Characterization of Surface Accessible, Catalytic, ^{27}Al, ^{119}Sn, and ^{17}O Species by DNP-Enhanced NMR Using Targeted Nitroxide Spin Probes as Reactant Models

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Introduction

The necessary requirement to achieve domain or surface-selective NMR is access to highly performing DNP instrumentation that will dramatically boost NMR sensitivities under magic angle spinning (MAS) conditions to achieve high spectroscopic resolution, while positioning the radical spin probes of choice as reactant model candidates within the local environment or interface of interest. We plan to explore the temperature and microwave power dependence of high-field DNP performance of ^{27}Al, ^{119}Sn, and ^{17}O nuclei, via direct electron-X (X = ^{27}Al, ^{119}Sn, and ^{17}O) and electron-^{1}H-X cross polarization processes in solution-imbibed mesoporous silica alumina.

Experimental

The NHMFL NMR facility has a modified, commercial 14.1 T DNP instrument operating in a temperature range >100 K with up to 40 Watts of microwave power at 395 GHz. As an initial trial we prepared SBA15 catalyst mixed with 10 mM TOTAPOL (in H_2O) that is packed into a 3.2 mm sapphire MAS rotor with a zirconia cap for e^--^{1}H-^{27}Al DNP CPMAS experiment at 100K. The sample rotor was spun at the spinning rate of 10 kHz and the e^--^{1}H DNP signal transfer during microwave irradiation was followed by ^{1}H-^{27}Al CP, utilizing a standard spin-lock CP sequence (mixing time = 100 μs) for obtaining an e^--^{1}H-^{27}Al CP spectrum.

Results and Discussion

Figure 1 shows our first e^--^{1}H-^{27}Al DNP CPMAS spectrum obtained at 14.1 T with a sample system of catalytic material, SBA15, that was mixed with 10 mM TOTAPOL in H_2O and packed into a 3.2 mm sapphire MAS rotor, which was spun at 10 kHz at 100K. The DNP signal enhancement factors (ε) were about 1.9 and 3.4 when the microwave irradiation power (395 GHz) was about 7 W and 20 W, respectively. We are expecting further signal enhancements by increasing the microwave power and optimizing the radical concentration.

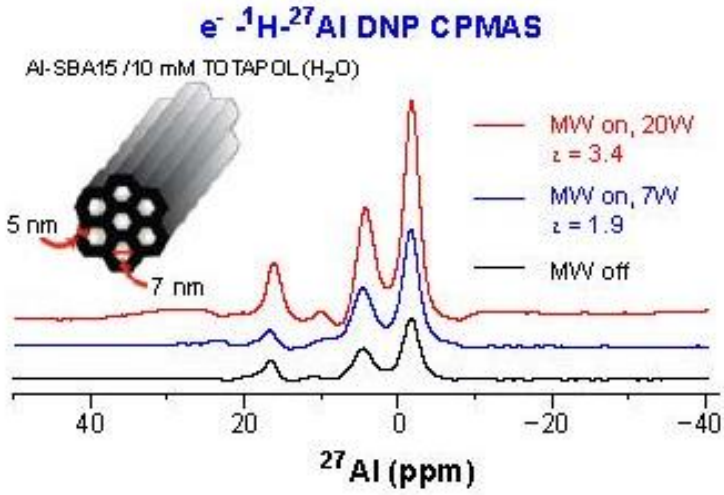

Fig.1 e^--^{1}H-^{27}Al DNP CPMAS spectra measured at 14.1 T (395 GHz microwave) spinning at ν_r = 10 kHz and at 100K sample temperature. The ppm chemical shift is not referenced to the peak of a standard sample.

Conclusions

We have successfully observed the e^--^{1}H-^{27}Al DNP CPMAS spectrum of a SBA15 catalytic sample system mixed with biradical TOTAPOL (10 mM in H_2O).

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