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 these new zeolites and fundamental questions concerning adsorption of gases in these zeolites are being addressed using neutron diffraction with Rietveld refinement and molecular dynamics simulations.

ACCOMPLISHMENTS TO DATE

Li-X zeolite (Si/Al = 1.0) is currently the best sorbent for use in the separation of air by adsorption processes. Silver is also known to strongly affect the adsorptive properties of zeolites; and it is known that thermal vacuum dehydration of silver zeolites leads to the formation of silver clusters within the zeolite. In this work we have synthesized type X zeolites containing varying mixtures of Li and Ag. The addition of very small amounts of Ag and the proper dehydration conditions resulted in the formation of silver clusters and enhanced adsorptive characteristics and increased energetic heterogeneity as compared to those of the near fully exchanged Li^+-zeolites. The performance for air separation by the best of these sorbents, containing, on average, only one Ag per unit cell, was compared to that of the near fully Li^+-exchanged zeolite using a standard PSA cycle by numerical simulation. The results show that the new sorbent provides a significantly higher (>10%)

product throughput, at the same product purity and recovery, when compared to that of the near fully Li^+-exchanged zeolite.

Further, silver zeolites of the types Y, X and low silica X have been synthesized. The zeolites were treated in such a way as to promote the formation of intracrystalline charged silver clusters. Equilibrium room temperature isotherms were measured for adsorption of nitrogen for each of the zeolites after various heat treatments and dehydration. These materials were structurally characterized via Rietveld refinement using neutron powder diffraction data. Color changes upon heat treatment and subsequent X-ray photoemission spectroscopy confirmed some reduction of $Ag^+ \rightarrow Ag^0$. The effects of various dehydration conditions, including the time, temperature and atmosphere, on the room temperature adsorption of nitrogen are discussed. Structural characterization, along with valence bond calculations, revealed the presence of cations in site II which are more active in Ag-LSX samples that were vacuum dehydrated at 450•C as compared to those which were vacuum dehydrated at 350•C.

The location of the extraframework silver in relation to the aluminosilicate framework is of primary importance for elucidating the effect of silver cations on the adsorptive characteristics of the zeolite. Hence we have also synthesized mixed Li,Ag ion-exchanged zeolites and treated these materials in ways that promote the formation of intracrystalline silver clusters. 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.

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. Success in this program will lead to oxygen at still lower costs.

PLANS FOR THE COMING YEAR

- To complete the characterization of Ag+ containing zeolites and the understanding of their interaction with nitrogen and oxygen.

- To complete the work on the synthesis and characterization of oxygen-binding Cobalt Complexes for advanced air separation.

ARTICLES, PRESENTATIONS AND STUDENT SUPPORT

Article and presentation

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).

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.

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