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

Keith V. Lawler¹, Amit Sharma¹, Breetha Alagappan¹, Paul M. Forster^{1,*}

Abstract

All 229 identified zeotype frameworks are screened in their siliceous form by grand canonical Monte Carlo simulation for their ability to separate a radio-chemically 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 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.

Keywords: Zeolites, Selectivity, Gas Adsorption, Gas Separation, Grand Canonical Monte Carlo

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, 2, 3] Zeolites have been shown to be useful in numerous separa-

*Corresponding author

Email address: Paul.Forster@unlv.edu (Paul M. Forster)

¹University of Nevada Las Vegas, Department of Chemistry, Las Vegas, NV 89154-4003, USA

tion applications, such as CO_2/CH_4 , [4, 5, 6, 7, 8] N_2/O_2 , [9, 10, 11, 12, 13] and CO_2/N_2 . [14, 15, 16, 17, 18, 19, 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 in two separations of interest. The first is the final separation of Kr and Xe from air; this mixture has a 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, noble gas fraction consists of 90:10 Xe:Kr. As Xe has no 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 Kr^{85} 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
 40 the initial experimental data why that specific zeolite exhibits good selectivity without performing additional experiments such as in-situ 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 modelling techniques such as grand canonical Monte Carlo (GCMC), an atomistic picture of adsorption can be acquired
 45 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
 50 MOFs, large selectivities are consistently associated with smaller pores or pockets of comparable size to Xe.[26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 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
 55 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 inter-
 60 action 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
 65 siliceous form would provide a reasonable approximation of the zeolite’s behavior. While siliceous zeolites are a natural point to begin modelling 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.

70 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.

75 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
80 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
85 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 hours. Gas adsorption isotherms were measured according to our previously published procedure[35] using a Mi-
90 cromeritics 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
95 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.

100 **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, 46, 47, 48] GCMC simulations were done with a modified version of the MUSIC
105 package.[49] The binary mixing parameters are found using the form of Coutinho et al.[50] In addition to the normal GCMC moves, a swap and exchange moves were moved to improve equilibration in the binary gas simulations.[51, 52, 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
110 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 struc-
115 tures 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
120 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 tetrahe-

dra. 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 sym-
metry inequivalent forms of the originally reported WEN experimental crystal
structure, and the lower energy ‘trans’ form is used in the screening.[59]

*** Table 1 about here ***

The internal energy was found using the following energy expression: $U = U_{framework-fluid} + U_{pol} + U_{fluid-fluid}$. 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 forcefield, [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 parameters were found using the principle of corresponding states using
the Ar parameters of Talu and Myers[62] and the critical parameters from the
CRC[63] as the starting point. Explicit fluid point dipole polarizability was
included as “ U_{pol} ” using the polarizability volumes in table 1.[1] The electric
field is computed with the Wolf Coulomb potential truncated at 15 Å, a damping
parameter of 0.1 Å⁻¹, and both the force and potential shifted.[64, 65, 66, 67] In
our own experiments, we have found that high loading regimes of isotherms for
Kr and Xe are better modeled with a 9-6 Lennard-Jones potential, therefore the
fluid-fluid potential interactions were modeled with the 9-6 fluid COMPASS[68]

force field (last section of table 1) cutoff at $15\text{\AA}$ and combined with 6^{th} order mixing rules.

3.2. Mapping the pore volume

In zeolites there are pores that are known experimentally to be accessible to
 160 guests while there are cages that are kinetically inaccessible. To correctly model
 the accessible volume within a zeolite, we developed our own void volume map-
 ping program which is very similar to a recently developed program.[69] Our
 program lays down a uniform grid of parallelepiped voxels laid in each crystallo-
 graphic dimension, evaluates the energy of the adsorbate-framework Lennard-
 165 Jones interaction for the center of each voxel, and uses a six way (no diagonal
 connections) 3-D flood fill algorithm connecting neighboring points that allows
 for the crossing of periodic boundaries. If a voxel has an energy below a certain
 threshold it is initially considered accessible and could be connected to other
 voxels; otherwise it is considered as belonging to the volume of the framework
 170 and could not be connected to other voxels. A void was determined to be part
 of a pore network if a path within the connected void volume made from 0
 to 1 along any crystallographic dimension including crossing other dimension's
 PBCs, if no such path could be made that connected volume was considered a
 closed-off cavity. Our pore volumes are taken as the sum of the volume of all
 175 accessible parallelepipeds. We found that a grid spacing of $0.15\text{\AA}$ and an energy
 cutoff of $+14\text{ kcal/mol}$ was sufficiently small to close off all CBUs that should be
 considered inaccessible. The pores produced in this manner have accessible pore
 volumes that typically agree to within 0.5% of those presented in the IZA-SC
 database.[70]

180 The GCMC moves were modified to have an auxiliary move rejection for use
 with the void maps. If the move placed the center of mass of the particle in a
 voxel within an open pore, the move is accepted by the conventional Metropolis
 algorithm. If the voxel is not part of an open pore, then the GCMC program
 checks whether the voxel is less than a certain number of voxels away (including
 185 diagonally). If any of the checked voxels are open, the move is accepted by the

conventional Metropolis algorithm; otherwise the move is outright rejected. We used a depth of 3 voxels away to resemble a translation move that has walked the particle into the wall of a framework.

