Identification of High-CO$_2$-Capacity Cationic Zeolites by Accurate Computational Screening

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Supporting Information

ABSTRACT: Solid porous materials such as cationic zeolites have shown great potential in energy-efficient separation processes. Conventional adsorbent design involves ad-hoc and inefficient experimental evaluation of a large structural and compositional space. We developed a computational methodology to screen cationic zeolites for CO$_2$ separation processes with quantitative accuracy, and identified a number of novel high-performing materials. This study enabled us to develop an intuitive design workflow for selecting optimal materials and dramatically accelerate the development of industrially relevant separation processes.

1. INTRODUCTION

Zeolites are produced in large volumes (>4.2 million metric tons/year)$^1$ and are vital in large-scale petrochemical catalysis, gas separations, environmental protection, and consumer products. Synthesis of new zeolites or advances in zeolite processing draw significant attention because of their potential for near-term industrial impact, including CO$_2$ capture and separation.$^2$–$^6$ Approximately 220 distinct zeolite topologies have been synthesized$^1$ and vast numbers of structures have been predicted in silico.$^8$–$^{10}$ This structural diversity makes systematic examination of large numbers of zeolites for specific applications valuable.

Multiple studies have used atomistic simulations to screen libraries of zeolites for adsorption applications.$^{11}$–$^{17}$ These studies have focused primarily on pure silica zeolites for reasons of computational simplicity. In contrast, however, almost all applications of zeolites use aluminosilicate compositions. This choice greatly broadens the range of available materials, since for each zeolite topology the Si:Al ratio (SAR) and the composition of the charge-balancing cations (Na, K, ...) can be varied. If only Na and K are used as cations, materials with composition Na$_x$K$_{1-x}$Si$_{1-x}$Al$_x$O$_4$ can be considered. However, this drastically increases the number of experimental systems to be synthesized and studied. Reliable computational predictions that are transferrable to a wide range of cationic zeolites are highly desirable.

In this paper, we show that quantitative methods can be used to screen cationic zeolites for realistic adsorption applications. Reaching this goal requires accurate, transferrable force fields (FFs), which we develop from extensive electronic structure calculations, and methods to efficiently sample cation positions. We illustrate these methods to select materials with high working capacity for CO$_2$ during cyclic adsorption processes. This application is important in its own right,$^18$ and our results not only identify a number of novel high-performing materials, but also result in intuitive design criteria to identify these high working capacity adsorbents. Our approach will be applicable to select optimal zeolites for a wide range of similar applications.

We acknowledge that the performance of cationic zeolites for CO$_2$ adsorption is likely in practical settings to be significantly affected by the presence of water, which adsorbs strongly on these materials. To perform a detailed evaluation of the performance of any specific cationic zeolite, information on the coadsorption of CO$_2$ and water would be necessary, as well as...
information about the water content of the feed streams of interest. The aim of our work is not to accomplish this task. Rather, we use adsorption of CO₂ in zeolites as an example to demonstrate how quantitatively accurate prediction of adsorption in large collections of cationic zeolites is now possible. As we discuss below, previous simulations of molecular adsorption in cationic zeolites fell short of the goal of quantitative accuracy for a variety of reasons. Our results for single-component adsorption of CO₂ address a specific example of adsorption in zeolites that has received considerable previous attention and the methods we use to treat these systems open the possibility of exploring a wide range of adsorbates and adsorbed mixtures with similar quantitative accuracy in the future.

Although experimental data on CO₂ adsorption in a variety of cationic zeolites is available, the extant data is insufficient to comprehensively consider the full range of zeolite structures. García et al. recently used breakthrough experiments and statistical analysis to study several Na-exchanged FAU and LTA zeolites with different SAR and their AlPO analogues for the separation of CO₂ from CO₂, CO, and CH₄. Lin et al. simulated Na-zeolites with three specific SAR values using calculations that fixed the cation positions. This approach overestimates the energy required for CO₂ capture processes in at least some materials. Kim et al. performed similar simulations for two SAR values in Na- and Ca-zeolites for 400 hypothetical zeolites. Developing accurate and transferable FFs for adsorbed molecules is challenging. Significant recent progress has occurred in deriving FFs from electronic structure calculations, an approach that can greatly improve on generic FFs or FFs fitted to specific experimental data. We previously used this approach to develop a FF for adsorption of CO₂ in siliceous and Na-containing zeolites. This FF accurately predicts experimentally observed adsorption properties and shows good transferability across different zeolite topologies. Below, we extend this FF to K-containing zeolites.

