Solid-State 67Zn NMR Characterization of Zincosilicates (CIT-6)

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Introduction

Zincosilicates are zeolite-like materials that possess an excellent ion exchange capacity for a broad range of ions with higher adsorption capacity, particularly for the divalent ions such as Pb^{+2}. The Davis group at Caltech has synthesized zincosilicate analogs of some of structures that are common in industry[1]. A single zinc atom present in the tetrahedral structure generates a -2 charge. It would thus be able to stabilize a divalent atom with a single heteroatom substitution. For example, the divalent metal counter-cations could be an element from the alkali-earth metal family, M = Mg, Ca, Sr, etc. The purpose of this user proposal is to utilize ^{67}Zn NMR spectroscopy, in addition to the conventional ^{19}Si and ^{27}Al NMR methods, in the high magnetic field strength at the NHMFL (18.8 and 19.5 T) to understand whether the divalent ion exchange offers the same enhancement in stability to thermal treatment that is seen with the silicoaluminate materials.

Experimental

We have employed the quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) NMR spectroscopy in solid state to enhance the signal sensitivity of a solid-state ^{67}Zn NMR spectrum, utilizing a home-built 4 mm MAS probe. The rf pulse strength of X-channel that is tuned at the Larmor frequency of ^{67}Zn at 19.5 T (ν_0 = 51.8 MHz) was about 40 kHz. The pulse calibration of a 90 degree pulse was carried out on a model compound (zinc perchlorate hexahydrate) that was purchased from the Sigma Aldrich.

Sample preparation: As a pilot study for setting up the QCPMG ^{67}Zn solid-state NMR spectroscopy, zinc-beta zeolites (CIT-6) materials were prepared with (calcined) and without (as made) thermal treatment. About 30 mg of each sample was packed into a 4 mm MAS rotor.

Results and Discussion

Fig. 1 shows the ^{67}Zn QCPMG NMR spectra of CIT-6 with (calcined) and without (as-made) thermal treatment. Each spectrum was obtained by co-adding the transient signals of 80,000 scans. Since the signal acquisition delay employed in this experiment was 1s, the total acquisition time of this experiment, 22 hours and 13 minutes, is still within a manageable period of time. Although the signal-to-noise (S/N) ratio of each spectrum shown in Fig. 1 is not sufficient yet, it is at least clear that the signal width of the calcined sample is broader than that of as-made sample as expected. We expect that the S/N ratio of the ^{67}Zn QCPMG NMR spectrum can considerably be improved if the experiment is carried out under the magic-angle spinning (MAS) condition. Thus, we anticipate that the capability found in this pilot study will make the ^{67}Zn solid-state NMR spectroscopy feasible to be utilized in our future study for investigating zincosilicate materials to fully characterize the structural changes around Zn atoms in the zeolite framework.

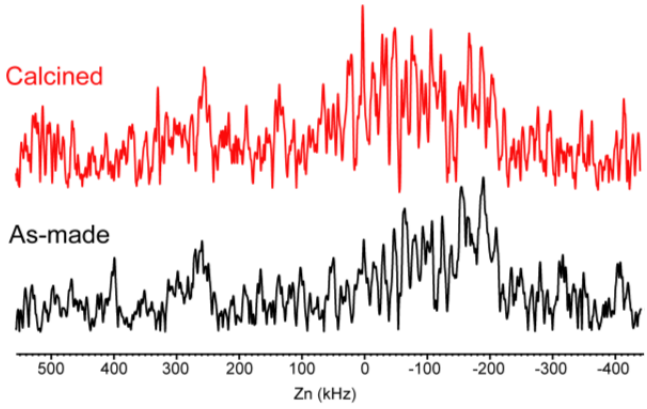

Fig. 1 Static ^{67}Zn CPMG NMR spectra of calcined (A) and as made (B) Zincosilicates (CIT-6) measured in the magnetic field strength 19.5 T.

Conclusions

Acquisitions of ^{67}Zn CPMG NMR spectra of zincosilicate materials at a high magnetic field strength, 19.5 T, were successful. We anticipate that a sufficiently strong ^{67}Zn NMR spectrum will be obtained successfully under MAS condition with an extended number of scans.

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References

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