4. Results and Discussion

190 4.1. Benchmarking a model chemistry

*** Figure 1 about here ***

To screen all of the siliceous zeolites for their ability to separate Kr/Xe, an appropriate parametrization needs to be done against experimental single gas adsorption data. Figures 1 and 2, and 3 contain our experimental and
 195 simulated isotherms and heats of adsorption for LTA, BEA, and FAU plotted on the same scales for easy visual comparison. The simulated heats of adsorption were found using fluctuation theory at the same median temperature used in the determination of the experimental heats of adsorption. It is important to carefully select the 12-6 Kr/Xe parameters for the framework-fluid interaction
 200 to correctly model the Henry’s law region of the isotherm. Very good results have been observed in MOFs using force fields derived from the two-parameter principle of corresponding states ($\epsilon \propto T_c$ and $\sigma \propto V_c^{1/3}$).[62] We found that the Kr force field produced in this matter predicted the HOA very well but under-predicted adsorption for these zeolites. To improve the fit, we increased
 205 the value of ϵ within 3 significant figures until a reasonable fit was found. Table 1 contains the determined force field parameters and the critical parameters.[63] We have also found that the softer repulsion term of a 9-6 Lennard-Jones for fluid-fluid interactions works well to describe the whole experimental Kr/Xe isotherm at higher loadings.[71] That result is the same here as a significant
 210 underestimation of adsorption at higher pressure (especially for Xe) when the same 12-6 potential used to build the fluid-framework interactions is used for the fluid-fluid interactions.

*** Figure 2 about here ***

BEA is known to be polymorphic, and we only performed simulations using the structure of polymorph A, the most representative polymorph. Given the similarity between the BEA polymorphs, we did not anticipate large differences with this approximation, as confirmed by the close agreement encountered. FAU is known to be a difficult material to produce in its siliceous form, as the process require dealumination and can lead to mesoporosity and aggregates of amorphous silica. This FAU sample seems to be high quality as a 77K N₂ pore size distribution (over the default range in the Micromeritics software) is trimodal, which is in line with the three primary topological features of FAU: the α cage (t-fau), sod(t-toc) the sodalite or β cage, and d6r (t-hpr) connecting the sodalite cages. The agreement between the FAU HOAs is of comparable quality to that of LTA and BEA, however the simulation model under-predicts total adsorption by 5-10%. We believe the discrepancy arises from two factors: the mass of the measured sample being too low giving too high measured quantities adsorbed, and the COMPASS fluid-fluid parameters being too weak as FAU is a large pore system where correctly describing fluid-fluid interactions will be more critical.

*** Figure 3 about here ***

The finalized model we employed yields excellent agreement for the isotherm and heat of adsorption for both gases at all tested temperatures. The predicted and measured heats of adsorption are both fairly flat, as expected of the relatively homogenous surface inside these zeolites. What is surprising is the similarity of the predicted heats of adsorption for Kr and Xe in both materials. A lack of small accessible pockets in the cells and a surface covered in 4-ring to 6-ring provides an easy explanation for the flatness and similarities in the heats of adsorption between these materials. The difference in heat of adsorption is consistent across all loadings which we have shown indicates a fairly uniform Xe/Kr selectivity at all loadings will be observed. We recognize that our approach neglects structural changes in response to gas uptake, as are known to occur in MFI, for example.[72, 73] However, the initial selectivities obtained from our calculations should still be valid.

245 *4.2. Screening the zeolites*

We carried out our screening at 298 K at five pressures on a logarithmic scale spanning the Henry’s law region (1 mmHg) to PSA useful pressures (10,000 mmHg). In table 1 of the Supplementary Information, we plot 1) the percent accessible pore volume of the framework, 2) the total loading at each point, 3) and the Xe/Kr selectivity at each point.

*** Figure 4 about here ***

Figures 4 and 5 summarize the screening results for both the initial adsorption (1 mmHg) and high loading (10,000 mmHg). The selectivities presented are for Xe over Kr, and the material’s percent accessible pore volume is used to shade the plotted points. In figure 4, a strong correlation between total loading and selectivity is evident, persisting to high loadings although with considerably more scatter. At low loadings, quantity adsorbed is primarily determined by the affinity of the zeolite for noble gases - frameworks with high HOAs for Kr and Xe also tend to have high selectivities. It is promising that zeolites with the highest selectivities tend to have relatively high adsorption for Kr and Xe as well. It is noteworthy that 10 zeolites have selectivities in excess of 10 - a value comparable to the most promising MOFs studied so far. At higher pressures, the zeolites stratify dramatically, as can be seen in figure 5. The zeolites with relatively low capacity (20-60 cm³/g) tend to be the most selective which is mainly due to a narrow small pore system. The zeolites with large capacity (≥ 100 cm³/g) are only moderately selective (~ 4 , the same as observed for HKUST-1 at high loadings). This is to be expected for large pore systems as they have space to accommodate large amounts of noble gas, but most of that gas cannot come into close enough contact with the unique framework topologies that provide sufficient dispersive interactions and to make the material selective.

*** Figure 5 about here ***

For some separations, a selectivity in favor of Kr is desirable. A recent review of MOF applicability to this problem highlighted FMOFCu, which could go from being Xe selective to Kr selective by lowering the temperature below 0 °C.[74] A few siliceous zeolites appear selective for Kr (Xe/Kr selectivity

less than 1), but none appear practical overall. At 298 K, four Kr-selective materials exhibited reasonable total gas loadings ($\geq 40 \text{ cm}^3/\text{g}$), yet they are only slightly selective for Kr. More selective frameworks all have low porosity and either modest uptake or low Kr selectivity at the highest pressures measured.

280 Additional simulations at a lower, yet potentially realistic PSA temperature (250 K), were performed to see if the loadings of the Kr selective materials could be improved. Table 2 shows the results for quantity adsorbed and Kr selectivity at the highest loading point (10,000 mmHg) for both temperatures evaluated. When cooled, the quantity adsorbed improved by no more than a
 285 factor of 5 for each of the zeolites examined. The Kr selectivity did not change appreciably for any materials with reasonable loadings. Remarkably high Kr selectivity is suggested in several topologies, including CHI and NPO, but the predicted total uptake is so small that these materials would be impractical for applications. Our simulations strongly suggest no siliceous zeolites would be
 290 competitive with FMOFCu.