Similar to our previous work on Na-zeolites, our FF was derived from the DFT/CC (density functional theory/coupled cluster) energies of CO₂ in selected zeolites. Below we refer to this FF as CCFF. We used K-CHA with SAR = 3 \((K_\text{Al}_2\text{Si}_3\text{O}_8)_2\) as the model for FF development, because of the small size of the CHA primitive unit cell. Experimental observations show that K cations prefer the center of eight-membered ring (8MR) windows (site SIII') in this material. Our DFT calculations used materials in which Al was distributed randomly subject to the Löwenstein rule and K was placed in site SIII'. CC correction functions for Al, Si, and O were taken from previous calculations, which were developed specifically for CO₂ adsorption in zeolites, and we developed similar correction functions for CO₂-K⁺ interactions. Our FF was fitted to energies calculated for 600 CO₂ configurations that sampled the full pore space in K-CHA. Further details on the FF development are given in the Supporting Information.

We have shown previously that accounting for mobility of extra-framework cations is critical for reproducing experimental CO₂ isotherms. We therefore developed a FF describing K⁺-zeolite interactions, again based on energies from electronic structure calculations. These used K-CHA with SAR = 11 \((K_\text{Al}_2\text{Si}_3\text{O}_8)_2\). DFT calculations were performed with the cation in the 8MR windows (site SIII'), the 6MR windows (site SII), and opposite the 4MR window (site SIII). Further details are given in the Supporting Information.

2. METHODS

2.1. Zeolite Structures. To screen materials for practical use, an important simplification can be made by noting that only a fraction of known zeolite topologies (and no hypothetical materials) have known aluminosilicate or siliceous synthesis routes. We therefore focus on these materials, ensuring that any materials selected from our calculations can be tested experimentally. We first studied ten-membered ring (10MR) zeolites. This choice avoids complications associated with pore blocking.

In the IZA database, there are 21 10MR topologies where aluminosilicate or silica analogues have been synthesized: DAC, EUO, FER, HEU, IMF, ITH, LAU, MFI, MFS, MRE, MTW, MMW, NES, RRO, SFF, STF, STI, SZR, TER, TON, TUN. For each topology, we fully optimized the siliceous structure using the Hill-Sauer FF. Using these optimized frameworks, we constructed aluminosilicate structures with SAR of 1, 2, 3, 5, 10, 25, and 50 with Si atoms randomly substituted by Al atoms obeying Löwenstein’s rule. For topologies including odd numbered window sizes (e.g., 3, 5, and 7MR), it is impossible to make structures with SAR = 1 within this scheme. For these topologies, the lowest SAR we chose was 2 or 3. Accurate experimental information on Al locations is not available for most zeolite structures. Numerical tests for several zeolites show that the assumption of random Al distribution is a reasonable starting point in structures where the locations of Al atoms are not known (see the Supporting Information).

For each SAR, K and/or Na extra-framework cations were introduced with the K/(K+Na) ratio of 0, 16.7, 33.4, 50, 66.7, 83.3, and 100%. In all, this procedure generated 910 distinct 10MR materials. To look beyond 10MR zeolites, we examined 16 other topologies from the IZA database with large pore volumes (or void fraction), including three 18MR (IRR, VFI, ITT), one 16MR (IRY), three 12MR (FAU, EMT, RWY), and nine 8MR (LTA, TSC, AFT, AFX, CHA, KFI, PAU, RH0, UFI) zeolites. IRR, VFI, ITT, IRY, RWY, and AFT topologies were included because of their large pore volumes, but their siliceous or aluminosilicate analogues have not been synthesized to date.

We label zeolites as ZEO_A_B, where ZEO indicates the topology, A the SAR, and B the percentage of K cations. Siliceous zeolites are denoted ZEO_Si. For example, MFI_10_50 represents a material with the MFI topology, SAR = 10, and 50% K cations.

2.2. Simulation Details. Classical simulations were performed using RASP, where our developed first-principles force fields were used for calculating the interactions between CO₂ and zeolite as well as the interactions between cation and framework. During the simulations all framework atoms were fixed at their crystallographic positions while cations were allowed to move.

