SODALITE ION EXCHANGE IN ETHYLENE OXIDE OLIGOMER SOLUTIONS

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Introduction

Sodalite has a simple aluminosilicate framework structure. Alternating SiO_4/AlO_4 tetrahedra are linked together through bridging oxygens creating a 3-dimensional network with pores of uniform size. [1] The resulting anionic framework requires a charge balancing cationic species. Sodalites, like more complex zeolites, are able to exchange their cationic species. However, traditional aqueous methods of ion exchange present complications for the exchange of catalytically important transition metal and rare earth ions such as precipitation of metal hydroxides and destruction of the zeolite framework due to the acidic metal complexes formed. [2] Ethylene oxide oligomers (polyethylene glycol, polyethylene glycol methyl ether, diglyme, tetraglyme, and polypropylene glycol) are being investigated as alternative media for ion exchange in hydrosodalite, $Na_6(AlSiO_4)_6 \cdot 8H_2O$, and dehydrated sodalite, $Na_6(AlSiO_4)_6$. Here we present initial results using lithium as the exchanged species to determine whether these solvents can be used successfully for zeolite ion exchange, and whether these reactions can be carried out in the absence of water. The extent of ion exchange was determined by measurement of the sodalite unit cell parameters using powder XRD and by elemental analysis using ICP-MS.

Experimental

Sodalite exchanges were carried out by adding either hydrosodalite or dehydrated sodalite to 1.0 M $LiNO_3$ solutions of each solvent (1 g : >100 mL). Each mixture was exchanged at 100°C overnight. The sodalite samples were then filtered, washed, and collected. Using these exchanged samples, this process was repeated for several cycles of exchange. Dehydrated sodalite reactions were carried out under completely dry conditions using a glove box. Unit cell parameters were determined for each sample after each exchange cycle using powder X-ray diffraction. Unit cell elemental compositions were determined for the samples using a FinniganMat ELEMENT 1 HR-ICP-MS at the Isotope Geochemistry Division, NHMFL.

Results and Discussion

Sodium hydrosodalite exchange data indicate that Li^+ ion exchange can be achieved using these oligomer solutions and that it is actually more efficient than traditional aqueous exchange. While water was only able to exchange 90% of the sodium ions, the oligomer solvents were able to exchange from 92 – 99% of the sodium ions after five exchange cycles. This is due to the fact that water molecules coordinate around the lithium ions very strongly making it difficult for their interactions to weaken and for the water molecules to shed. This shifts the equilibrium of the exchange to the left, thus hindering exchange in aqueous solution. On the other hand, the oligomers do not coordinate around the lithium ion as strongly, they mobilize the ion without forming a tightly bound coordination sphere making it easier to shed the ligand. This allows for the exchange to proceed forward more efficiently in the oligomer solvents. [3, 4] Sodium dehydrated sodalite data indicate that ion exchange is possible and quite efficient using oligomer solvents under dry conditions as well as they were able to exchange from 88 – 91% of the sodium ions after three to four cycles of exchange. The presence of water is not required for oligomer ion exchange; the oligomers alone can complex and transport the ion sufficiently. The exchanging ion then sheds the large oligomer before its stabilized exchange and coordination into the dehydrated cage.

Conclusions

These results confirm that ion exchange using ethylene oxide oligomer solvents is possible and quite efficient for hydrosodalite and for dehydrated sodalite under completely dehydrated conditions as well. A new method is now provided that can be used for the exchange of transition metals and rare earths into zeolites that eliminates previous problems associated with traditional ion exchange methods.

References

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