*** Table 2 about here ***

Figure 6 shows a strong correlation between the initial selectivities compared against the difference in the Xe and Kr heats of adsorption into the material. The heats of adsorption were computed with multi-component fluctuation
 295 theory.[75] There appears to be a maximal initial selectivity possible for a given difference in initial HOA, although many materials show lower selectivities than this. Normalizing the difference in heat of adsorption to either the Kr, Xe, or total heat of adsorption does not yield a more linear or tightly correlated data set. The same effect is observed at all loadings with a similarly narrow spread
 300 in the results. This plot directly demonstrates the established rule of thumb for using single gas adsorption measurements to estimate a material’s selectivity. Figure 6 indicates that, for a material to have a Xe selectivity ≥ 10 , the difference in heat of adsorption needs to be at least $\geq 8 \text{ kJ/mol}$.

*** Figure 6 about here ***

305 Compiling the most selective materials at the both initial and high loadings, we selected 23 frameworks for more detailed study: AFO, **ATN**, ATO, BOF,

CAN, **CDO**, EAB, EDI, EON, EPI, ESV, **FER**, **LAU**, LTF, MAZ, **MRE**, MTF, OFF, OWE, **PCR**, **PSI**, UFI, and **ZON** (those in bold are among the most selective at both initial and final loading). Examining these structures, we
 310 have identified two different sets of adsorption behavior that correspond with distinct structural motifs responsible for the high selectivity. The first category of selective zeolite frameworks, comprising the majority of the best performers, exhibits flat or slightly increasing selectivity and is associated with a narrow pore system. The remaining highly selective zeolites exhibit a high initial selectivity
 315 which drops, often dramatically, as loading increases. This type of behavior is associated with the presence of small pockets capable of adsorbing a single gas atom that are accessible off larger channels.

The first group, where selectivities increase or remain nearly constant as a function of loading, contain narrow pore systems. Snurr and coworkers, conducting a survey of 134,000 hypothetical MOFs, concluded that this mechanism
 320 lead to the best selectivities for this separation.[29] We later showed that porous transition metal formates exhibit among the highest selectivities Kr/Xe selectivities reported, and that this selectivity gently improves with increased loading, due to this mechanism.[36] This result was further enforced by a recent survey of 670,000 materials by Smit and co-workers, which did analyze the IZA
 325 zeolites but only for initial selectivity.[40] ATN is an example of a narrow channel pore system with 1-D ~ 6 Å diameter pores. The Xe loading is centralized in the t-ocn (atn) composite building unit (CBU) maximizing the Xe atoms dispersion interaction with the 2 8-ring windows of the t-ocn (figure 7). The
 330 constricted pores provide a site (or sites) with a large amount of contact between the pore wall and the adsorbed gas, leading to high dispersive interactions good selectivity.[29, 36, 40] Typically, only one or several crystallographically distinct gas adsorption sites are present in compounds with this type of adsorption. If only one site is present, the only energetic difference between the first
 335 gas molecule to adsorb and the last are fluid-fluid interactions, resulting in a gradual increase in HOA and selectivity. While slightly more complicated, similar overall behavior generally occurs when several adsorption sites are present,

especially with the sites are chemically similar. 8-ring pores are common in this group with examples of cylindrical, elliptical or zig-zag cross sections. 10-ring pores tend to be distorted. The zeolites EPI, ESV, MTF, and OWE show fall-offs in selectivity at high loadings. OWE and EPI are 2-dimension materials with limited wall surface for adsorption whereas ESV and MTF have undulating pore volumes that resemble a series of pockets connected by smaller windows. As these features saturate, the decrease in selectivity is observed.

*** Figure 7 about here ***

The second category of topological features leading to high selectivity are small pockets or secondary pores connected to larger pores. Features comparable in size to Xe provide a region with very high dispersive interactions favoring Xe. We have previously shown that this is the mechanism behind high initial HOAs and selectivities for Kr and Xe in HKUST-1, but that it also leads to lower HOAs and selectivities at higher loadings. In our survey, this mechanism leads to the highest initial selectivities, but these may not be ideal adsorbents for PSA-type processes as the selectivities drop as loading increases. We illustrate this mechanism with UFI, which has the highest predicted initial selectivity for siliceous zeolites. UFI has a 2D pore system consisting of large lta cages connected through 8-ring pores. A number of t-ufi cages are accessible through this pore system; this is where the simulations show gas density building up at low loadings (figure 8). This is analogous to the mechanism for high initial selectivity observed in HKUST-1.[35]

*** Figure 8 about here ***

Figure 9 shows the results from the more thorough selectivity simulations for each of the top zeolites as a function of percent loading, with 100% defined as the respective loading at 10,000 mmHg. As all of the simulated adsorption data has been corrected to reflect the excess adsorption, a turnover in the isotherm should be expected when the density of the adsorbed fluid very closely matches that of the bulk fluid.[76] By collecting some data points beyond 10,000 mmHg, we have determined that this turnover occurs around 10,000 mmHg in almost all of these zeolites thus indicating the loading at 10,000 mmHg is close to the

asymptotic limit. The results have been divided into two sets corresponding to
370 either narrow pores or cavities off larger pores, and for visual clarity the narrow
pore materials have been further sub-divided based off of their loading at 10,000
mmHg. Note that the noise at low loadings is due to very low total Kr uptake.

*** Figure 9 about here ***

Each of the materials with a small pocket adsorption mechanism are shown
375 in figure 9a. In these materials, small cages accessible from larger channels result
in high initial selectivities as these pockets fill. Once the majority of the pockets
have filled, larger fractions of adsorbed gas atoms occupy less selective sites in
the larger pores, leading to lower selectivities at higher loadings. For example,
the t-ufi cages in UFI are nearly saturate at 10-20% of the total possible loading.
380 Once the t-ufi cages are close to saturated, the majority of the adsorption occurs
in the t-grc cages. These t-grc cages are not expected to be as selective based on
our screening results for LTA, which only can adsorb into t-grc CBUs and has
a selectivity of ~ 4.5 at all loadings. Interestingly enough, UFI had the highest
capacity of any of the zeolites closely examined at $88.0 \text{ cm}^3/\text{g}$. An exception to
385 dramatically falling selectivities is EAB where the selectivity remains essentially
flat across all selectivities studied. As EAB contains large channels that connect
smaller t-gme pockets off the main pores, this behavior came as a surprise.
Examining predicted adsorption sites, Xe indeed occupies the t-gme pocket as
anticipated, but also occupies two well-defined sites in the larger t-eab cavities
390 of the main pore. This is the only instance we are aware of where a pocket large
enough to accommodate two Xe atoms provides comparable selectivities to a
pocket which only accommodates one.

