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PROBING THE STRUCTURE OF METAL-SUBSTITUTED MOLECULAR SIEVES BY SOLID-STATE NMR

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PROBING THE STRUCTURE OF METAL-SUBSTITUTED MOLECULAR SIEVES BY SOLID-STATE NMR.

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Paramagnetic metal ions exert large influences on the NMR spectra of neighboring nuclei. We are using these effects to probe metal sites in zeolites and $AlPO_4$ molecular sieves. In particular, we are studying [Co]-$AlPO_4$-5 because similar cobalt substituted $AlPO_4$ sieves are reported in the literature. We have extended that work to probe the titanium zeolite TS-1 by comparing spectra of normal TS-1 to samples where the titanium has been reduced to the paramagetic Ti^{3+}. This promises to be a useful technique for determining framework substitution in many zeolite systems.

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INTRODUCTION

We are interested in the catalytic activity of zeolites with heteroatoms in the framework, especially those which are oxidation-reduction catalysts. The titanium substituted zeolites are of particular interest because of their utility in selective oxidation. In spite of numerous spectroscopic and structural studies, there are virtually none that conclusively place titanium in the framework. Diffuse reflectance UV demonstrates that the titanium is not in the form of anatase but not that it is in the framework. Infra-red spectroscopy of these samples has a band at about 960 cm^{-1}, the source of which is debated. X-ray spectroscopies (EXAFS and XANES) are equivocal, with different authors offering different interpretations[1-3]. The ^{29}Si NMR spectrum has no peak which can be assigned to silicon that is next nearest neighbor to titanium. In summary, these interesting catalysts elude all attempts at spectroscopic structural characterization. Additionally if a structural tool were to present itself, it would be most useful to follow the structure of titanium under reaction conditions (structure function relationships). To those ends we have attempted several different types of NMR experiments ($^{47,49}Ti$ and ^{29}Si) all with negative results. However, an EPR experiment by Tuel, et al[4] combined with recent ^{31}P NMR experiments on cobalt-containing aluminum phosphate molecular sieves by Peeters[5] as well as work by Sananes, et al[6,7] and Canesson, et al[8,9] led us to think about the potential of using the influence of a paramagnetic cation to probe the structure of TS-1.

The interesting thing realized in the cobalt-$AlPO_4$ work is that much of the ^{31}P signal in these samples is rendered "NMR invisible" by the Co paramagnetism. They also realized that if the cobalt is in the framework, the reason for loss of signal lies in the contact interaction between the ^{31}P and the paramagnetic electrons. It is possible to recover this signal, albeit very broad, through a spin echo NMR technique. The ^{31}P resonance of the "invisible" phosphorus is greatly shifted and broadened by the paramagnetic influence. The French group has pursued this methodology and refined the spin echo technique to the point where they believe that they can reconstruct a quantitatively accurate NMR spectrum.

Analogous NMR experiments should be possible using ^{29}Si NMR rather than ^{31}P. The difficulty is that the intrinsic sensitivity of ^{31}P is about 15 times that of ^{29}Si which translates to a factor of 225 more time required for the ^{29}Si experiment. To get around this time requirement we resorted to quantitative ^{29}Si NMR and measured the loss of signal between paramagnetic and diamagnetic samples. This is where Tuel's EPR experiment becomes interesting. We can measure the ^{29}Si NMR spectrum of TS-1 before and after reduction of the Ti^{4+} (diamagnetic) to Ti^{3+} (paramagnetic).

EXPERIMENTAL

The samples used were $AlPO_4$-5 and [Co]-$AlPO_4$-5 synthesized using literature procedures and TS-1 synthesized with two different levels of incorporation of titanium. All samples were characterized by powder x-ray diffraction, diffuse reflectance UV, and elemental analysis. The analyses of the TS-1 samples give Si:Ti ratios of 30:1 and 120:1. The [Co]-$AlPO_4$-5 sample has a P:Al:Co ratio of 14:13:1. The [Co]-$AlPO_4$-5 was also steamed for 72 hours at 720 K which removes most of the cobalt from the structure, leaving it in the pores of the sieve.