To get reliable cation distributions, we performed pre-equilibration simulations prior to the adsorption of CO₂. Parallel tempering was used in these simulations. For each cationic material, nine replicas were included in simulations at temperatures of 300, 390, 507, 659, 857, 1114, 1448, 1882, and 2447 K. Adjacent temperatures are in a ratio of 1.3 as suggested in previous work. Test calculations indicated that this approach was far more efficient than conventional MC methods, and critically, that adequate sampling of cation positions had a strong influence on adsorption isotherms (see the Supporting Information). This observation calls into question the precision of earlier simulation studies of CO₂ adsorption in cationic zeolites.

Adsorption isotherms and isosteric heats of adsorption were predicted computationally using standard Grand Canonical Monte Carlo (GCMD) methods, where volume \((V)\), temperature \((T)\), and chemical potential \((\mu)\) are held constant and the number of adsorbate molecules fluctuates. Geometrical properties of the empty zeolite structures were calculated, including pore size, accessible pore volume, and surface area. More details can be found in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Validation of Force Fields. The FFs described above do not rely on any experimental adsorption data. We show
below comparison with experimental data for pure K- and mixed Na/K-zeolites that these FFs quantitatively predict CO2 adsorption in these materials.

Figure 1 compares predictions from our simulations with experimental data for CO2 adsorption in four different K-containing zeolites. Individual isotherms for each material are shown in the Supporting Information. We emphasize that our FF was not fitted to this experimental data in any way. Overall, the agreement between our computational predictions and the experimental data is very good, although CCFF slightly overestimates the CO2 loading at low pressures for K/Na-X (SAR = 1.23, 88.7% K). Similar data for Na-containing zeolites are shown in our earlier work.27

Figure 1 also compares CCFF predictions to experiments for K/Na-LTA (SAR = 1). K cations make it difficult for CO2 to diffuse in LTA because they block 8MR windows.32 GCMC simulations alone cannot account for this blockage effect. We chose data from a sample with composition K17Na79Al96Si96O384 (17.4% K) for which the blockage effect is likely to be small. The predicted isotherms at 298 and 343 K agree well with the experimental data of Liu et al.,32 but are significantly overestimated at 253 K relative to the experiments. Analysis of the heat of adsorption from the experimental data (see the Supporting Information) strongly indicates that the experimental data at 253 K was not fully equilibrated, presumably due to kinetic window blockage. Thus, Figure 1 shows that GCMC results from our FF quantitatively predicts equilibrium adsorption uptake of CO2 in a wide range of Na- and K-containing zeolites.

3.2. CO2 Capture Using Ten-Membered Ring (10MR) Zeolites. Cyclic processes such as pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and temperature swing adsorption (TSA) are widely used for gas separations.40 We considered the four prototypical processes listed in Table 1 for CO2 capture, where adsorption and desorption conditions were chosen for industrial relevance.41,42 Our aim is not to develop detailed process models of gas capture, but instead to examine some of the key factors influencing these prototypical processes. Detailed modeling of gas capture requires modeling multicomponent adsorption of the gas mixtures of interest. As a first step, however, it is useful to focus simply on the capacity for the primary component of interest (in this case, CO2). On this basis for each process the working capacity (ΔN), defined as the difference between the adsorbed amounts at adsorption (Nads) and desorption (Ndes) conditions, is used to evaluate CO2 capture performance of materials.

We first studied the 10MR zeolites. To illustrate our approach, Figure 2 shows our results for MWW zeolites. For each process, the CO2 gravimetric working capacity varies with SAR and cation composition, with SAR having a stronger influence on the working capacity. For PSA, siliceous MWW...
has higher working capacity than the cationic materials with high SAR, which are in turn better than those with medium and low SAR. Even though the cationic forms of MWW adsorb more CO₂ than the siliceous form at the adsorption condition, the cationic structures have lower working capacities due to the larger residual amounts of CO₂ at the desorption condition (Figure S10). The stronger CO₂ interactions created by the presence of extra-framework cations result in a trade-off between high adsorption capacities and reduced working capacities. This trend holds for most of 10MR zeolites we studied, and is consistent with experimental observations for LTA.⁴³ In the VSA process (Figure 2b), however, the cationic forms of MWW with SAR ~ 25 perform better than those with lower and higher SAR, including siliceous MWW. In the PTSA and VTSA processes, the optimal SAR lie at 50 and 10. From our calculations, the optimal MWW structures are MWW_Si, MWW_25_100, MWW_50_100, and MWW_10_17 for PSA, VSA, PTSA, and VTSA, respectively. These result indicate that PTSA and VTSA favor lower SAR materials compared to PSA and VSA, respectively. Conceptually, it is useful to consider PTSA as a combination of PSA and TSA. In TSA, stronger CO₂/zeolite interactions lead to a larger CO₂ working capacity as the temperature increases. Very strong CO₂ interactions, however, hinder the performance in PSA. As a result, a trade-off exists in the most suitable CO₂ interactions (i.e., Si/Al ratio) between PSA and TSA. Overall, PTSA favors a lower Si/Al ratio compared to PSA. A similar conceptual interpretation can be used to understand the outcomes for VTSA and VSA.

