Tailoring the Adsorption Properties of Hierarchical Porous Silicas for High-Capacity Water Sorbents

Pasquale F. Fulvio,[1] JiaJi Lin,[1] and Krista S. Walton[1]

[1] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
email for correspondence: pfulvio@gatech.edu

Hierarchical mesoporous-macroporous silica materials (HS-PEG) were prepared via a one-pot hydrothermal synthesis method using tetraethyl orthosilicate (TEOS) as the silica source, NH_4OH as condensation catalyst, and a combination of alkylammonium bromide surfactants (C_nTAB) and different polyethylene glycols (PEG) as structure directing agents (SDAs). Once the SDAs were removed by calcination in air, periodic and wormhole mesopores within primary particle units, and macropores formed by particle agglomerates were obtained. Similar to MCM materials [1], we report the control over the mesopore size using different alkyl chain lengths within 2 to 4nm range. Moreover, the solvent system used, namely, water, and water-ethanol, also dictated the adsorption properties of the materials. For instance, when water was the single solvent used, mesopores were nearly 1nm larger and pore volumes were nearly double than the counterparts prepared in water-ethanol. Higher ratios of NH_4OH also led to higher mesopore volumes. Hygroscopic salts including anhydrous LiCl, $MgCl_2$, $MgSO_4$, $CaCl_2$, and $SrCl_3.6H_2O$ and $SrBr_3.6H_2O$, were then impregnated in these silicas by a modified incipient wetness method with pre-determined salt to silica weight ratios. For LiCl containing composites, the water uptake increased proportionally to the LiCl target contents [2]. Moreover, composites having different pore volumes and pore widths were found to adsorb similar amounts of water. The composites were found stable for salt loadings of up to 60wt.%. As for Mg salts, composites did not deliquesce for loadings of less than 40wt.%. Such salts form hydrates as $MgCl_2.6H_2O$ and $MgSO_4.7H_2O$, that have larger unit cells, and cannot be dehydrated unless thermally treated to temperatures greater than 300°C, which exceed the operation range of atmospheric water harvesting (AWH) or of thermal energy storage (TES) devices. These results indicate that the free mesopore volume in the composites is required for the strong nanoconfinement of salt hydrates, and to the high-water uptakes exceeding 150wt.% at 80% relative humidity, as in case of LiCl composites. Finally, the current synthesis method for HS-PEG represents an improvement over previously reported monolith syntheses [2, 3] that required multiple steps. The present method yields powders with fine distributions of sizes, and that can be easily integrated with AWH or TES devices.

References:

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Acknowledgements:

The authors acknowledge financial support from the DARPA Advanced Research Project Agency Atmospheric Water Extraction Program under Grant No. HR001120S0014.