NMR spectra were obtained on a Varian Unity-400 with a 9.4 T magnet and a Varian (7 mm) MAS probe. The nominal resonance frequencies are 161.9 and 79.5 MHz for phosphorus and silicon. Many spectra were obtained without MAS (static). Spectra were obtained using standard Bloch decays (single pulse) and modified Hahn echoes. We used small chips of the titanosilicate mineral, titanite, ($CaTiOSiO_4$) and $AgPF_6$ as internal intensity reference standards for ^{29}Si and ^{31}P, respectively. The titanium in TS-1 was reduced by soaking in CO at 673 K for 12 hours in a glass tube on a vacuum line[4]. The samples were packed in NMR rotors in a dry, oxygen free atmosphere. The Varian NMR rotors have a double o-ring cap which effectively excludes air during transfer of the sample from the glove box to the spectrometer. We used dry nitrogen as a drive gas for the NMR turbine to minimize the potential of reoxidation of the Ti^{3+}. After obtaining ^{29}Si spectra of the reduced samples they were exposed to room air to reoxidize and another ^{29}Si NMR spectrum obtained.

RESULTS AND DISCUSSION

^{31}P NMR experiments

The ^{31}P NMR experiments on $AlPO_4$-5 were done to establish the technique and demonstrate that a decrease in the ^{31}P resonance intensity is a useful means of establishing that Co is in the $AlPO_4$ framework. Figure 1 contains several NMR spectra for pure $AlPO_4$-5 and [Co]-$AlPO_4$-5. The spectrum of $AlPO_4$-5 (figure 1A) has a relatively sharp peak at about - 30 ppm and only a few spinning sidebands. The signal corresponding to the internal reference is at - 145.6 ppm. Knowing the weights of the sample and reference, it is possible to quantify the observed ^{31}P MAS NMR signal by integrating the peaks and all corresponding spinning sidebands. The $AlPO_4$-5 sample is the case where 100% of the phosphorous NMR signal is "visible". Figure 1B shows the ^{31}P MAS spectrum obtained for the [Co]-$AlPO_4$-5 sample. This spectrum contains a large number of spinning sidebands. From the integrals, we conclude that ca. 50% of the ^{31}P NMR signal is "invisible" relative to the pure $AlPO_4$-5 sample. This agrees with Peeters et al's results. Figure 1C is the ^{31}P spectrum of [Co]-$AlPO_4$-5 after steaming. The normalized intensity of the ^{31}P signal is the same as that of the pure $AlPO_4$-5. Note that the peak height of the central resonance is less than in 1A but there is significant intensity in the sidebands which must be accounted for in spin counting. The increased sideband intensity is expected in samples with paramagnetic "impurities". This data demonstrates that the cobalt has been removed from the framework by steaming.

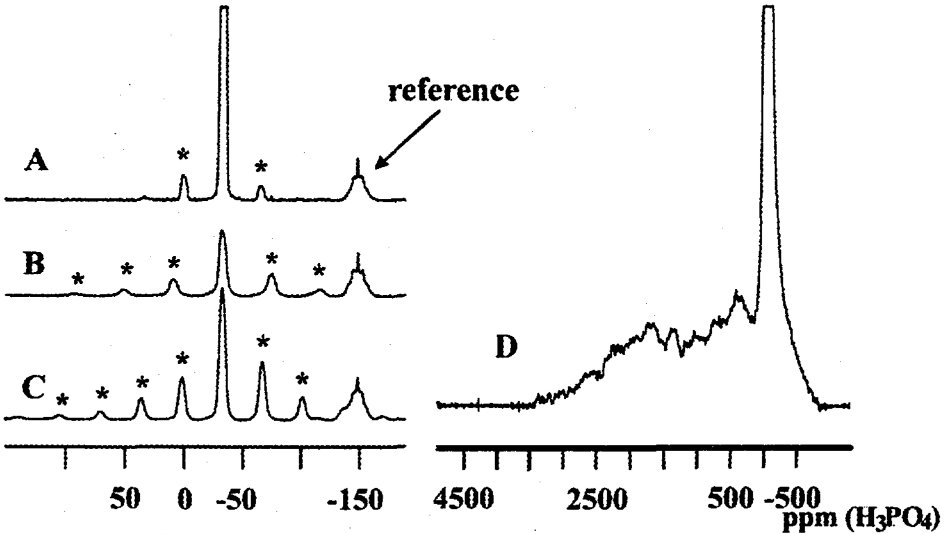

FIGURE 1: The ^{31}P NMR spectra of $AlPO_4$-5. Spectra are: 1A pure $AlPO_4$-5, 1B [Co]-$AlPO_4$-5. 1C [Co]-$AlPO_4$-5 after steaming and removal of Co from the structure. Figure 1D is the spin echo mapping (SEM) spectrum of [Co]-$AlPO_4$-5 (static).