The GCMC results presented above represent a significant step towards iden-
tifying zeolitic adsorbents for practical separations, although more than was
395 determined above will ultimately be required. Practical adsorbents need to be
available economically and show reasonable kinetics. While the selectivities as
over useful loading ranges are most promising with narrow pore zeolites, these
zeolites may also show much lower adsorption/desorption kinetics compared
with zeolites containing larger pores and selective pockets. EAB represents a

400 potentially important framework as it has both large channels, which should
lead to superior kinetics, and also flat selectivity at all loadings. Further experi-
mental studies are needed to determine whether these zeolites would be practical
in real-world separations.

We are also well-aware that most zeolite frameworks have not been syn-
405 thesized in purely siliceous forms. To our surprise, a number of zeolites do
exhibit selectivities that are competitive with the best MOF adsorbents stud-
ied so far. One of the promising structures to emerge from this effort is FER,
which is well-known in a pure silica form. Other frameworks (e.g. MRE, UFI)
occur in high Si/Al ratios, as germanosilicates (e.g. PCR), or as an AIPO (e.g.
410 ATO, ZON), where performance may be comparable to the pure silica form.
The promising germanosilicates and pure AIPO results here should be trans-
ferable as they have no mobile cations, the dispersion interactions should be
similar (especially if the T-atom approximation is made), and the distribution of
framework partial charges will have little effect on the adsorption of noble gases
415 as polarizability only accounted for 1-2% of the total energetics in this study
(owing to the cancellation of electric fields caused by neighboring charges). Ad-
ditionally, H-exchanged versions of these frameworks are likely to offer similar
overall performance. Even in cases where compounds resembling the SiO₂ form
do not exist, such frameworks remain promising for follow-up studies where mo-
420 bile cations are present. A final substantial advantage that siliceous zeolites have
over aluminosilicates is that they are sufficiently hydrophobic that separations
could be run in the presence of humidity without need for periodic reactivation.

The screening results presented here are a first step towards screenings with
cations present. For realistic results from such screenings, cation mobility must
425 be included, which represents a considerable challenge on its own. Good agree-
ment between our experimental and simulated data on several SiO₂ structures
provides important validation that our model is indeed sufficiently accurate.
The screening has also provided important clues as to which frameworks may
be promising as cations are included in later simulations. Finally, in order to cor-
430 relate our results with the recent study by Smit,[40] we compared our predicted

performance for air separation ($\text{Xe/Kr} = 20:80$) to results for the radiochemical separation. The Xe selectivities remained comparable, except in compounds showing high selectivity due to small pockets, where the high loading selectivity greatly improved for the 20:80 ratio. Figures are presented in the SI.

435 5. Conclusions

An initial screening demonstrated that many siliceous zeolites have promise for a Kr/Xe separation. In the case of EAB, EON, LTF, MAZ, OFF and UFI, a high initial selectivity results from the presence of a small cage off of the main pore system that is about the right size to adsorb a single Xe atom. However
 440 these small cages quickly saturate with increased gas loading. Zeolites with only small cages are expected to have limited utility as practical PSA sorbents as their selectivity is limited by the adsorption into the small cages. The most promising zeolites for selective Xe adsorption at PSA relevant pressures were ones that contained narrow pore systems with either zig-zags or elliptical cross
 445 sections. We suggest the most promising topologies for further study are CDO, MRE, and PSI as they have selectivities greater than 10 at all loadings and high capacities. CDO, FER, MRE, and MTF are of particular interest as these frameworks can be made as pure SiO_2 . AFO, ATO, PSI, and ZON are also of interest as they can be made as pure AlPOs to test the transferability of the
 450 pure silica results.

It is also important to note that a good parametrization of the force field is essential to using multi-component GCMC as a screening tool. TraPPE-zeo provides an excellent transferable description of fluid-framework interactions. The fluid-fluid interactions need to be correctly modeled to get good isother-
 455 mal agreement at both low and high loadings, in particular for Kr/Xe a softer repulsion term than that of a 12-6 Lennard-Jones is needed. This problem is not unique to this work, and can be seen in many of the previously published Kr/Xe adsorption isotherms into MOFs and zeolites. In the future, we intend to extend our findings to some of the more complex zeolitic topologies, i.e. cation

460 containing aluminosilicates, and to include framework flexibility to better describe materials known to distort on adsorption like MFI.

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References

- 470 [1] J.-R. Li, R. J. Kuppler, H.-C. Zhou, Selective gas adsorption and separation in metal-organic frameworks, *Chem. Soc. Rev.* 38 (5) (2009) 1477–1504. doi:10.1039/B802426J.
- [2] J.-R. Li, J. Sculley, H.-C. Zhou, Metal-organic frameworks for separations, *Chem. Rev.* 112 (2) (2012) 869–932. doi:10.1021/cr200190s.
- 475 [3] P. K. Thallapally, J. W. Grate, R. K. Motkuri, Facile xenon capture and release at room temperature using a metal-organic framework: a comparison with activated charcoal, *Chem. Commun.* 48 (3) (2012) 347–349. doi:10.1039/C1CC14685H.
- [4] M. Palomino, A. Corma, F. Rey, S. Valencia, New insights on co₂-methane
480 separation using lta zeolites with different si/al ratios and a first comparison with mofs, *Langmuir* 26 (3) (2009) 1910–1917. doi:10.1021/la9026656.
- [5] M. Palomino, A. Corma, J. L. Jordá, F. Rey, S. Valencia, Zeolite rho: a highly selective adsorbent for co₂/ch₄ separation induced by a structural phase modification, *Chem. Commun.* 48 (2012) 215–217. doi:10.1039/C1CC16320E.
485

