



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Assessing zeolite frameworks for noble gas separations through a joint experimental and computational approach



Keith V. Lawler, Amit Sharma, Breetha Alagappan, Paul M. Forster*

University of Nevada Las Vegas, Department of Chemistry, Las Vegas, NV 89154-4003, USA

ARTICLE INFO

Article history:

Received 22 June 2015

Received in revised form

30 September 2015

Accepted 2 October 2015

Available online 22 October 2015

Keywords:

Zeolites

Selectivity

Gas adsorption

Gas separation

Grand canonical Monte Carlo

ABSTRACT

All 229 identified zeolite frameworks are screened in their siliceous form by grand canonical Monte Carlo simulation for their ability to separate a radiochemically relevant Kr/Xe mixture in a pressure swing adsorption process. Prior to screening, our model was benchmarked against experimental single gas adsorption measurements, and it was found that for Kr and Xe a Lennard-Jones 9-6 potential with a softer repulsion than an equivalently parameterized Lennard-Jones 12-6 potential was necessary to accurately model fluid–fluid interactions. Examination of the most promising candidate materials, we concluded that zeolites with small, accessible cages about the size of a Xe atom performed the best initially. Zeolites with narrow pore channels with spots along the pore wall with high local surface area are the best performers across all loadings.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Alongside activated carbons and metal-organic frameworks (MOFs), zeolites represent a major family of adsorbents critical to non-cryogenic gas separation technologies [1–3]. Zeolites have been shown to be useful in numerous separation applications, such as CO₂/CH₄ [4–8], N₂/O₂ [9–13], and CO₂/N₂ [14–20].

Our group is studying the non-cryogenic separation of Kr and Xe through pressure-swing adsorption (PSA) [21,22] and related techniques. Development of a viable process has implications for two separations of interest. The first is the final separation of Kr and Xe from air; this mixture has an 80:20 Kr:Xe molar ratio after the noble gases have been isolated. The other process of interest is encountered during processing of spent radioactive fuel [23,24]. Once all other gases are purged, the noble gas fraction consists of 90:10 Xe:Kr. As the Xe present in fission gas has no radioactive isotopes with half-lives longer than 30 days, Xe is expected to contain essentially no radioactive isotopes at the time of separation. In the Kr fraction however, some radioactive Kr⁸⁵ is present. Storage of the entire mixture is impractical when only the Kr fraction needs to be sequestered. In addition, this separation could serve as a new source for commercial Xe which has a very high cost \$5000/L owing

to its rarity as a minor byproduct from cryogenic distillation of air. Cryodistillation is prohibitively expensive due to high cost and large space requirements associated with the necessary equipment, making PSA an attractive method to accomplish this separation.

Zeolites present several advantages for a practical separation compared to MOFs. A number of zeolite adsorbents are available commercially. The majority of these are inexpensive, stable, less toxic, and well-characterized for large-scale use. In comparison to MOFs, zeolites tend to be more robust materials. This is a particularly useful trait when separating radiowaste that will constantly be emitting high energy decay particles that would damage or destroy most MOFs. The challenge for selecting a gas adsorbent among zeolites lies in determining which framework topology, composition, and extra-framework cation(s) provide ideal adsorption properties for the specific separation. Currently 229 topologies are recognized by the IZA [25]. While this number is much lower than for MOFs, most zeolites may be synthesized over a range of Si/Al ratios and their adsorption properties may be further altered by ion exchange, leading to a very large number of potential adsorbents.

A purely experimental approach to searching for adsorbents is not optimal for several reasons. Assessing one specific zeolite is labor intensive in terms of synthesis, ion exchange, characterization, and extended gas adsorption analysis. Even when a zeolite is found to be promising, it is generally not clear from the initial experimental data why that specific zeolite exhibits good selectivity without performing additional experiments such as *in-situ*

* Corresponding author.

E-mail address: Paul.Forster@unlv.edu (P.M. Forster).

crystallography with gas loading. Without an atomistic picture of gas adsorption, it is not straightforward to take a positive result for one adsorbent and use that information to select better adsorbents. Using modeling techniques such as grand canonical Monte Carlo (GCMC), an atomistic picture of adsorption can be acquired which leads to an understanding of the adsorption behavior in materials known to perform well for certain separations, guiding the search for better adsorbents.

Recent work on heavy noble gas separations by our group and others have previously studied MOF materials for Kr/Xe separation. Across a range of MOFs, large selectivities are consistently associated with smaller pores or pockets of comparable size to Xe [26–39]. From this observation, we were able to target structures with such adsorption sites for study, and determined that a family of porous transition α -metal formates show both reasonable capacity and consistently high selectivities over a wide range of loadings [36]. Recently, an impressive screening study was performed that screened 670,000 different known and hypothetical porous zeolites, MOFs, ZIFs, PPNs, and COFs for their selectivity at an initial loadings of an 20:80 mixture of Xe:Kr at room temperature [40]. Their results supported the conclusion that topologies with smaller pores and pockets that maximized interaction with Xe had improved Xe selectivities, and one of their top performers is SIZ-3 (CSD code: JAVTAC) which is an AlPO-11 (AEL) zeolite analogue [41].

