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Kr/Xe separation over Metal Organic Framework Membranes

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ABSTRACT:

Objectives

The central thrust of this proposal is to establish a solid fundamental science program leading to the rational design of a novel family of continuous membranes, composed of metal organic frameworks which offer the possibility of demonstrating high separation performance for Kr/Xe gas mixtures.

The specific objectives of the proposed work are:

(1) The development of continuous and reproducible MOF membranes on porous tubular supports displaying high Kr permeabilities and high Kr/Xe separation selectivities.

(2) Demonstrating the membrane performance long term stability.

(3) Establish the basic structure/separation relationships of MOF membranes in Kr/Xe separations.

(4) Demonstrating that membrane synthesis could be amenable to large scale production.

Description/Methods

The separation of krypton (Kr) from xenon (Xe) is a relevant problem for nuclear industries. Separating Kr from Xe is a critical step in removing radioactive ^{85}Kr during treatment of spent nuclear fuel. The conventional method to separate these two gases is fractional distillation at cryogenic temperatures, which is an energy intensive process. In addition, even after cryogenic distillation, trace levels of radioactive Kr in the Xe-rich phase are too high to permit further use. In this respect, membrane technology could play a key role in making this separation less energy intensive and therefore economically feasible. Membrane separation processes have several advantages over conventional fractional distillation; for instance, it is a viable energy-saving method, since it does not involve any phase transformation, furthermore, the required membrane process equipment is simple, easy to operate, control and scale-up. Metal organic frameworks (MOFs) consisting of metal cations or metal-based-clusters linked by organic molecules forming a crystalline porous network, have emerged as a novel type of crystalline porous materials which combine highly desirable properties, such as uniform micropores, high surface areas, and exceptional thermal and chemical stability, making them ideal candidates for molecular gas separation applications.

Herein, we propose to develop continuous and robust type of membranes, composed of metal organic frameworks, which show great promise for Kr/Xe separation. The particular MOF compositions to be explored have been chosen based on two important criteria: (1) limiting pore aperture (or window openings) and/or (2) Differences in adsorption capacities. Based on the kinetic diameter of Kr (~3.60 Å) and Xe (~3.96 Å), in principle, MOFs with limiting pore apertures in the ~3.5-3.9 Å range should be suitable candidates for Kr molecular sieving over Xe. In the ideal case scenario, Kr molecules would diffuse rapidly through the pores, while Xe at most will diffuse slowly meaning that high Kr selectivities

could be potentially achieved based on *molecular diffusion differences*. Another key parameter to consider is the adsorption capacities of the gas molecules to be separated. In this respect, ideal materials should be those exhibiting Kr *preferential adsorption* over Xe. The CoPI of this project has recently found that a particular type of MOF denoted as FMOFCu displays unprecedented high Kr/Xe selectivy, making this MOF highly appealing to be prepared on membrane form. It is important to mention that although crystalline porous phases in powder form have been reported as selective Xe adsorbents for separating Xe/Kr mixtures, the focus of this work under NEUP is to demonstrate the preparation of *defect free continuous MOF membranes* for Kr/Xe separation which is not a trivial issue. Even if a MOF phase displaying unique and remarkable separation properties is prepared in powder or particle form, the same material may be not suitable for membrane preparation due to limited adhesion of the membrane to the support, induced stresses developed at the membrane-support interface, poor crystal intergrowth, etc. Therefore, the preparation of continuous MOF membranes for gas separations is challenging.

MOF membranes will be prepared inside tubular porous α-alumina and stainless steel supports by different synthesis approaches that could lead to continuous, reproducible and robust membranes. Porous tube is a highly desirable configuration for scale-up. The different synthesis approaches include: *secondary seeded growth: using physical and chemical approaches, and evaporation-induced self-assembly.* These three approaches (fundamentally different) may potentially result in the successful growth of continuous membranes on the porous tubular supports. MOF membranes and crystals will be characterized by XRD, SEM, HRTEM, EDS, ICP, and porosimetry mainly. Other useful complimentary techniques will include TGA, FTIR and CHN analysis.A continuous flow system coupled with a gas chromatograph will be used for measurements of single gas permeation and of mixtures separations.
To gain a better understanding on the structure/separation property relationships, *the role of key membrane properties such as composition, membrane thickness, Kr and Xe adsorption capacities, and membrane defects on the separation performance for Kr/Xe gas mixtures will be studied*. These properties should impact the overall separation performance of the membranes. Having a fundamental understanding of these structure/separation relationships will allow us to rationally design better membranes. Finally, optimum MOF membranes will be grown in 25 cm long porous tubes to prove the potential of the membranes for scale up. More specifically, we will study systematically appropriate synthesis conditions for scale up from 6 cm to 25 long membranes.

Benefits/Outcomes

If successful, the proposed research will result in the development of novel membranes capable of effectively separating Kr from Xe with high flux and selectivity. The ability to fabricate thin, chemically and mechanically stable MOF membranes for nuclear gas treatment constitutes an important new direction in membrane science with the goal of achieving higher combinations of selectivity and permeability overcoming current conventional fractional distillation approach. This research may result in the development of robust membranes, as a viable energy saving approach for the effective removal of ^{85}Kr during processing of spent nuclear fuel.

Participants

The PI (Colorado School of Mines) and CoPI (PNNL) are uniquely qualified to execute the proposed work. The PI has established expertise in the molecular engineering design of porous nanocrystalline particles, films and membranes for diverse functional applications in molecular gas separations. The CoPI has extensive experience in the synthesis, characterization, and application of metal organic framework materials, with particular emphasis on gas sorption.Their complimentary sets of skills provide a remarkable combination of talents that enable the proposed research.