- [6] J. Kim, A. Maiti, L.-C. Lin, J. K. Stolaroff, B. Smit, R. D. Aines, New materials for methane capture from dilute and medium-concentration sources, *Nat. Commun.* 4 (2013) 1694. doi:10.1038/ncomms2697.
- [7] L. Ohlin, P. Bazin, F. Thibault-Starzyk, J. Hedlund, M. Grahm, Adsorption of co₂, ch₄, and h₂o in zeolite zsm-5 studied using in situ atr-ftir spectroscopy, *J. Phys. Chem. C* 117 (33) (2013) 16972–16982. doi:10.1021/jp4037183.
- [8] F. Gholipour, M. Mofarahi, Gas adsorption separation of co₂/ch₄ system using zeolite 5a, *Microporous Mesoporous Mater.* 200 (2014) 1–10. doi:10.1016/j.micromeso.2014.08.022.
- [9] S. P. Nandi, P. L. Walker Jr., Separation of oxygen and nitrogen using 5a zeolite and carbon molecular sieves, *Sep. Sci. Technol.* 11 (5) (1976) 441–453. doi:10.1080/01496397608085334.
- [10] J. Cejka, H. van Bekkum, A. Corma, F. Schueh, *Introduction to Zeolite Molecular Sieves*, Elsevier, 2007.
- [11] P. Li, F. H. Tezel, Adsorption separation of n₂, o₂, co₂ and ch₄ gases by β -zeolite, *Microporous Mesoporous Mater.* 98 (1-3) (2007) 94–101. doi:10.1016/j.micromeso.2006.08.016.
- [12] H. Karge, J. Weitkamp (Eds.), *Molecular Sieves: Science and Technology*, Vol. 7, Springer, 2008.
- [13] V. J. Inglezakis, A. A. Zorpas (Eds.), *Handbook of Natural Zeolites*, Bentham Science, 2012.
- [14] E. D. Akten, R. Siriwardane, D. S. Sholl, Monte carlo simulation of single- and binary-component adsorption of co₂, n₂, and h₂ in zeolite na-4a, *Energy Fuels* 17 (4) (2003) 977–983. doi:10.1021/ef0300038.
- [15] R. Siriwardane, M.-S. Shen, E. P. Fisher, Adsorption of co₂, n₂, and o₂ on natural zeolites, *Energy Fuels* 17 (2003) 571–576. doi:10.1021/ef0201351.

- [16] M. P. Bernal, J. Coronas, M. Menéndez, J. Santamariá, Separation of co₂/n₂ mixtures using mfi-type zeolite membranes, *AIChE J.* 50 (1) (2004) 127–135. doi:10.1002/aic.10012.
- [17] X. Gu, J. Dong, T. M. Nenoff, Synthesis of defect-free fau-type zeolite membranes and separation for dry and moist co₂/n₂ mixtures, *Ind. Eng. Chem. Res.* 44 (4) (2005) 937–944. doi:10.1021/ie049263i.
- [18] E. García-Pérez, J. B. Parra, C. O. Ania, A. García-Sánchez, J. M. van Baten, R. Krishna, D. Dubbeldam, S. Calero, A computational study of co₂, n₂, and ch₄ adsorption in zeolites, *Adsorption* 13 (2007) 469–476. doi:10.1007/s10450-007-9039-z.
- [19] B. Liu, B. Smit, Comparative molecular simulation study of co₂/n₂ and ch₄/n₂ separation in zeolites and metal-organic frameworks, *Langmuir* 25 (10) (2009) 5918–5926. doi:10.1021/la900823d.
- [20] M. Fischer, R. G. Bell, Influence of zeolite topology on co₂/n₂ separation behavior: Force-field simulations using a dft-derived charge model, *J. Phys. Chem. C* 116 (50) (2012) 26449–26463. doi:10.1021/jp3099768.
- [21] R. T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley, Hoboken, NJ, 2003. doi:10.1002/047144409X.
- [22] S. Sircar, Basic research needs for design of adsorptive gas separation processes, *Ind. Eng. Chem. Res.* 45 (16) (2006) 5435–5448. doi:10.1021/ie051056a.
- [23] J. Izumi, Waste gas treatment using zeolites in nuclear-related industries, in: S. Auerbach, K. Carrado, P. Dutta (Eds.), *Handbook of Zeolite Science and Technology*, Marcel Dekker, New York, 2003. doi:10.1201/9780203911167.ch20.
- [24] N. R. Soelberg, T. G. Garn, M. R. Greenhalgh, J. D. Law, R. Jubin, D. M. Strachan, P. K. Thallapally, Radioactive iodine and krypton control for

- 540 nuclear fuel reprocessing facilities, *Sci. Technol. Nucl. Install.* 2013 (2013) 702496. doi:10.1155/2013/702496.
- [25] International zeolite association-structure commission database of zeolite structures [cited June 5, 2014].
URL <http://www.iza-structure.org/databases/>
- 545 [26] U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, Metal-organic frameworks—prospective industrial applications, *J. Mater. Chem.* 16 (7) (2006) 626–636. doi:10.1039/B511962F.
- [27] R. Bazan, M. Bastos-Neto, A. Moeller, F. Dreisbach, R. Staudt, Adsorption equilibria of o₂, ar, kr and xe on activated carbon and zeolites: single
550 component and mixture data, *Adsorption* 17 (2010) 371–383. doi:10.1007/s10450-011-9337-3.
- [28] P. Ryan, O. K. Farha, L. J. Broadbelt, R. Q. Snurr, Computational screening of metal-organic frameworks for xenon/krypton separation, *AIChE J.* 57 (7) (2011) 1759–1766. doi:10.1002/aic.12397.
- 555 [29] B. J. Sikora, C. E. Wilmer, M. L. Greenfield, R. Q. Snurr, Thermodynamic analysis of xe/kr selectivity in over 137,000 hypothetical metal-organic frameworks, *Chem. Sci.* 3 (7) (2012) 2217–2223. doi:10.1039/C2SC01097F.
- [30] T. Van Heest, S. L. Teich-McGoldrick, J. A. Greathouse, M. D. Allendorf, D. S. Sholl, Identification of metal-organic framework materials for ad-
560 sorption separation of rare gases: Applicability of ideal adsorbed solution theory (iast) and effects of inaccessible framework regions, *J. Phys. Chem. C* 116 (24) (2012) 13183–13195. doi:10.1021/jp302808j.
- [31] J. Liu, P. K. Thallapally, D. M. Strachan, Metal-organic frameworks for removal of xe and kr from nuclear fuel reprocessing plants, *Langmuir* 28 (31)
565 (2012) 11584–11589. doi:10.1021/la301870n.