Figure 2 represents a detailed, quantitative description of CO₂ adsorption in a wide range of MWW zeolites that would require enormously time-consuming synthesis and testing to establish experimentally. Further, high performing regions of SAR and cation content might still be missed due to practical limitations on the number of experimental samples. This kind of data, which we calculated for all of the 21 zeolite topologies

Table 2. CO₂ Gravimetric Working Capacity of the Optimal Composition for the Ten-Membered Ring (10MR) topologies in the Four CO₂ Capture Processes

<table>
<thead>
<tr>
<th>zeolite</th>
<th>ΔN (mol/kg)</th>
<th>zeolite</th>
<th>ΔN (mol/kg)</th>
<th>zeolite</th>
<th>ΔN (mol/kg)</th>
<th>zeolite</th>
<th>ΔN (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFF_Si</td>
<td>1.95</td>
<td>RRO_Si</td>
<td>2.03</td>
<td>STF_Si</td>
<td>3.43</td>
<td>SFF_5_0</td>
<td>2.96</td>
</tr>
<tr>
<td>STF_Si</td>
<td>1.95</td>
<td>DAC_Si</td>
<td>2.01</td>
<td>DAC_Si</td>
<td>3.21</td>
<td>DAC_50_17</td>
<td>2.79</td>
</tr>
<tr>
<td>MWW_Si</td>
<td>1.89</td>
<td>STF_50_100</td>
<td>1.93</td>
<td>MWW_50_100</td>
<td>3.11</td>
<td>SFF_Si</td>
<td>3.06</td>
</tr>
<tr>
<td>ITH_Si</td>
<td>1.53</td>
<td>HEU_Si</td>
<td>1.73</td>
<td>SFF_Si</td>
<td>3.06</td>
<td>SFF_5_0</td>
<td>2.96</td>
</tr>
<tr>
<td>NES_Si</td>
<td>1.49</td>
<td>MWW_25_100</td>
<td>1.67</td>
<td>NES_Si</td>
<td>2.56</td>
<td>DMS_5_0</td>
<td>2.49</td>
</tr>
<tr>
<td>TUN_Si</td>
<td>1.43</td>
<td>SFF_25_67</td>
<td>1.64</td>
<td>NES_Si</td>
<td>2.56</td>
<td>STI_2_0</td>
<td>2.68</td>
</tr>
<tr>
<td>TER_Si</td>
<td>1.36</td>
<td>TER_50_100</td>
<td>1.38</td>
<td>STI_2_0</td>
<td>2.68</td>
<td>NES_5_0</td>
<td>2.49</td>
</tr>
</tbody>
</table>

*Only the top 7 structures are shown.*
listed above, greatly extends the number of zeolites for which thorough information is available regarding CO₂ adsorption. Using our results, we determined the optimal composition for each 10MR zeolite topology in each process listed above.

Table 2 summarizes the top 7 structures for each process. More information on these 10MR optimal compositions is given in Tables S5−S8. In PSA, the siliceous form is the optimal composition for most topologies, while in the other three processes the optimal composition is topology-dependent. Among the optimal structures in Table 2, SFF_Si (and STF_Si), RRO_Si, STF_Si, and STF_5_0 are predicted to yield the largest CO₂ working capacity in the PSA, VSA, PTSA, and VTSA processes, respectively. Except for STF_5_0, these materials have previously been synthesized, so they can be readily used in experiments.44,45 MWW_10_17 also stands out in VSTA, and its aluminosilicate analogues have been successfully synthesized.46

It is useful to consider the relationship between geometric characteristics such as pore volume, surface area, pore limiting diameter (PLD), and largest cavity diameter (LCD) and the CO₂ working capacity for the materials described above. We first discuss the PSA process. Figure 3 shows the computed working capacity as a function of several geometrical parameters, the isosteric heat of adsorption at zero coverage (Qst₀), (c) average isosteric heat at adsorption and desorption conditions, Qstavg, (d) surface area, (e) largest cavity diameter, and (f) pore limiting diameter in 10MR zeolites with different SAR.