Additionally, we have applied the spin echo-mapping technique (SEM) as proposed by Sananes and coworkers to the [Co]-$AlPO_4$-5 sample. This technique essentially a Hahn echo at different carrier frequencies in a static sample. We used a 90 pulse length of 6 μs, a 180 pulse length of 12 μs and an echo time, tau, of 20 μs. The quantitative ^{31}P NMR spectrum is the sum of all the spectra obtained at different irradiation frequencies. Figure 1D shows the total ^{31}P NMR spectrum obtained for the [Co]-$AlPO_4$-5 sample using the SEM technique. As can be seen, the total ^{31}P NMR signal spreads over 2000 ppm. The sharp (truncated) peak at the left of the spectrum corresponds to the center peak in spectrum 1B. In these early experiments we have not attempted to quantify the intensities in the SEM spectrum, 1D.

^{29}Si MAS NMR experiments

Figure 2 shows ^{29}Si MAS NMR spectra before and after reduction with CO and reoxidized for the two TS-1 samples investigated in this study. For comparison purposes we obtained spectra of the TS-1 samples prior to reduction to establish the intensity where 100% of the ^{29}Si NMR signal is observed. As noted by Tuel, et al, when a TS-1 sample is exposed to carbon monoxide if oxygen and water are excluded, the majority of the diamagnetic Ti^{4+} atoms are reduced to paramagnetic Ti^{3+}. Then, depending on the titanium concentration, different amounts of the ^{29}Si NMR signal become "NMR invisible". In the TS-1 sample with a Si:Ti ratio of 30:1 ca. 95% of the silicon NMR signal becomes "invisible" following CO reduction. Thus, the spectra are plotted at high gain to show the small ^{29}Si peak for the remaining signal. Reoxidation with O_2 or air changes Ti^{3+} back to Ti^{4+} and the entire ^{29}Si NMR signal becomes observable again. For the sample with a Si:Ti ratio of 120:1 only 50% of the ^{29}Si signal vanishes.

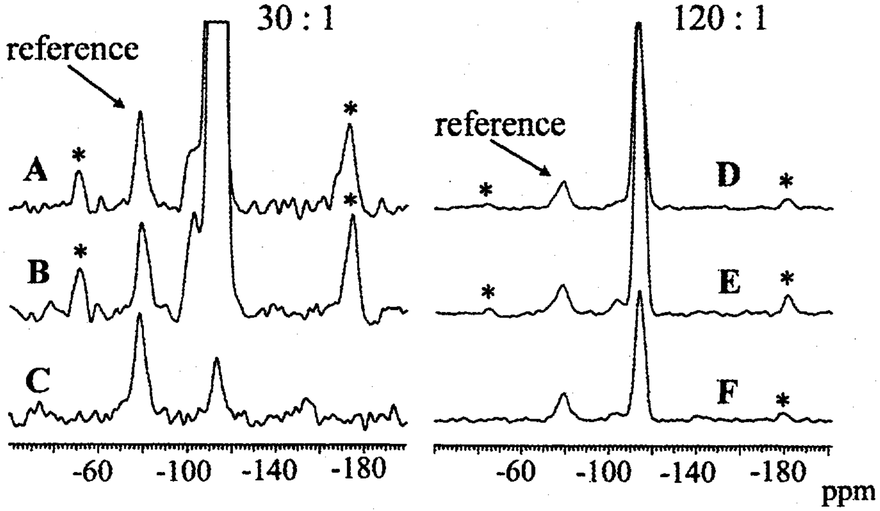

FIGURE 2: Quantitative ^{29}Si NMR spectra of the two TS-1 samples. Asterisks indicate spinning sidebands. The spectra are: 2A prior to reduction, 2B after reduction and reoxidation, 2C after reduction, 2D prior to reduction, 2E after reduction and reoxidation, and 2F after reduction.

CONCLUSIONS

This is evidence that titanium is in the zeolite framework because were it simply in the pores the ^{29}Si NMR resonance would not disappear when Ti^{4+} (diamagnetic) is reduced to Ti^{3+}.

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