- [32] C. A. Fernandez, J. Liu, P. K. Thallapally, D. M. Strachan, Switching kr/xenon selectivity with temperature in a metal-organic framework, *J. Am. Chem. Soc.* 134 (22) (2012) 9046–9049. doi:10.1021/ja302071t.
- [33] M. Parkes, C. Steiger, J. Perry, IV, M. Allendorf, J. Greathouse, Screening
570 metal-organic frameworks for selective noble gas adsorption in air: effect of pore size and framework topology, *Phys. Chem. Chem. Phys.* 15 (2013) 9093–9106. doi:10.1039/c3cp50774b.
- [34] Y.-S. Bae, B. G. Hauser, Y. J. Colon, J. T. Hupp, O. K. Farha, R. Q. Snurr, High xenon/krypton selectivity in a metal-organic framework with
575 small pores and strong adsorption sites, *Microporous Mesoporous Mater.* 169 (2013) 176–179. doi:10.1016/j.micromeso.2012.11.013.
- [35] Z. Hulvey, K. V. Lawler, Z. Qiao, J. Zhou, D. Fairen-Jimenez, R. Q. Snurr, S. V. Ushakov, A. Navrotsky, C. M. Brown, P. M. Forster, Noble gas adsorption in copper trimesate, hkust-1: An experimental and
580 computational study, *J. Phys. Chem. C* 117 (39) (2013) 20116–20126. doi:10.1021/jp408034u.
- [36] K. V. Lawler, Z. Hulvey, P. M. Forster, Nanoporous metal formates for krypton/xenon separation, *Chem. Commun.* 49 (2013) 10959–10961. doi:10.1039/C3CC44374D.
- [37] J. J. Perry, IV, S. L. Teich-McGoldrick, S. T. Meek, J. A. Greathouse, M. Haranczyk, M. D. Allendorf, Noble gas adsorption in metal-organic
585 frameworks containing open metal sites, *J. Phys. Chem. C* 118 (22) (2014) 11685–11698. doi:10.1021/jp501495f.
- [38] H. Wang, K. Yao, Z. Zhang, J. Jagiello, Q. Gong, Y. Han, J. Li, The first
590 example of commensurate adsorption of atomic gas in a mof and effective separation of xenon from other noble gases, *Chem. Sci.* 5 (2) (2014) 620–624. doi:10.1039/C3SC52348A.

- [39] J. Liu, D. Strachan, P. Thallapally, Enhanced noble gas adsorption in ag@mof-74ni , *Chem. Commun.* 50 (2014) 466–468. doi:10.1039/C3CC47777K.
- [40] C. M. Simon, R. Mercado, S. K. Schnell, B. Smit, M. Haranczyk, What are the best materials to separate a xenon/krypton mixture?, *Chem. Mater.* Just Accepted (2015) 1. doi:10.1021/acs.chemmater.5b01475.
- [41] E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues, *Nature* 430 (2004) 1012–1016. doi:10.1038/nature02860.
- [42] A. Corma, F. Rey, J. Ruis, M. J. Sabater, S. Valencia, isupramolecular self-assembled molecules as organic directing agent for synthesis of zeolites, *Nature* 431 (2004) 287–290. doi:10.1038/nature02909.
- [43] J. A. Hriljac, High-pressure synchrotron x-ray powder diffraction studies of zeolites, *Crystallogr. Rev.* 12 (2) (2006) 181–193. doi:10.1080/08893110600772032.
- [44] A. Corma, M. E. Domine, L. Nemeth, S. Valencia, Al-free sn-beta zeolite as a catalyst for the selective reduction of carbonyl compounds (meerwein-ponndorf-verley reaction), *J. Am. Chem. Soc.* 124 (13) (2002) 3194–3195. doi:10.1021/ja012297m.
- [45] D. Peng, D. Robinson, A new two-constant equation of state, *Ind. Eng. Chem. Fundamen.* 15 (1) (1976) 59–64. doi:10.1080/0892702031000065719.
- [46] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, Equation of state calculations by fast computing machines, *J. Chem. Phys.* 21 (1953) 1087–1092. doi:10.1063/1.1699114.
- [47] M. P. Allen, D. J. Tildesley, *Computer Simulations of Liquids*, Clarendon, Oxford, 1987.

- [48] D. Frenkel, B. Smit, Understanding Molecular Simulation, 2nd Edition, Academic Press, San Diego, 2002.
- [49] A. Gupta, S. Chempath, M. Sanborn, L. Clark, R. Snurr, Object-oriented programming paradigms for molecular modeling, *Mol. Simul.* **29** (1) (2003) 29–46. doi:10.1080/0892702031000065719.
- [50] J. a. A. P. Coutinho, E. H. Kontogeorgis, Georgios M. Stenby, Binary interaction parameters for nonpolar systems with cubic equations of state: a theoretical approach 1. co₂/hydrocarbons using srk equation of state, *Fluid Phase Equilib.* **102** (1994) 31–60. doi:10.1016/0378-3812(94)87090-X.
- [51] R. Q. Snurr, A. T. Bell, D. N. Theodorou, Prediction of adsorption of aromatic hydrocarbons in silicalite from grand canonical monte carlo simulations with biased insertions, *J. Phys. Chem.* **97** (1993) 13742–13752. doi:10.1021/j100153a051.
- [52] R. Cracknell, P. Gordon, K. Gubbins, Influence of pore geometry on the design of microporous materials for methane storage, *J. Phys. Chem.* **97** (2) (1993) 494–499. doi:10.1021/j100104a036.
- [53] M. Jeffroy, E. Borissenko, A. Boutin, A. Di Lella, F. Porcher, M. Souhasou, C. Lecomte, A. H. Fuchs, Evidence of a framework induced cation redistribution upon water adsorption in cobalt exchanged x faujasite zeolite: A joint experimental and simulation study, *Microporous Mesoporous Mater.* **138** (1-3) (2011) 45–50. doi:10.1016/j.micromeso.2010.09.031.
- [54] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, Olex2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* **42** (2009) 339–341. doi:10.1107/S0021889808042726.
- [55] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136** (1964) B864. doi:10.1103/PhysRev.136.B864.

