Title: **Air Separation by Pressure Swing Adsorption Using Superior Adsorbent**
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OBJECTIVE

The separation of air for the production of oxygen is an important operation in the chemical processing industry as well as for energy conversion processes. This separation has been done predominately by cryogenic distillation; though, as adsorption systems have become more efficient and new, more effective sorbents have been synthesized, separation by adsorption processes (*e.g.*, pressure swing adsorption (PSA), and vacuum swing adsorption (VSA)) have become increasingly competitive and are already favorable for small-to-medium scale operations. Currently, approximately 20% of air separations are accomplished using adsorption technologies. In this program we are synthesizing and characterizing new materials to be used in this important gas separation. Further, the structures of new zeolites and Co-Complexes immobilized on nanoporous materials and fundamental questions concerning adsorption of gases in these new sorbents are addressed.

ACCOMPLISHMENTS TO DATE

Before the past year, we synthesized mixed Li,Ag ion-exchanged zeolites and treated these materials in ways that promote the formation of intracrystalline silver clusters. Using these new zeolites for air separation by standard pressure swing adsorption (PSA), it was determined that the oxygen productivity was increased by 12% when compared with the best sorbents in industry, Li-LSX zeolite. These samples were also structurally characterized using Rietveld refinement of neutron powder diffraction data. Structural characterization revealed the presence of cations in a novel site II* in mixed Li,Ag-LSX zeolites that were vacuum dehydrated at 450•C. Cations in this site II* are more interactive with the atmospheric sorbates of interest than silver at the conventional site II location. Vacuum dehydration at 450•C induced thermal migration of Ag^+ from site II to site II* and gives rise to the superior properties for air separation.

During the past year, we focused on the synthesis of oxygen selective sorbents. The inherent advantage for using oxygen-selective sorbent for air separation is that much less work is to be done for the same separation as comapred with using nitrogen selective sorbents, since air conatins mush less oxygen. Following our original plan, cobalt (II) bis(3-fluoro-salicylaldehyde) ethylenediamine (Co(fluomine)), an organometallic complex of known oxygen-binding capacity, has been synthesized in such a way as to anchor this material on the anion sites of selected nanoporous substrates. The O_2 and N_2 binding capacities of the resulting bulk materials were then characterized. The resulting O_2 sorption isotherms of these materials were more reversible than those of the free material. They also exhibit the positive slope with oxygen pressure that is desirable for PSA applications. X-ray photoemission spectroscopy (XPS) analysis indicated a difference in the electronic nature of the cobalt atoms present in the free Co(fluomine) as compared to those of the material immobilized on the surface of type X zeolite, indicating possible coordination of Co(II) at the axial position by zeolitic framework oxygen. Stability testing of these materials, however, did not seem to result in increased stability over that observed in the free Co(fluomine).

A number of related and important issues in PSA air separation have also been addressed, such as the use of molecular sieve carbon as the sorbent, criterion for sorbent selection for PSA, and diffusion rates of nitrogen/oxygen in zeolites.

In the remaining months, we plan to evaluate the best sorbents for air separation specifically for producing oxygen or enriched oxygen for fossil energy applications.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Advanced and efficient coal conversion and power generation systems require an inexpensive source of oxygen. Pressure swing adsorption is a commercially proven technology that can generate oxygen at a wide range of concentrations at low costs. In this work, we aim at developing the best sorbents for air separation by pressure swing adsorption. The best sorbent developed in this program is the Ag-Li mixed cation X zeolites. PSA using these sorbents will yield 12% higher sorbent productivity than the best zeolite sorbent that is used in industry today.

ARTICLES, PRESENTATIONS AND STUDENT SUPPORT

Articles and presentations

N.D. Hutson and R. T. Yang, "Synthesis and Characterization of the Sorption Properties of Oxygen-Binding Cobalt Complexes Immobilized in Nanoporous Materials," *Ind. Eng. Chem. Res.*, **39**, 2252 (2000).

N. D. Hutson and R. T. Yang, "Structural Effects on the Adsorption of Atmospheric Gases in Mixed Ag,Li -X Zeolite," *AIChE J.*, **46,** 2305 (2000).

N. D. Hutson, S. U. Rege and R. T. Yang, "Mixed Cation Zeolites: Li_xAg_y-X as a Superior Adsorbent for Air Separation", *AIChE J.* , 45, 724 (1999).

N. D. Hutson, S. C. Zajic and R. T. Yang, "The Influence of Residual Water on the Adsorption of Atmospheric Gases in Li-X Zeolite: Experiment and Simulation," *Ind. Eng. Chem. Res.*, **39**, 1775 (2000).

N. D. Hutson, R. T. Yang, B. A. Reisner and B.H. Toby, "Silver Ion-exchanged Zeolites Y, X and Low Silica X: Observations of Thermally Induced Cation/Cluster Migration and the Resulting Effects on the Equilibrium Adsorption of Nitrogen," *Chem. Mater,* **12**, 3020 (2000).

N. Sundaram and R. T. Yang, "Binary Diffusion of Unequal Sized Molecules in Zeolites," *Chem. Eng. Sci.*, **55**, 1747 (2000).

S. U. Rege and R. T. Yang, "Kinetic Separation of Oxygen and Argon using Molecular Sieve Carbon," *Adsorption*, **6**, 15 (2000).

S. U. Rege and R. T. Yang, "A Simple Parameter for Selection of Sorbent for Gas Separation by Pressure Swing Adsorption," *Separ. Sci. Tech*., in press.

R. T. Yang, N. D. Hutson, B. A. Reisner and B. H. Toby, "New Sorbents for New Separations by Weak Chemical Bonds," Plenary Lecture, Second Pacific Basin Conference on Adsorption Science and Technology, Brisbane, Australia, May 14-18, 2000.

R. T. Yang, "New Sorbents for New Separations by Weak Chemical Bonds," AIChE Meeting, Los Angeles, David Cooney Memorial Session, November 16, 2001.

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