Figure 3. PSA gravimetric working capacity of CO₂ as a function of the (a) pore volume, (b) isosteric heat of adsorption at zero coverage, Qst₀, (c) average isosteric heat at adsorption and desorption conditions, Qstavg, (d) surface area, (e) largest cavity diameter, and (f) pore limiting diameter in 10MR zeolites with different SAR.
MWW_10_0) that have similar pore volumes to these siliceous materials, however, have much lower working capacities. The PSA working capacity generally decreases as $Q_{st0}$ increases, but the correlation is not strong, especially for siliceous materials (Figure 3b). For instance, $Q_{st0}$ for MFI_Si (24 kJ/mol) is close to that for STF_Si (22 kJ/mol), but their PSA working capacities differ by about 40%. A similar trend is observed between the working capacity and $Q_{stavg}$ (Figure 3c). The relationship between the PSA working capacity and surface area and pore sizes (LCD and PLD) was also investigated (Figure 3d–f). A moderate correlation with working capacity is found for surface area, but the correlation with pore sizes is weak. Structures with the same topology but different SAR and cation compositions may have very similar LCD and PLD. Thus, pore volume is a more reliable geometrical predictor than surface area or pore size. We also similarly analyzed the other three CO$_2$ capture processes (Figures S11–S13). The correlations between CO$_2$ working capacity and the geometrical and energetic parameters listed above are not strong, so none of these parameters can be used alone for predicting the highest-performing structures in all four processes.

### Table 3. CO$_2$ Gravimetric Working Capacity of the Optimal Composition for Each Zeolite Topology with Large Pore Volume in the Four CO$_2$ Capture Processes$^a$

<table>
<thead>
<tr>
<th>zeolite</th>
<th>$\Delta N$ (mol/kg)</th>
<th>zeolite</th>
<th>$\Delta N$ (mol/kg)</th>
<th>zeolite</th>
<th>$\Delta N$ (mol/kg)</th>
<th>zeolite</th>
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<tr>
<td>RWY_5_100</td>
<td>7.48</td>
<td>RWY_3_17</td>
<td>6.18</td>
<td>RWY_3_0</td>
<td>13.02</td>
<td>RWY_3_17</td>
<td>8.25</td>
</tr>
<tr>
<td>IRY_10_50</td>
<td>4.26</td>
<td>IRY_3_0</td>
<td>3.55</td>
<td>IRY_3_0</td>
<td>7.13</td>
<td>IRY_2_0</td>
<td>7.02</td>
</tr>
<tr>
<td>IRR_10_100</td>
<td>3.62</td>
<td>FAU_5_0</td>
<td>3.14</td>
<td>IRR_5_50</td>
<td>6.46</td>
<td>IRR_2_0</td>
<td>6.28</td>
</tr>
<tr>
<td>FAU_5_67</td>
<td>3.41</td>
<td>IRR_5_50</td>
<td>3.01</td>
<td>FAU_5_0</td>
<td>5.19</td>
<td>FAU_2_0</td>
<td>5.14</td>
</tr>
<tr>
<td>TSC_50_83</td>
<td>3.36</td>
<td>EMT_5_0</td>
<td>2.77</td>
<td>TSC_10_0</td>
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<td>EMT_2_0</td>
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<tr>
<td>EMT_50_100</td>
<td>3.18</td>
<td>UFI_25_100</td>
<td>2.69</td>
<td>ITT_10_0</td>
<td>5.06</td>
<td>ITT_2_0</td>
<td>5.04</td>
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<tr>
<td>RHO_Si</td>
<td>2.90</td>
<td>KFI_25_100</td>
<td>2.64</td>
<td>EMT_10_17</td>
<td>5.05</td>
<td>RHO_5_0</td>
<td>4.56</td>
</tr>
</tbody>
</table>

$^a$Only the top 7 structures are shown.

Figure 4. PSA gravimetric working capacity of CO$_2$ as a function of the (a) pore volume, (b) isosteric heat of adsorption at zero coverage, $Q_{st0}$, (c) average heat at adsorption and desorption conditions, $Q_{stavg}$, for all siliceous zeolites, and (d) the adsorbed amount of CO$_2$ as a function of the pore volume at adsorption and desorption conditions in PSA.