- [56] W. Kohn, L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133. doi:10.1103/PhysRev.140.A1133.
- [57] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953. doi:10.1103/PhysRevB.50.17953.
- [58] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865. doi:10.1103/PhysRevLett.77.3865.
- [59] S. Merlino, The crystal structure of wenkite, Acta Crystallogr B30 (1974) 1262–1266. doi:10.1107/S056774087400464X.
- [60] P. Bai, M. Tsapatsis, J. I. Siepmann, Trappe-zeo: Transferable potentials for phase equilibria force field for all-silica zeolites, J. Phys. Chem. C 117 (46) (2013) 24375–24387. doi:10.1021/jp4074224.
- [61] R. T. Cygan, J.-J. Liang, A. G. Kalinichev, Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field, J. Phys. Chem. B 108 (4) (2004) 1255–1266. doi:10.1021/jp0363287.
- [62] O. Talu, A. Myers, Reference potentials for adsorption of helium, argon, methane, and krypton in high-silica zeolites, Colloids Surf., A 187 (2001) 83–93. doi:10.1016/S0927-7757(01)00628-8.
- [63] Crc handbook of chemistry and physics, 95th ed, 2014-2015 [cited Dec. 16, 2014].
URL <http://www.hbcpnetbase.com>
- [64] D. Wolf, P. Keblinski, S. R. Phillpot, J. Eggebrecht, Exact method for the simulation of coulombic systems by spherically truncated, pairwise r^{-1} summation, J. Chem. Phys. 110 (17) (1999) 8254–8282. doi:10.1063/1.478738.

- [65] D. Zahn, B. Schilling, S. M. Kast, Enhancement of the wolf damped
675 coulomb potential: Static, dynamic, and dielectric properties of liquid wa-
ter from molecular simulation, *J. Phys. Chem. B* 106 (41) (2002) 10725–
10732. doi:10.1021/jp025949h.
- [66] H. Yu, W. F. van Gunsteren, Accounting for polarization in molecular
simulation, *Comput. Phys. Commun.* 172 (2005) 69–85. doi:10.1016/j.
680 cpc.2005.01.022.
- [67] C. J. Fennell, J. D. Gezelter, Is the ewald summation still necessary? pair-
wise alternatives to the accepted standard for long-range electrostatics, *J.*
Chem. Phys. 124 (2006) 234104. doi:10.1063/1.2206581.
- [68] J. Yang, A.-M. Tian, H. Sun, Compass force field for 14 inorganic molecules,
685 he, ne, ar, kr, xe, h2, o2, n2, no, co, co2, no2, cs2, and so2, in liquid phases,
J. Phys. Chem. B 104 (2000) 4951–4957. doi:10.1021/jp992913p.
- [69] R. L. Martin, M. Prabhat, D. D. Donofrio, J. A. Sethian, M. Haranczyk,
Accelerating analysis of void space in porous materials on multicore and
gpu platforms., *Int. J. High Perform. Comput* 26 (2012) 347–357. doi:
690 10.1177/1094342011431591.
- [70] M. D. Foster, I. Rivin, M. M. Treacy, O. D. Friedrichs, A geometric solu-
tion to the largest-free-sphere problem in zeolite frameworks, *Microporous*
Mesoporous Mater. 90 (1-3) (2006) 32–38. doi:10.1016/j.micromeso.
2005.08.025.
- [71] K. V. Lawler, Z. Hulvey, P. M. Forster, On the importance of a precise crys-
695 tal structure for simulating gas adsorption in nanoporous materials, *Phys.*
Chem. Chem. Phys. 17 (2015) 18904–18907. doi:10.1039/C5CP01544H.
- [72] D. G. Hay, H. Jaeger, G. W. West, Examination of the mono-
clinic/orthorhombic transition in silicalite using xrd and silicon nmr, *J.*
700 *Phys. Chem.* 89 (7) (1985) 1070–1072. doi:10.1021/j100253a005.

- [73] E. García-Pérez, J. B. Parra, C. O. Ania, D. Dubbeldam, T. J. Vlugt, J. M. Castillo, P. J. Merkling, S. Calero, Unraveling the argon adsorption processes in mfi-type zeolite, *J. Phys. Chem. C* 112 (27) (2008) 9976–9979. doi:10.1021/jp803753h.
- 705 [74] D. Banerjee, A. J. Cairns, J. Liu, R. K. Motkuri, S. K. Nune, C. A. Fernandez, R. Krishna, D. M. Strachan, P. K. Thallapally, Potential of metal-organic frameworks for separation of xenon and krypton, *Acc. Chem. Res.* 48 (2015) 211–219. doi:10.1021/ar5003126.
- 710 [75] F. Karavias, A. Myers, Isosteric heats of multicomponent adsorption: Thermodynamics and computer simulations, *Langmuir* 7 (12) (1991) 3118–3126. doi:10.1021/la00060a035.
- [76] A. Myers, P. Monson, Adsorption in porous materials at high pressure: theory and experiment, *Langmuir* 18 (26) (2002) 10261–10273. doi:10.1021/la026399h.
- 715 [77] K. Momma, F. Izumi, Vesta 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Cryst.* 44 (2011) 1272–1276. doi:10.1107/S0021889811038970.

