Molecular Dynamics in the Solid-State for $KMnO_4$ Observed Using ^{17}O MAS NMR

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Introduction

Recent investigations on tetraoxoanion salts (e.g., Cs_2WO_4 [1], $KReO_4$ and NH_4ReO_4 [2]) by ^{17}O NMR show that the anions all exhibit unusual dynamic behaviour. Their high-field ^{17}O magic-angle spinning (MAS) NMR spectra change drastically with temperature as compared to their corresponding room temperature (RT) spectra. These observations lead us to perform a variable temperature (VT) ^{17}O MAS NMR study on $KMnO_4$, which shows a narrow singlet ^{17}O MAS NMR resonance at RT [3]. Here we report some preliminary results obtained from VT ^{17}O MAS and 2D 3QMAS experiments.

Experimental

^{17}O VT MAS NMR spectra of ^{17}O-enriched $KMnO_4$ (using 10% $H_2{}^{17}O$) powders were recorded at 21.1 T (121.50 MHz) using the NHMFL 900 MHz ultra-widebore magnet and a 3.2 mm transmission-line VT MAS probe designed and constructed at the NHMFL.

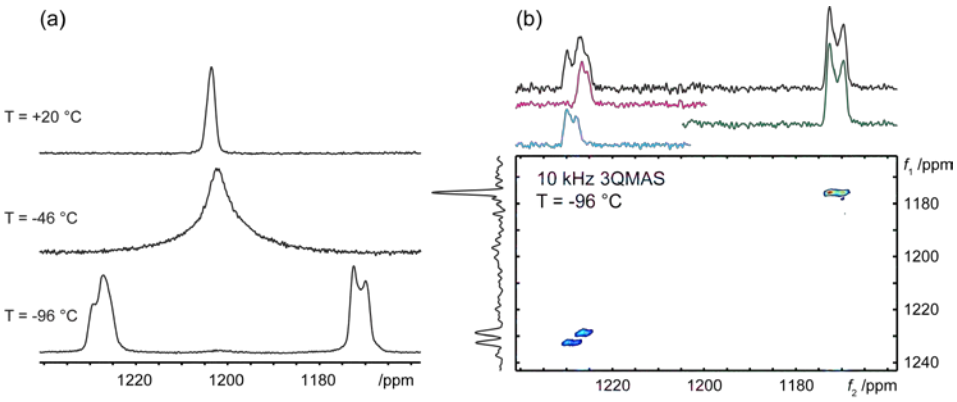

Figure 1. (a) ^{17}O 1D variable-temperature MAS NMR spectra of $KMnO_4$. (b) 2D MQMAS spectrum obtained at -96 °C with slice projections along the three peaks. A sum of the three slices is shown on the top. The MAS frequency was 10 kHz.

Results and Discussion

Figure 1 shows the ^{17}O MAS NMR spectra of $KMnO_4$ acquired at 21.1 T when varying the temperature. A narrow ^{17}O singlet resonance (FWHM = 260 Hz) was observed at RT. The peak gets broadened extensively upon cooling and then splits into two equal-intensity resonances at –96 °C. The two resonances are positioned almost symmetrically with respect to the RT peak and are separated by ~ 55 ppm. To further characterize the ^{17}O resonances, a ^{17}O 3QMAS NMR experiment was performed at this low temperature. The 3QMAS spectrum and its traces show that the high-frequency peak resolves into two non-equivalent ^{17}O sites (~1232 and 1228 ppm) and the low-frequency peak exhibits one ^{17}O sites (~1175 ppm) with double the intensity, in agreement with the 1:1:2 ratio of oxygen sites in the *Pnma* crystal structure of $KMnO_4$. Details of the molecular dynamics is under investigation and will be reported in the future.

Conclusions

Preliminary VT ^{17}O MAS and 2D 3QMAS NMR experiments indicate the presence of three different ^{17}O sites in $KMnO_4$ at low temperature. At high temperature, the molecule undergoes reorientation and averages the different sites into a single resonance.

Acknowledgements

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References

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