

Separation of Oxygen and Nitrogen by Porous Cyanometallates

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The adsorption-based separation in porous solids takes place through steric, kinetic, or equilibrium effect selectivity. In this contribution the oxygen-nitrogen separation by four porous frameworks representative of cyanometallates was studied by inverse gas chromatography. The following materials were considered: $\text{Cd}_3[\text{Co}(\text{CN})_6]_2$ (cubic), $\text{Zn}_3[\text{Co}(\text{CN})_6]_2$ (rhombohedral), $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ (rhombohedral) and $\text{Co}[\text{Fe}(\text{CN})_5\text{NO}]$ (cubic). Chromatographic separation profiles from gases mixtures using columns of these materials were recorded. For columns prepared from rhombohedral zinc hexacyanocobaltate(III) excellent separation of O_2 and N_2 was observed. Such behavior was attributed to a kinetic-based selectivity related to the size and shape for the pore windows of this material. The porous framework of this zinc phase is formed by ellipsoidal cavities ($12.5 \times 9 \times 8 \text{ \AA}$) communicated by elliptical windows of $\sim 5 \text{ \AA}$. For $\text{Cd}_3[\text{Co}(\text{CN})_6]_2$ and $\text{Co}[\text{Fe}(\text{CN})_5\text{NO}]$ also kinetic-based selectivity was observed while for $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$ the K^+ ion located close to the cavity windows hinders the porous windows accessibility for nitrogen and oxygen molecules. All the samples to be studied were characterized from X-ray diffraction, infrared spectroscopy, thermogravimetric and adsorption data.

Keywords adsorption; air separation; porous solids; prussian blue analogue

INTRODUCTION

The large-scale technologies for oxygen and nitrogen production are based on cryogenic distillation of air. These technologies consume relatively large amount of energy. For small and intermediate scales the separation by adsorption is probably the most attractive alternative, and after cryogenic distillation, it is the most widely used process for air separation, particularly when very high product purity is not required. The separation by adsorption is based on the adsorbent selectivity for a given component in the considered mixture. The adsorption is an exothermic

process and it is favored at low temperatures. In consequence, the removal of the adsorbed species (desorption) is an endothermic process and requires a temperature increase. The adsorption equilibrium is reached for equal chemical potential for both adsorbed and gaseous phases. A reduction for the chemical potential in the gaseous phase leads to partial desorption for the adsorbed species. This fact supports the gas separation by pressure swing adsorption (PSA) cycles (1,2). For oxygen-nitrogen separation by adsorption five classes of adsorbent materials are currently used: molecular-sieve zeolites, activated carbons, silica gel, activated alumina, and coordination compounds (3). Several of these materials can be integrated in a given PSA-based technology where a feed dryer stage including the CO_2 removal is always incorporated.

The adsorption-based separation is achieved by at least one of the following mechanisms: steric, kinetic, or equilibrium effect. In the steric mechanism the pass of a given species through the porous framework is determined by its size and shape. Oxygen and nitrogen are both ellipsoidal shape molecules but of slightly different size, 3.46 and 3.64 Å (kinetic diameter), respectively (4). Kinetic separation results from a different diffusivity for the adsorbates that are present in the considered mixture. The diffusivity of a given adsorbate through a porous framework depends on its size and also on the nature and strength for the guest-host interactions. Related to their ellipsoidal shape, nitrogen and oxygen are molecules with permanent quadrupole moment, which, in $10^{-26} \text{ esu.cm}^2$ units, is 1.52 for nitrogen and 0.30 for oxygen (5). Molecules with quadrupole moment interact with an electric field gradient. The interaction will be stronger for nitrogen. The large majority of oxygen-nitrogen adsorption-based separation processes are carried out through the control of the adsorption equilibrium, varying the pressure between two extreme values (PSA) under practically isothermal conditions.

Regarding materials, zeolites and activated carbons are among the most widely used. Zeolites with exchangeable alkaline and alkaline earth metals (groups 1 and 2,

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