Tables

Framework parameters for framework-fluid interactions

	LJ type	$R_0(\text{\AA})$	$\varepsilon(\text{K})$	Charge(e)
Si ^a	12-6	2.5817	22.0	+1.500
O ^a	12-6	3.7041	53.0	-0.750
H ^b	12-6	0.0	0.0	+0.375

Noble Gas parameters for framework-fluid interactions

	LJ type	$R_0(\text{\AA})$	$\varepsilon(\text{K})$	$\alpha(\text{\AA}^3)$	$T_c(\text{K})$	$P_c(\text{MPa})$	$V_c(\frac{\text{cm}^3}{\text{mol}})$
Ar ^c	12-6	3.8220	119.80	1.6411	150.687	4.863	75
Kr ^d	12-6	4.0768	180.00 ^e	2.4844	209.48	5.525	91
Xe ^d	12-6	4.4449	230.30	4.0440	289.733	5.842	118

Noble Gas parameters for fluid-fluid interactions

	LJ type	$R_0(\text{\AA})$	$\varepsilon(\text{K})$	$\alpha(\text{\AA}^3)$	$T_c(\text{K})$	$P_c(\text{MPa})$	$V_c(\frac{\text{cm}^3}{\text{mol}})$
Kr ^f	9-6	4.3000	140.90	2.4844	209.48	5.525	91
Xe ^f	9-6	4.2600	196.26	4.0440	289.733	5.842	118

Table 1: Force Field and Critical Simulation Parameters. ^aFrom TraPPE-zeo[60]. ^bFrom Clay-FF, charge lowered for charge neutrality. ^cFrom Talu and Myers[62]. ^dObtained from principle of corresponding states, critical parameters from the CRC[63]. ^eIncreased to match experiment. ^fFrom COMPASS[68].

Code	298 K 10,000 mmHg		250 K 10,000 mmHg	
	N (cm ³ /g)	S _{Kr/Xe}	N (cm ³ /g)	S _{Kr/Xe}
ABW	1.42	48.44	5.84	39.85
ACO	76.58	1.68	134.68	1.30
AEN	2.46	9.12	10.09	8.97
APC	4.15	9.48	18.36	10.66
BIK	2.01	13.85	7.66	15.59
CHI	0.11	214.98	0.29	470.88
CZP	14.27	3.59	36.22	3.88
JBW	7.89	5.13	26.62	5.43
LTJ	2.30	11.41	10.34	12.94
MON	2.44	14.27	10.38	14.61
NAB	0.98	16.42	2.35	107.50
NAT	69.63	0.91	101.08	0.74
NPO	0.30	76.32	0.84	148.52
NSI	0.56	43.63	1.87	75.53
PAR	0.99	14.46	3.34	14.69
RRO	12.26	2.78	33.97	2.85
RWR	35.48	1.91	83.39	1.53
VSV	6.50	3.68	19.94	4.04
WEI	1.93	20.88	7.59	18.39
YUG	30.52	1.11	43.57	1.03

Table 2: Simulated Total Quantities Adsorbed (cm³/g) and Kr/Xe selectivities for initially Kr selective zeolite framework types calculated at 10,000 mmHg at both 298 K and 250 K.

Figure Captions

720 **Figure 1** Comparisons of experimental (solid) and simulated (dashed) Kr and Xe isotherms and heats of adsorption for LTA.

Figure 2 Comparisons of experimental (solid) and simulated (dashed) Kr and Xe isotherms and heats of adsorption for BEA.

725 **Figure 3** Comparisons of experimental (solid) and simulated (dashed) Kr and Xe isotherms and heats of adsorption for FAU.

Figure 4 Initial selectivities of a 90:10 Xe/Kr mixture. The dashed line indicates a selectivity of 1, below which the materials are selective for Kr instead of Xe.

730 **Figure 5** High loading selectivities of a 90:10 Xe/Kr mixture. The dashed line indicates a selectivity of 1, below which the materials are selective for Kr instead of Xe.

Figure 6 Initial selectivities of a 90:10 Xe/Kr mixture as a function of the difference in the Xe and Kr heats of adsorption. The dashed line indicates a selectivity of 1, below which the materials are selective for Kr instead of Xe.

735 **Figure 7** Xe loading density into ATN at 10 mmHg and 298 K.

Figure 8 Xe loading density into UFI at 10 mmHg and 298 K.

Figure 9 Selectivity vs. Percent Loading of a 90:10 Xe:Kr mixture into the top zeolites.

740 **Figures**

Figure 1: Comparisons of experimental (solid) and simulated (dashed) Kr and Xe isotherms and heats of adsorption for LTA.

Figure 2: Comparisons of experimental (solid) and simulated (dashed) Kr and Xe isotherms and heats of adsorption for BEA.

Figure 3: Comparisons of experimental (solid) and simulated (dashed) Kr and Xe isotherms and heats of adsorption for FAU.

Figure 4: Initial selectivities of a 90:10 Xe/Kr mixture. The dashed line indicates a selectivity of 1, below which the materials are selective for Kr instead of Xe.

Figure 5: High loading selectivities of a 90:10 Xe/Kr mixture. The dashed line indicates a selectivity of 1, below which the materials are selective for Kr instead of Xe.

Figure 6: Initial selectivities of a 90:10 Xe/Kr mixture as a function of the difference in the Xe and Kr heats of adsorption. The dashed line indicates a selectivity of 1, below which the materials are selective for Kr instead of Xe.

Figure 7: Xe loading density into ATN at 10 mmHg and 298 K.

Figure 8: Xe loading density into UFI at 10 mmHg and 298 K.

(a) Zeolites with small cages

(b) Zeolites with channels and loading $\geq 45 \text{ cm}^3/\text{g}$

(c) Zeolites with channels and loading $\leq 45 \text{ cm}^3/\text{g}$

Figure 9: Selectivity vs. Percent Loading of a 90:10 Xe:Kr mixture into the top zeolites.