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MOLECULAR MODELING INVESTIGATION OF CATION SITING IN CRYSTALLINE SILICOTITANATE AND POLYOXONIOBATE MATERIALS

Edward J. Maginn and James P. Larentzos
Department of Chemical and Biomolecular Engineering,
University of Notre Dame, Notre Dame, IN 46556
ed@nd.edu

INTRODUCTION

Separation of radionuclides from high-level nuclear waste solutions is a vital step to minimize disposal volume. A number of inorganic ion exchangers have shown promise for selective removal of trace radionuclides in the presence of high sodium ion concentrations under alkaline conditions.

Various classes of ion exchangers, such as crystalline silicotitanates (CST), pharmacosiderates and polyoxoniobates, are being synthesized by collaborators at Texas A&M and Sandia National Laboratories. Ultimately, the objective is to design a novel material with improved ion exchange capacity and kinetics that can reduce the amount of separation processes needed for sufficient radionuclide removal. The ion exchange performance of these materials may be improved by introducing suitable structural modifications. For example, by partially substituting niobium for titanium in the CST structures, Tripathi *et al.*[1] have shown that the selectivity for cesium is enhanced.

In this work, the origins of ion exchange selectivity and kinetics are investigated through atomistic level simulations, which provide an additional design tool for the synthesis of novel ion exchangers. The primary focus has been to develop a transferable potential model that can be used to accurately predict structural characteristics of the ion exchangers of interest. The developed potential model is based upon the ion pair, shell model[2] and is extended to a more efficient fixed charge model. Energy minimizations and molecular dynamic simulations are applied to determine structural characteristics,

such as cation and water sites, coordinating environments and the energetics associated with the sites. Upon validation of a reliable potential model, these techniques are applied to the polyoxoniobate structures to assist in the determination of the crystal structure.

MODELING APPROACH

The potential model is based upon previous work in which crystalline structures such as silicalite, rutile and various zeolites have been simulated[3,4]. To account for polarizability in the lattice, a shell model potential is added to all oxygen atoms in the system. Although the shell model is accurate in predicting crystal structure, it tremendously increases computational cost relative to simpler fixed charge models. This severely limits simulation time and length scales. To overcome this, a more efficient fixed charge model is developed that is capable of predicting crystal structure with comparable accuracy to the shell model.

Energy minimization studies were conducted with the fixed charge model to predict the crystal structure of CST materials. Molecular dynamic simulations were also carried out to determine a time-averaged position of the cation and water sites, which provide a better estimation of the sites determined by x-ray diffraction. In addition, through molecular dynamic simulations, dynamic properties of the materials were obtained. Finally, a simulated annealing molecular dynamics approach was implemented in order to ensure efficient sampling of configuration space.

RESULTS

The CST structures have been well characterized through the use of powder x-ray diffraction techniques[1,6] and provide excellent test cases for the validation and optimization of a transferable potential model for all ion exchangers of interest. The first simulations were performed on the sodium exchanged and cesium exchanged CST structures and later extended to the 25% niobium substituted CST structures. The potential model parameters for the initial simulations were taken from the literature[7,8] and tested. Modifications to the potential parameters and atomic partial charges were made in order to capture the important interactions observed experimentally.

Through simulations, experimental findings were confirmed and additional insight into the cation and water sites was provided. For example, in the cesium exchanged CST structure, the exchangeable sodium cation sites were unable to be determined through powder x-ray diffraction. Molecular dynamic simulations were able to provide a reasonable position and coordinating environment for the exchangeable sodium cations, in addition to accurately predicting the cesium and water sites. In applying the model to the 25% niobium substituted cesium exchanged CST structure, the model confirms experimental results suggesting that cesium attains a higher coordination in the niobium substituted CST than in the pure CST structure, which leads to an enhancement of the selectivity for cesium. Table 1 and Table 2 compare the experimental and predicted cation and water sites in the cesium exchanged CST and cesium exchanged Nb-CST.

Table 1. Fractional atomic coordinates obtained for Cs exchanged CST.

	Experimental			Predicted			Deviation (Å)
	x	y	z	x	y	z	
Cs	0.5000	0.5000	0.2500	0.501	0.499	0.223	0.324
Na							
Na							
O(water1)	0.2738	0.2738	0.5000	0.285	0.285	0.487	0.199

Table 2. Fractional atomic coordinates obtained for Cs exchanged Nb-CST.

