In Situ High Temperature MAS NMR Characterization of a Titanosilicate UPRM-5 Prepared Using Tetrapropylammonium and Tetrabutylammonium Cations

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Introduction

Hernandez-Maldonado developed a titanium silicate material (UPRM-5) with a pore aperture that could be tailored with minimal impact on adsorption capacity.[1-4] This is possible due to the inclusion of quaternary ammonium cations to the synthesis, acting as structure-directing agents (SDAs). The structural contraction process upon thermal treatment has been the subject of collaborations between Hernández-Maldonado and Fu, which included the use of *in situ* high temperature MAS NMR to monitor the appearance of new titanium coordination environments upon dehydration of UPRM-5 prepared with tetraethylammonium (TEA^+) acting as SDA (report dated December 2010). The work described in this report focuses on elucidating the effect that larger quaternary ammonium SDAs have on the coordination environment of the UPRM-5 framework at high temperatures. In particular, SDAs tetrapropylammonium (TPA^+) and tetrabutylammonium (TBA^+).

Experimental

In situ high temperature ^{29}Si MAS NMR experiments were performed on a Bruker DMX300 spectrometer with the ^{29}Si Larmor frequency of 59.64 MHz and using a 4 mm Bruker double-resonance variable temperature probe. A 2.0 μs pulse (~30˚ flip angle) was used for excitation of the ^{29}Si magnetization. The samples were spun at 6 kHz using N_2 gas. Each temperature set point was stabilized for about half an hour before data acquisition. The chemical shift was referenced to DSS.

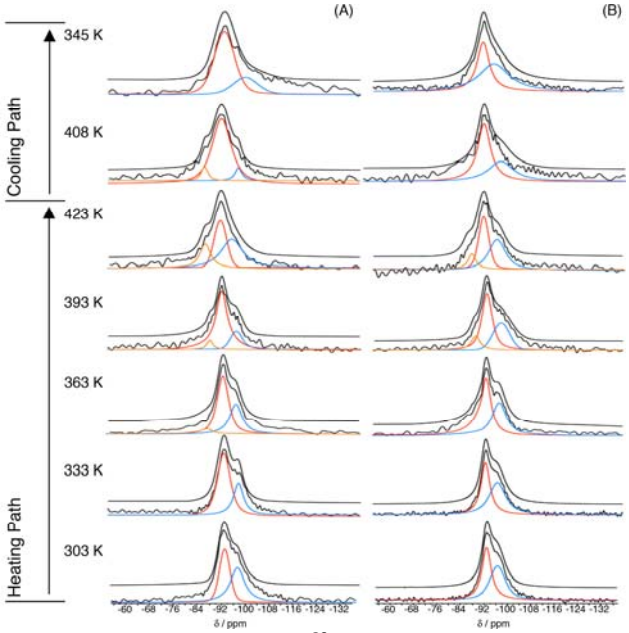

Fig. 1 *In situ* high temperature ^{29}Si MAS NMR spectra for (A) Sr^{2+}-UPRM-5 (TPA^+) and (B) Sr^{2+}-UPRM-5 (TBA^+).

Results and Discussion

Fig. 1 shows stacks of spectra gathered for Sr^{2+}-UPRM-5 samples prepared using tetrapropylammonium (TPA^+) and tetrabutylammonium (TBA^+). Two silicon environments associated with specific titanium coordination were initially found in both UPRM-5 variants, similar to what was reported for the material synthesized with tetraethylammonium (TEA^+).[2] A third resonance appeared around -87.0 ppm between 363 and 423K, and was related to a Si(2Si, $2Ti_{oct}$) environment. A shifting of the original resonances and the presence of a third resonance at -87.0 ppm evidenced the sensitivity of these materials to thermal dehydration. The reversibility of the formation of the new titanium coordination was verified with the aid of NMR data gathered upon cooling of the sample (see Fig. 1). The spectral data gathered for Sr^{2+}-UPRM-5 (TPA^+) under these conditions revealed the presence of only two Si-Ti environments, probably due to exposure of the sample to ambient moisture during the *in situ* test. However, the data also showed a decrease in resonance intensity and shift relative to the one initially found at -97.0 ppm, probably indicating a degree of irreversibility. For the case of Sr^{2+}-UPRM-5 (TBA^+), the data gathered upon cooling is nearly identical to that of the material tested prior to the heating stage. The results suggest that the materials synthesized with TBA^+ have a better thermal recovery than the samples synthesized with TPA^+, probably due to the higher amount of semi-octahedral titanium chains in the latter and their association to tenacious water typically present in flexible titanium silicates.

Acknowledgements

This work was supported in part by the NHMFL and by NSF HRD 0833112.

References

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