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

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Introduction

The work presented in this report is a continuation of a collaboration between Fu and Hernández-Maldonado to elucidate the effects that larger quaternary ammonium SDAs (Structure Directing Agents) have on the coordination environment of UPRM-5[1-3] (a soft titanium silicate) frameworks at high temperatures. In particular, SDAs tetrapropylammonium (TPA^+) and tetrabutylammonium (TBA^+).[4,5] These materials have been designed to selectively remove CO_2 from natural gas streams as well as air (closed volume system).

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 half an hour before data acquisition. The chemical shift was referenced to DSS.

Results and Discussion

Fig. 1 shows ^{29}Si NMR chemical shifts and peak relative areas for Sr^{2+}-UPRM-5 samples prepared using TPA^+ and TBA^+ as a function of material activation temperature.[5] Chemical shifts for both materials remained similar and nearly constant up to temperature of 60°C. However, as the temperature was increased further, peak relative areas underwent significant changes. As the temperature is increased, the relative area of the resonance associated to the semi-octahedral titanium centers decreases. Semi-octahedral titanium chains (or larger amount of structural faulting) are also associated to tenacious or coordinated water present in flexible titanium silicates. Sr^{2+}-UPRM-5 (TPA) exhibited the most significant reduction in the amount of semi-octahedral titanium centers, from ca. 50% to ca. 28%, within the 30 - 150°C range. Since faulting in these materials will translate to significant differences in textural properties, the NMR data suggests that such properties plausibly correlate with the level of dehydration of the semi-octahedral titanium centers. Peak relative areas associated to octahedral titanium centers reached maxima at 90 and 120°C for Sr^{2+}-UPRM-5 (TPA) and Sr^{2+}-UPRM-5 (TBA), respectively. It is also worth noting that the peak relative area associated to the Si(2Si, $2Ti_{oct}$) environment increased when the temperature was increased, markedly in the case of Sr^{2+}-UPRM-5 (TPA). The appearance of the corresponding resonance (i.e., initially centered at -89.0 ppm) and further increase in the peak relative area may be the consequence of perturbations of the octahedral titanium centers due to the release of coordinated water. This also seems to affect the semi-octahedral titanium centers.

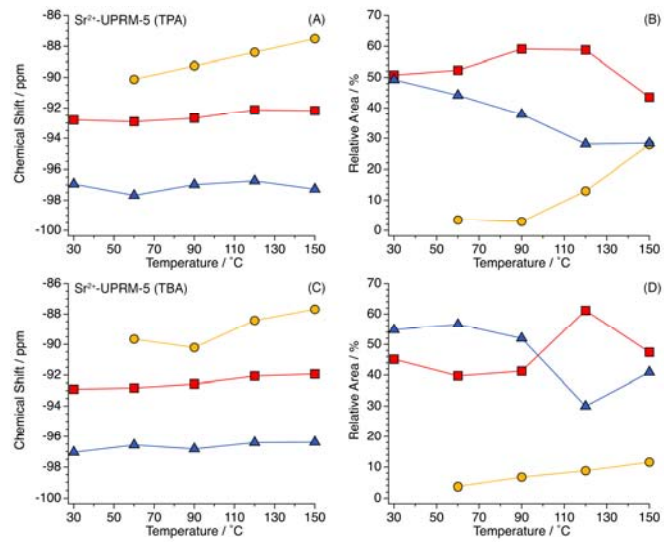

Fig. 1 ^{29}Si MAS NMR chemical shifts and relative peak area as function of temperature of deconvoluted spectra for (A, B) Sr^{2+}-UPRM-5 (TPA) and (C, D) Sr^{2+}-UPRM-5 (TBA). Circle, square and triangle markers correspond to NMR resonances initially located at ca. -89, -93 and -97 ppm, respectively.

Acknowledgements

This research was supported in part by the NHMFL which is supported by the National Science Foundation (DMR-1157490), the State of Florida, and the U.S. Department of Energy, and by NSF Grant No. HRD 0833112.

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