NMR characterization of quadrupolar nuclei in solids

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Ultrahigh-field NMR was integral in five publications, including development of $^{209}$Bi SSNMR as a structural characterization method, a preliminary investigation of $^{137}$Ba SSNMR, characterization of metallocenes with $^{35}$Cl NMR, and acquisition of ultra-wideline $^{14}$N SSNMR spectra. We also received assistance in the form of CASTEP calculations for several projects. We are continuing work on pharmaceuticals ($^{35}$Cl, $^{23}$Na, $^{14}$N), nanoparticle samples (multinuclear), metallocenes ($^{91}$Zr, $^{49}$Ti, $^{27}$Al and $^{35}$Cl), and initiating new projects on amino acids ($^{14}$N), low-valent indium complexes ($^{115}$In), and other assorted materials.

Metallocenes. We have amassed a large amount of $^{35}$Cl, $^{47/49}$Ti and $^{91}$Zr NMR data for a series of titanocenes, zirconocenes and hafnocenes. These metallocenes are important in homogeneous and heterogeneous catalysis for polyethylene production; however, little is known about the precise mechanism of these catalytic processes. Probing the metal centers of these metallocenes may provide rich insight into initiation, polymerization and termination processes. The chemical shift and quadrupolar parameters extracted from $^{35}$Cl, $^{47/49}$Ti and $^{91}$Zr NMR spectra are very sensitive to slight structural modifications, ligand substitution and variation in substituents on the cyclopentadienyl rings (Figure 1). High-field spectra of these insensitive nuclei can be acquired quite rapidly, suggesting that the high field will be instrumental in conducting studies on metallocenes loaded onto micro- and mesoporous support materials.

Adiabatic Pulses. Last year, we initiated a series of projects for S/N enhancement of ultra-wideline patterns, using adiabatic pulses and microcoils (manuscript will be shortly submitted). Our new WURST-QCPMG techniques have been implemented successfully on the 900 MHz NMR spectrometer. In particular, we have been focussing on $^{14}$N and $^{35}$Cl SSNMR on the 900, but we expect this work to expand over numerous different nuclei over the next year.

$^{14}$N solid-state NMR. We have published three papers in this area over the past year, and plan to extend our work to pharmaceutical polymorphs, amino acids and other systems over the next year. In particular, our $^{14}$N DEISM technique, which enhances the S/N of broad $^{14}$N NMR spectra, is of particular interest. While the ultra-high field does not narrow the spin-1 powder patterns, it certainly will be useful for boosting S/N and allow increasingly efficient spectral acquisitions. We plan to run a series of pharmaceuticals at the 900 MHz spectrometer over the coming year.

$^{115}$In solid-state NMR. With the assistance of the 900 NMR Facility staff, we have been collecting NMR data at 21.1 T (and 9.4 T here at Windsor) for a series of low-valent In(I) compounds. We have completed data acquisition at the 900, including new VT $^{115}$In NMR experiments. A manuscript is currently being written on this topic.
Figure 1: Static $^{47/49}$Ti SSNMR spectra of CpTiCl$_3$ and Cp*TiCl$_3$ acquired at 21.1 T and 9.4 T. Black traces - experimental spectra, red traces - analytical simulations shown with deconvolutions of the $^{49}$Ti (green traces) and $^{47}$Ti (blue traces) powder pattern simulations. Spectra were acquired with a standard echo sequence. For more information see [1].

References

