{+}, (−O−Al)$^{2+}$, and AlOOH have been suggested to act as true Lewis sites in zeolite structures.[2,3] However, the spectroscopic characterization of true Lewis sites by, for instance, nuclear magnetic resonance (NMR), infrared (IR), or electron spin resonance (ESR) is a much more demanding task than that of Brønsted or cationic Lewis centers, and unambiguous information about the nature of these centers is still missing.

A series of papers suggest the investigation of such aluminum species using nitric oxide (NO) as small paramagnetic π radical probe molecule.[4−7] On the basis of ESR results on Na−NO[4,5,7] and Cu−NO[8] adsorption complexes in Y and ZSM-5 type zeolites, the spectrum of the Al−NO complex should display at least 18 hyperfine (hf) lines due to the interaction between the unpaired electron spin at the nitric oxide and the nucleus spins of the ^{14}N ($I = 1$) and ^{27}Al ($I = {}^{5}/_{2}$) nuclei. However, typical ESR spectra of such Al−NO adsorption complexes are only poorly resolved as illustrated in Figure 1a. Simulations of the Al−NO signal do not provide unambiguous evidence for an Al hf coupling because of the low spectral resolution of the experimental spectra (Figure 1b). Therefore the assignment of the observed ESR signals to Al−NO complexes was intuitively deduced from a comparison of the observed ESR signals with those of NO adsorbed on γ alumina.[7] However, strict experimental evidence for an aluminum hf interaction is still lacking from an ESR spectroscopic point of view up to now. In this work, we present the first pulsed electron nuclear double-resonance (ENDOR) study of the Al (true Lewis site)−NO adsorbate complex in H-ZSM-5. The Davies ENDOR experiment[9] was employed to measure the ^{27}Al hf interaction of the NO−Al complex. The Mims-type ENDOR sequence[10] was used to study the interaction of the adsorbate complex with distant protons and aluminum nuclei.

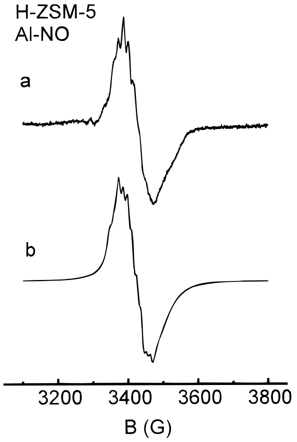

Figure 1. ESR spectra at 77 K of the Al−NO complex in H-ZSM-5 activated at 1073 K: (a) experimental spectrum and (b) simulated spectrum. The simulation parameters are $g_{xx} = 1.997$, $g_{yy} = 1.997$, $g_{zz} = 1.950$, $A_{xx}^{\mathrm{Al}} = 13$ G, $A_{yy}^{\mathrm{Al}} = 13$ G, $A_{zz}^{\mathrm{Al}} = 0$, $A_{xx}^{\mathrm{N}} = 0$, $A_{yy}^{\mathrm{N}} = 28$ G, $A_{zz}^{\mathrm{N}} = 0$.

The H-ZSM-5 zeolite with a Si/Al ratio of 15 was dehydrated at 673 K for 3 h and subsequently treated in an oxygen atmosphere at the same temperature for 2 h to remove organic residuals. The subsequent activation was performed in a vacuum of 10^{-6} Pa for 2 h at 1073 K. Nitric oxide was adsorbed onto activated samples at room temperature at a pressure of 3×10^{-2} Pa. ESR spectra were taken on a Bruker ESP 300 spectrometer at 77 K. The pulsed ENDOR experiments have been performed on a Bruker ESP 380 spectrometer at 6 K. Selective microwave pulses of 100 or 200 ns for $\pi/2$ and π pulses, respectively, were used for both pulse sequences. All experiments were done at X band frequencies.

Figure 1a illustrates the ESR spectrum of the Al−NO adsorbate complex. The spectrum shows a pure resolution, and the assignment of the weak splittings to an aluminum hf coupling seems to be vague. A simulated spectrum of the Al−NO complex is presented in Figure 1b. The simulation parameters were taken from the literature,[4,6,7] and a Gaussian line shape was used in the simulation procedure with highly anisotropic line widths ($\Delta B_{xx} = \Delta B_{yy} = 10$ G, $\Delta B_{zz} = 60$ G). The tensor coordinate frames were chosen in such a way that z axes points along the N−O bond direction and the y axes corresponds to the symmetry axes of the NO Π_y^* orbital having the unpaired electron. We have to note that even a careful adjustment of the simulation parameters does not provide a satisfying accordance of the simulated spectrum with the experimental one and a considerable uncertainty in the simulation parameters remains.