3.3. Extension to Zeolites with Large Pore Volumes. One interesting observation from the 10MR zeolites is that in every process, the best-performing materials have topologies...
with large pore volumes in their siliceous form. This motivated us to extend our work to other zeolites with large pore volumes. To look beyond 10MR zeolites, we examined 16 other topologies from the IZA database with large pore volumes or void fractions. Similar to the 10MR topologies, the optimal compositions of these large-pore topologies were identified for each CO2 capture process. The results for the top 7 structures are summarized in Table 3. More information is given in Tables S9–S12. The working capacities for these structures are much larger than those from the 10MR zeolites (Table 2). RWY with SAR of 5 or 3 performs best for all the four processes. The highest working capacities are predicted to be 7.5, 6.2, 13.0, and 8.3 mol/kg for the PSA, VSA, PTSA, and VTSA process, respectively. These values exceed the working capacities of typical adsorbents (such as FAU and LTA zeolites) by up to a factor of 3. IRY and IRR aluminosilicates with SAR from 2 to 10 also stand out in these processes, yielding higher or comparable working capacities compared to the FAU zeolites.

Because volumetric capacities are important for the process design, we also calculated the volumetric capacities for each zeolite. The volumetric results for the optimal compositions are given in Tables S13–S20. They differ from the gravimetric case, especially for the materials with low framework density. While RWY aluminosilicates with SAR of 5 or 3 (i.e., RWY_5_100, RWY_3_17) still perform best for PSA, VSA, and PTSA processes, IRY_2_0 stands out for the VTSA process. The highest volumetric working capacities are predicted to be 6.5, 5.3, 11.2, and 8.8 mmol/cm3 for the PSA, VSA, PTSA, and VTSA process, respectively, which exceed those of FAU and LTA zeolites by up to 50%.

To date, the RWY framework has been synthesized only as a sulfide or selenide material, while IRY and IRR as a germanosilicate or germanoaluminosilicate. Synthesis routes for the aluminosilicate analogues of these materials are being developed. Among the experimentally known materials we examined, EMT and TSC aluminosilicates yield similar predicted CO2 working capacities to FAU zeolites. For 10MR zeolites, siliceous structures typically gave the highest PSA working capacities. This is not true for the large-pore topologies, especially for RWY, IRY, IRR, ITT, and VFI. We compared the PSA gravimetric working capacity for all the siliceous structures. For most of them, a linear correlation exists between the working capacity and pore volume (Figure 4a). Large deviations, however, exist for RWY_Si, IRY_Si, IRR_Si, ITT_Si, and VFI_Si. For these materials, $Q_{st}$ was found to be 15–20 kJ/mol, noticeably smaller than for other siliceous materials, for which $Q_{st}$ was 22–34 kJ/mol (Figure 4c). These weaker host/guest interactions leads to smaller adsorbed amounts of CO2 at both adsorption and desorption conditions and therefore reduce CO2 capture performance (Figure 4d).

It is useful to note that the isosteric heat of adsorption at dilute loading, $Q_{st}^0$, cannot account for the observations just discussed; $Q_{st}^0$ of ITT_Si is similar to most other siliceous materials (Figure 4b). This situation arises because $Q_{st}^0$ is...
loading dependent in many of these materials, and it is \( Q_{\text{st}} \) under process conditions that is most relevant to process performance. Instead of the siliceous analogs, RWY_5_100, IRY_10_50, IRR_10_100, ITT_25_67, and VFI_10_100, are found to be optimal for these topologies in PSA (Table 3 and Table S9). \( Q_{\text{st}}^{\text{avg}} \) of these aluminosilicates are 25 − 27 kJ/mol (Table S9), a value similar to the optimal 10MR structures.

Figure 5a shows the PSA gravimetric working capacity of \( \text{CO}_2 \) as a function of \( Q_{\text{st}}^{\text{avg}} \) for all the zeolite topologies we considered. \( Q_{\text{st}}^{\text{avg}} \) varies from 15−47 kJ/mol, but the optimal compositions fall into a narrow range. For the optimal structures for this process, \( Q_{\text{st}}^{\text{avg}} \) is 28 ± 3 kJ/mol. Similar narrow ranges of \( Q_{\text{st}}^{\text{avg}} \) are observed for the optimal structures in other three processes (Figure Sb−d): 32 ± 2, 29 ± 3, and 39 ± 3 kJ/mol for VSA, PTSA, and VTSA, respectively. The same observations hold true for the volumetric working capacities and \( Q_{\text{st}}^{\text{avg}} \) (Figure S14). The observation that different cyclic processes will have different optimal heats of adsorption can be understood from analysis of Bhatia and Myers for model adsorbents governed by Langmuir adsorption isotherms.\(^{52}\) A key outcome of our results is that we have determined these optimal heats of adsorption from accurate data for a large set of materials without imposing assumptions regarding the functional form of the adsorption isotherms.