Zeolites exist across a range of compositions with the simplest possible form containing only Si and O. A significant number of zeolites have been synthesized in either purely siliceous forms, or very high silica compositions where the siliceous form would provide a reasonable approximation of the zeolite's behavior. While siliceous zeolites are a natural point to begin modeling efforts, they may well represent practical adsorbents as well. Since they are hydrophobic, they are particularly stable and robust, may be activated and reactivated under simple conditions, and are relatively tolerant to trace water during separations. As adsorbents, they may offer good selectivity through dispersive interactions for Kr and Xe, which have no standing multipolar moments to strongly interact with cations. In contrast, the separation of N₂ and O₂ is best done in zeolites with small, highly charged cations (Li, Mg, Ca) because of the four-fold difference in standing quadrupole moment of the two gases.

A vital part of studying Kr/Xe adsorption in the vast family of zeolites is developing a transferable description of adsorption into the pure TO₂ frameworks. Here we develop such a model which we show can generally predict gas adsorption isotherms to excellent agreement with experiment. We then apply the model to all 229 siliceous zeolites to determine their ability to separate 90:10 Xe:Kr across the range of loadings relevant to an actual PSA process.

2. Experimental

We obtained a sample of calcined and activated siliceous LTA (ITQ-29) from Avelino Corma's group [42]. We obtained a sample of siliceous FAU from Joseph Hriljac [43]. We obtained a sample of siliceous BEA from Dr. Laszlo Nemeth that was synthesized, calcined, activated, and characterized using a modification of a previously published procedure with tetraethylorthosilicate as the only silica metal source [44]. About 150 mg of each sample was initially activated under dynamic turbopump vacuum at 400 °C for 24 h. Gas adsorption isotherms were measured according to our previously published procedure [35] using a Micromeritics ASAP 2020 instrument fitted with a He cryostat with a stability of better than ± 0.01 K. Isotherms were collected up to ~ 710 mmHg with 5 cm³/g incremental volumetric doses and long equilibration times. Desorption measurements were taken at the end of each isotherm.

Each measurement displayed negligible hysteresis, indicating equilibrium had been achieved. Samples were reactivated for an hour under dynamic vacuum at 150 °C and allowed to equilibrate in the cryostat for an hour between each measurement. Kr isotherms were measured at 230 K, 240 K, and 250 K. Xe isotherms were measured at 280 K, 290 K, and 300 K. The Clausius–Clapeyron equation was used to obtain isosteric heats of adsorption.

3. Simulation

3.1. GCMC details

Gas adsorption was simulated with Monte Carlo in the grand canonical ensemble using the multi-component Peng–Robinson equation of state for fugacities [45–48]. GCMC simulations were done with a modified version of the MUSIC package [49]. The binary mixing parameters are found using the form of Coutinho et al. [50]. In addition to the normal GCMC moves, swap and exchange moves were added to improve equilibration in the binary gas simulations [51–53]. Each simulation employed 200,000 equilibration cycles and 300,000 production cycles. A cycle here consists of N moves, where N is the number of adsorbed particles (minimum 20). The zeolites are held as rigid during the simulations.

We carefully considered potential options for obtaining crystal structures for the 229 zeolites. While experimental structures are attractive in some respects, they are not available for the majority of SiO₂ zeolites and vary in accuracy. For a comparative screening effort, we anticipate that a self-consistent set of structures would provide the best means of comparing zeolitic topologies directly. Computational lattice energy minimization is particularly well-developed in the case of SiO₂ zeolites, and should provide reasonably accurate structures that are fully self-consistent with each other. We used structures taken from the IZA-SC Database of Zeolite Structures [25]. Those structures were optimized using the DLS76 program for a pure SiO₂ composition in a pre-dominant symmetry of the zeolite. Some of the frameworks (CHI, CLO, EWT, IRY, ITN, ITV, LIT, PAR, RON, SSO, SVR, and WEN) are acknowledged by the IZA-SC as interrupted frameworks that cannot be made as four-connected frameworks (stoichiometrically SiO₂) and therefore have dangling oxygens around the broken tetrahedra. For these frameworks, Olex2 was used to place the hydrogens to form silanol groups to terminate the dangling oxygens which would be the calcined form of the framework [54]. The hydrogen positions in the primitive cell were refined with a selective dynamics plane-wave density functional theory [55,56] optimization with the Vienna ab-initio Simulation Package 5.3.5 (VASP) using the projector-augmented wave (PAW) [57] method and the generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) [58]. Just the Γ point was used to describe k-space. The WEN structure in the database does not include the experimental disorder and omits two of the would be silanol oxygens. To solve this, we constructed both symmetry inequivalent forms of the originally reported WEN experimental crystal structure, and the lower energy 'trans' form is used in the screening [59].

The internal energy was found using the following energy expression: $U = U_{\text{framework-fluid}} + U_{\text{pol}} + U_{\text{fluid-fluid}}$. Table 1 includes all of the single species parameters used in this work. The framework-fluid potential was computed using a 12-6 Lennard-Jones with a low cutoff of 1.5 Å and a high cutoff at 15 Å. The atomic parameters for the framework-fluid potential are from the first two sections of Table 1 and combined using the Lorentz-Berthelot mixing rules. The framework Si and O parameters come from the recently developed TraPPE-zeo force field [60], and the silanol hydrogen parameters are taken from ClayFF with the charge lowered to ensure charge neutral unit cells [61]. The Kr and Xe

Download English Version:

<https://daneshyari.com/en/article/72037>

Download Persian Version:

<https://daneshyari.com/article/72037>

[Daneshyari.com](https://daneshyari.com)