	Experimental			Cs-Nb-CST Predicted			Deviation (Å)
	x	y	z	x	y	z	
Cs	0.5000	0.5000	0.2500	0.500	0.500	0.250	0.000
O(water1)	0.2824	0.2824	0.5000	0.347	0.347	0.505	0.717
O(water2)	0.5916	0.5916	0.5000	0.653	0.653	0.505	0.682

In the polyoxoniobate structures, $(Nb_{12}SiO_{40})^{-16}$ clusters (*i.e.* keggin clusters) are linked together by M_2O_2 [M = Nb, Ti] bridges to form keggin ion chains[9]. The keggin ion chains are counterbalanced by sodium cations. Experimentally, powder x-ray diffraction is unable to distinguish between the sodium and water sites in the polyoxoniobate structures. It is known that the water and sodium sites are located over four distinct sites. Through charge neutrality, the amount of sodium cations is known, while the amount of water is unknown. The newly developed fixed charge potential was applied to the polyoxoniobate materials in order to assist in the determination of crystal structure. Molecular dynamic simulations were used to resolve and characterize the sodium and water sites. In the Ti_2O_2 bridging structure, it was found that two of the four different sites are fully occupied with sodium cations. Additionally, these sites are located very close to the keggin clusters and allow the sodium cations to become highly coordinated, thereby increasing the stability of the structure. The remaining two sites are partially occupied with sodium and water. In addition, the sodium cations are more diffuse as compared to the sodium cations in the highly coordinated, fully occupied sites. It was found that this higher mobility allows the sodium cations to attain a higher coordination and increased stability. Simulations show that the site nearest to the Ti_2O_2 bridges is 50% occupied with sodium. The sodium position depends upon arrangement of the Ti_2O_2 bridges, where the sodium cations in this site will move to coordinate with one of the oxygen atoms in the Ti_2O_2 bridge. The remaining sodium cations are located in the fourth site, where the cations occupy 25% of the sites.

By substituting niobium for titanium in the bridges of the keggin clusters, there is a decrease in the amount of counterbalancing sodium cations. Again, there are four distinct sites for the sodium and water molecules. Molecular dynamic simulations again show that there are two fully occupied, sodium cation sites located near the keggin clusters. However, there are no sodium cations located in the site nearest the Nb_2O_2 bridges, whereas this site was 50% occupied with Ti_2O_2 bridges. It is shown through

simulations that the additional charge introduced into the bridges by substituting niobium for titanium causes the sodium to depopulate from the site and prefer the more stable, fourth site.

SUMMARY

A new, transferable potential model has been developed which accurately predicts the siting of cations and water in crystalline ion exchange materials. The model has been validated with the CST structures and has been extended to the polyoxoniobate materials. Molecular simulations have demonstrated the ability to provide experimentalists with additional insight into the origins of selectivity, which will hopefully lead to the design of an optimal ion exchanger for cesium, strontium and actinide separation from high-level waste solutions.

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REFERENCES

1. Tripathi, A., Medvedev, D., Nyman, M. and Clearfield, A.; Selectivity for Cs and Sr in Nb-substituted titanosilicate with sitinakite topology. *J. Solid State Chem.*, 2003, **175**(1), 72-83.
2. Dick, B.G. and Overhauser, A.W.; Theory of the Dielectric Constants of Alkali Halide Crystals. *Phys. Rev.*, 1958, **112**, 90-103.
3. Sanders, M.J., Leslie, M. and Catlow, C.R.A.; Interatomic Potentials for SiO_2. *J. Chem. Soc., Chem. Commun.*, 1984, 1271-1273.
4. Jentys, A. and Catlow, C.R.A.; Structural Properties of Titanium Sites in Ti-ZSM5. *Catal. Lett.*, 1993, **22**, 251-257.
5. Poojary, D.M., Cahill, R.A. and Clearfield, A.; Synthesis, Crystal Structures, and Ion-Exchange Properties of a Novel Porous Titanosilicate. *Chem. Mater.*, 1994, **6**, 2364-2368.
6. de Leeuw, N.H. and Parker, S.C.; Molecular Dynamics Simulation of MgO Surfaces in Liquid Water Using a Shell-Model Potential for Water. *Phys. Rev. B*, 1998, **58**, 13901-13908.
7. Higgins, F.M, de Leeuw, N.H. and Parker, S.C.; Modeling the Effect of Water on Cation Exchange in Zeolite A. *J. Mater. Chem.*, 2002, **12**, 124-131.
8. Woodley, S.M., Battle, P.D., Gale, J.D. and Catlow, C.R.A.; The Prediction of Inorganic Crystal Structures Using a Genetic Algorithm and Energy Minimisation. *Phys. Chem. Chem. Phys.*, 1999, **1**, 2535-2542.
9. Nyman, M., Bonhomme, R., Alam, T.M., Rodriguez, M.A., Cherry, B.R., Krumhansl, J.L., Nenoff, T.M. and Sattler, A.M.; A General Synthetic Procedure for Heteropolyniobates. *Science*, 2002, **297**, 996-998.