These results indicate that suitable \( Q_{\text{st}}^{\text{avg}} \) are required for maximizing the working capacity of each zeolite topology in a specified process. A high \( Q_{\text{st}}^{\text{avg}} \) will lead to a large amount of residual adsorption at the desorption condition, whereas a low \( Q_{\text{st}}^{\text{avg}} \) gives a low adsorbed amounts at both adsorption and desorption conditions. This conclusion is similar to that drawn by Bhatia and Myers based on simplified models of storage of \( \text{H}_2 \) in porous materials.\(^{52}\) An optimal heat of adsorption was also found to exist for \( \text{H}_2 \) in MOF materials\(^{53}\) and for the separation of \( \text{CO}_2 \) from mixtures of \( \text{CO}_2 \), \( \text{CO} \), and \( \text{CH}_4 \) using Na-exchanged zeolites.\(^{22}\) Simon et al. pointed out, however, that an optimal heat of adsorption does not guarantee that a material will exhibit a large working capacity because this also depends on the density of adsorption sites.\(^{54}\)

The difference in \( \text{CO}_2 \) working capacity among these optimal compositions originates from differences in their pore volumes, as illustrated in Figure 6. Although no clear correlations exist between working capacity and pore volume if all the zeolites are included, simple correlations are observed for the optimal structures in all four processes. The high-performing materials possess large pore volumes and concurrently yield the optimal heat of adsorption for the defined process.

Figure 6. \( \text{CO}_2 \) gravimetric working capacity as a function of the pore volume for all the zeolite structures in (a) PSA, (b) VSA, (c) PTSA, and (d) VTSA processes. Red circles indicate the optimal structure of each zeolite topology, and the dashed lines indicate linear fits for the optimal structures in each process.
from only Na- and K-containing zeolites, we anticipate that they are also applicable to zeolites containing other cations for the adsorption processes considered here.

From a design standpoint, once a target adsorption process is identified, selecting topologies with large pore volumes and then tuning the composition to the optimal average heat is the path to maximizing the working capacity. Our results indicate that SAR is a more significant factor than the $K/(K+N)$ ratio in determining the working capacity. These intuitive design criteria are the same for maximizing both volumetric and gravimetric capacities.

4. CONCLUDING REMARKS

In summary, we used accurate transferable force fields to screen siliceous, Na-, K-, and mixed Na/K-exchanged zeolites for CO$_2$ capture in four prototypical cyclic processes. We studied 10MR zeolites and other topologies with large pore volumes but different water. By focusing on real materials, our results make direct predictions about high performing materials that can be targeted for synthesis. For each zeolite topology and process there is an optimal composition (SAR and $K/(K+N)$ ratio) that outperforms other compositions. In each process, the optimal composition is topology-dependent, but the average heats of adsorption for the optimal compositions are similar among all topologies. The highest performing materials exhibit the optimal heat of adsorption and have large pore volume. Once a target adsorption process is identified, selecting topologies with large pore volumes and then tuning the composition to the optimal average heat defines a clear path to maximizing the gravimetric or volumetric CO$_2$ working capacity. We have reported on over 1000 distinct zeolite compositions, which greatly increases the number of zeolites for which reliable CO$_2$ adsorption data is available. Obtaining the same information from experiments would have been vastly time-consuming. Detailed process design clearly requires information that goes beyond the single component adsorption data we used for screening. In particular, the performance of cationic zeolites for adsorbing CO$_2$ may be strongly affected by the presence of other polar species such as water. Despite the complications associated with detailed modeling of cyclic adsorption processes for realistic chemical mixtures, the methods we have demonstrated create a strong foundation for using quantitative computational approaches for this purpose in the future.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b01132.

Detailed description of DFT-derived force fields for CO$_2$ in cationic zeolite, classical simulations, and CO$_2$ capture results (PDF)

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Notes

The authors declare the following competing financial interest(s): The authors have filed a patent application covering applications of some of the materials described in this manuscript.

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