Therefore, the Davies ENDOR technique was employed to justify the assignment of the observed splittings to an aluminum hf interaction. Five ENDOR lines from each electron spin manifold are potentially observable for aluminum nuclei, since ^{27}Al has a nuclear spin $I = {}^{5}/_{2}$. The nuclear quadrupole (nq) coupling enters the ^{27}Al $\pm{}^{5}/_{2} \leftrightarrow \pm{}^{3}/_{2}$ and $\pm{}^{3}/_{2} \leftrightarrow \pm{}^{1}/_{2}$ nuclear transitions in first-order perturbation theory, whereas for the central $-{}^{1}/_{2} \leftrightarrow {}^{1}/_{2}$ transition, the nq interaction gives only a second-order contribution. Therefore, if the nq coupling is large, all transitions except the $-{}^{1}/_{2} \leftrightarrow {}^{1}/_{2}$ transition have broad line shapes in disordered systems and may be undetectable.[11] We expect this to be the case here because of the low symmetry at the aluminum nucleus in the proposed structures of the true Lewis site. Figure 2 illustrates two Davies ENDOR spectra which were measured near the g_{xx}/g_{yy} (Figure 2a) and g_{zz} (Figure 2b) spectral positions of the ESR spectrum of the Al−NO complex. A well-resolved doublet with a spacing of about 7.9 MHz was observed in the spectrum taken near the g_{xx}/g_{yy} position. We may assign this doublet to the central $-{}^{1}/_{2} \leftrightarrow {}^{1}/_{2}$ transition of the aluminum hf coupling as its splitting corresponds to the double nuclear

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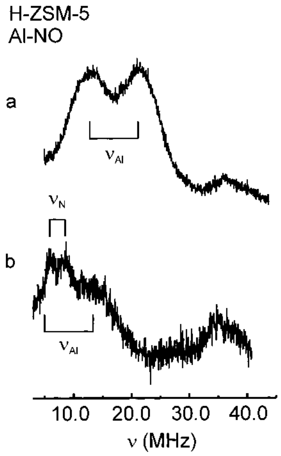

Figure 2. Davies ENDOR spectra at 6 K of the Al−NO complex in H-ZSM-5 activated at 1073 K: The spectra were measured at (a) 3471 G and (b) 3620 G corresponding to the g_{xx}/g_{yy} and g_{zz} spectral positions of the ESR spectrum of the Al−NO complex.

Larmor frequency $2\nu_{\rm Al}$ of the aluminum nuclei. An aluminum hf coupling $A^{\rm Al}_{xx/yy} = 34.2$ MHz was estimated from the center of gravity of the doublet as the strong coupling case $A \gg 2\nu_{\rm Al}$ holds.[11] The coordinate frame of the Al hf tensor refers to the electron **g** tensor coordinate system of the NO adsorbate complex.[4,6,7] It is worth to note that this aluminum hf coupling of $A^{\rm Al}_{xx/yy} = 12.2$ G given in magnetic field units corresponds to the poorly resolved splitting of about 13 G which are observed at the g_{xx}/g_{yy} position of the ESR spectrum of the Al−NO complex. Therefore, the pulsed ENDOR experiments provide a first unambiguous evidence for a strong aluminum hf interaction in the NO adsorption complex in activated H-ZSM-5 zeolites and support the interpretation where a true Lewis site (Al)−NO complex is formed upon nitric oxide adsorption onto activated H-ZSM-5. The Davies ENDOR spectrum recorded near the g_{zz} position displays two types of low intense signals (Figure 2b). The low signal/noise ratio is due to the weak ESR intensity at the high field edge of Al−NO ESR spectrum. The broad signal centered at about 10 MHz may again be assigned to aluminum nuclei based on its spectral width of about $2\nu_{\rm Al} = 8$ MHz. We determine from the center of gravity $A^{\rm Al}_{zz} = 20$ MHz. The double peak structure of the Al signal is less pronounced, since it is overlapped by another doublet signal centered at 7.2 MHz. The splitting of this doublet is about 2 MHz, which is indicative for ^{14}N nuclei ($2\nu_{\rm N} = 2.01$ MHz). We estimate a nitrogen hf coupling along the z axis of electron **g** tensor of $A^{\rm N}_{zz} = 14.4$ MHz from the center of gravity of the doublet. This value compares to those of the Cu$^+$−NO complex in Cu-ZSM-5 ($A^{\rm N}_{zz} = 15$ MHz).[8]

The **g** tensor theory of NO adsorption complexes predicts a slightly orthorhombic **g** tensor.[4,5] Unfortunately, the resolution in the X band ESR spectrum is not sufficient to separate the g_{xx} from the g_{yy} component in the spectrum of the Al−NO complex. Therefore, we cannot distinguish between the ^{27}Al hf couplings along the x and y axes of the **g** tensor. Nevertheless, the ENDOR experiments allow to put some constraints on the aluminum hf tensor. It seems to be natural to assume that the deviation of the z axis of the dipolar aluminum hf tensor from the intermolecular axis of the NO molecule (g_{zz} axis) is small because metal−nitrosyl complexes have only a slightly bent structure.[8,12] Furthermore, the well-resolved doublet in the ^{27}Al ENDOR spectrum (Figure 2a) suggests that the deviation of the aluminum hf tensor from an axial symmetry is small. If we assume $A^{\rm Al}_{xx} \approx A^{\rm Al}_{yy}$, we can roughly estimate the isotropic and dipolar aluminum hf coupling to be $A^{\rm Al}_{\rm iso} = -29$ MHz and $T^{\rm Al} = 4.5$ MHz. This translates into an approximated Al−N distance of about $r_{\rm Al-N} = 1.6$ Å using a simple point dipole approximation. Of course, $r_{\rm Al-N}$ has to be considered as a lower limit for the Al−N bond length as our simple approach neglects spin density contributions in the aluminum orbitals. We have to note that this value is in contradiction with a Al−N distance of about 1.1 Å which was deduced from ESR data alone.[7] However, such a short bond length seems to be unreasonable, since typical bond length in aluminum compounds and nitrosyl complexes are in the range from 1.5 to 2.1 Å.[12,13]

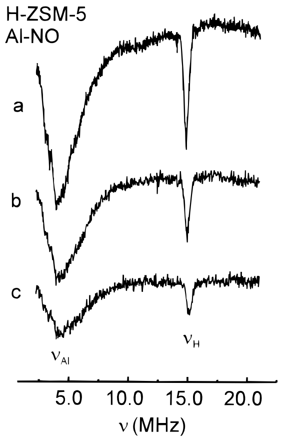

Figure 3. Mims ENDOR spectra at 6 K of the Al−NO complex in H-ZSM-5 activated at 1073 K: The spectra were measured at (a) 3471 G, (b) 3550 G, and (c) 3500 G within the ESR spectrum of the Al−NO complex. The delay between the first and second microwave pulses was $\tau = 808$ ns.

The estimated aluminum hf coupling parameter allow more detailed conclusions about the structure of the Al−NO complex than former X band ESR experiments. However, ESR experiments at various frequencies, which provide more information about orthorhombic distortions and distributions of the principal values of the **g** tensor, are necessary to improve the simulated ESR spectra and to derive a conclusive model of the complex structure. This problem will be addressed in a forthcoming paper.

Whereas the Davies ENDOR sequence detects strongly coupled nuclei, Mims ENDOR experiments are more suitable for the measurement of weak hf interactions. A series of Mims ENDOR spectra recorded at various field positions within the Al−NO ESR spectrum is illustrated in Figure 3. All spectra display signals at the aluminum and proton free nuclear Larmor frequency, which are assigned to weakly coupled ^{27}Al and ^{1}H nuclei. It seems to be worthwhile to discuss briefly the proton ENDOR signals with respect to the proposed structures of the true Lewis sites in more detail. The line width of the proton ENDOR signals is 0.5 MHz for all three spectra which were recorded at different field positions within the ESR powder pattern. This line width corresponds to a maximum dipolar hf coupling between proton and Al−NO complex of about $T^{\rm H}_{\rm max} = 0.25$ MHz which in turn yields a lower limit for the distance between the true Lewis site (Al)−NO complex and the weakly coupled protons of about $r_{\rm N-H} = 6.6$ Å. In zeolite materials, such a relatively long distance is indicative for matrix protons which are not associated with the paramagnetic complex. Therefore, we can exclude from our experiments structural models for true Lewis sites which have protons directly coordinated to the acid center such as for instance AlOOH. Presumably the distant protons can be assigned to Brønsted centers which were not destroyed by the high-temperature sample activation.

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