

## **In Silico Screening of Carbon Capture Materials**

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**One of the main bottlenecks to deploying large-scale carbon dioxide capture and storage (CCS) in power plants is the energy required to separate the CO<sub>2</sub> from flue gas. For example, near-term CCS technology applied to coal-fired power plants is projected to reduce the net output of the plant by some 30% and to increase the cost of electricity by 60-80%. Developing capture materials and processes that reduce the parasitic energy imposed by CCS is therefore an important area of research. We have developed a computational approach to rank adsorbents for their performance in CCS. Using this analysis, we have screened hundreds of thousands of zeolite and zeolitic imidazolate framework (ZIF) structures and identified many different structures that have the potential to reduce the parasitic energy of CCS by 30-40% compared to near-term technologies.**

Reducing anthropogenic global CO<sub>2</sub> emissions is a complex issue. The scale of the problem, the costs, its interdependence with energy production, and the intrinsic uncertainties in making long-term predictions about something as complex as the climate are a few of the factors contributing to one of the biggest challenges of our time.<sup>1</sup> Despite advances in alternative energy, most, if not all, future energy scenarios include continuing growth in the absolute use of fossil energy.<sup>2</sup> CCS, deployed at an industrial scale, is one of the few viable technologies that mitigate anthropogenic CO<sub>2</sub> emissions.<sup>3</sup> For power plants, post combustion CCS involves the separation of CO<sub>2</sub> from flue gas, followed by its compression and then sequestration in geological formations. CCS is very energy intensive, and capture dominates both the energy consumption and the cost.<sup>3,4</sup>

One can use simple thermodynamics to estimate the minimum energy required to separate CO<sub>2</sub> from flue gases (typically, 70-75% N<sub>2</sub>, 13% CO<sub>2</sub>, 5-7% H<sub>2</sub>O, 3% O<sub>2</sub> at 40°C and 1 atm). If we capture 90% of the CO<sub>2</sub> from a coal-fired power plant with the separation performed at 40°C, the minimum energy required is of the order of 4-5% of the energy

produced by the power plant.<sup>5</sup> Near-term capture technologies are projected to use five times the thermodynamic limit.<sup>5</sup> This suggests that capture processes that use less energy may be feasible. The technology for CO<sub>2</sub> capture considered near-term for power plants was developed as far back as the 1930s.<sup>6,7</sup> This technology uses aqueous solutions of amines that react with CO<sub>2</sub> to form carbamates and are therefore highly selective in capturing CO<sub>2</sub>. One drawback of these amine solutions is that they contain 70% water by weight, and the regeneration cycle involves heating and evaporating large volumes of water, making the process energy intensive. Alternative separation processes that use other solvents, solid adsorbents, or membranes have the potential to require less energy.<sup>5</sup> One of the main challenges here is that many properties of CO<sub>2</sub> and N<sub>2</sub> are relatively similar, and hence success of such approaches relies on the development of novel materials sensitive to these small differences.

For adsorbent-based gas separations, it is important to have adsorbents with a large internal surface;<sup>8</sup> examples of such material include zeolites, metal-organic frameworks (MOFs), and zeolitic imidazolate frameworks (ZIFs).<sup>9-12</sup> The number of possible structures of these materials is very large: hundreds of thousands of possible zeolites with different pore topologies exist in the zeolite database,<sup>13</sup> and a nearly infinite number of different types of MOFs can be created by changing the type of the metal and the organic linker. In practical terms, synthesizing and testing all these structures for CO<sub>2</sub> separation would be an impossible task. Therefore, we have developed a viable computational strategy to characterize large databases of carbon capture materials and identify optimal materials for CO<sub>2</sub> separation.

Several articles on screening for optimal separation materials have been published.<sup>14-16</sup> These articles consider a limited set of 10-20 different materials, which is insufficient to characterize the hundreds of thousands of different possible topologies.<sup>13</sup> In addition, these studies often focus on a single material property, such as selectivity or residence time, at a

specific condition. However, optimizing the residence time<sup>15</sup> or uptake<sup>16</sup> in the adsorption step, for example, ignores that a material effective at adsorbing CO<sub>2</sub> might be difficult to regenerate. More importantly, these studies do not consider that different materials perform optimally at different conditions. In this work, we take another approach. For each material we determine the optimal process conditions by minimizing the electric load that a temperature-pressure swing capture process using that material followed by compression would impose on a power plant. This minimum load, which we call parasitic energy, is introduced as a metric to compare different materials.

Separation of gases using nanoporous materials exploits the fact that at flue gas conditions CO<sub>2</sub> selectively adsorbs in the pores of these materials. By increasing the temperature, decreasing the pressure, or a combination of both, nearly pure CO<sub>2</sub> can be recovered. Figure 1 illustrates such a temperature-pressure swing separation process. Regardless of the regeneration method, the parasitic energy of a CCS process can be readily modeled if equilibrium adsorption and desorption are assumed. While there are many possible process configurations, they all rely on the difference between adsorption and desorption conditions to capture CO<sub>2</sub>. The processes vary primarily in their method of gas-solid contacting and heat transfer, though neither of those factors affects performance under equilibrium assumptions. The energy required for this process has three main components: (1) energy to heat the material, (2) energy to supply the heat of desorption (equal to the heat of adsorption), and (3) energy required to pressurize CO<sub>2</sub> to 150 bar, which is a standard requirement for transport and storage.<sup>4</sup> For a specific material and a fixed adsorption condition, we vary the desorption conditions and calculate the CO<sub>2</sub> and N<sub>2</sub> loading differential between the adsorption and desorption conditions to compute the quantity and purity of CO<sub>2</sub> produced. The thermal energy requirement ( $Q$ ) of the process per unit mass of CO<sub>2</sub> captured ( $\Delta q_{CO_2}$ ) is the sum of the sensible energy needed to heat the bed to the desorption temperature and the energy needed to supply the heat of adsorption.

$$Q = \frac{C_p m_{\text{sorbent}} (T_{\text{final}} - T_{\text{flue}}) + (\Delta q_{\text{CO}_2} \Delta h_{\text{CO}_2} + \Delta q_{\text{N}_2} \Delta h_{\text{N}_2})}{\Delta q_{\text{CO}_2}}$$

where  $C_p$  is the specific heat capacity of the adsorbent,  $m_{\text{sorbent}}$  is the mass of the adsorbent,  $T_{\text{final}} - T_{\text{flue}}$  is the temperature differential between the adsorption and desorption conditions,  $\Delta q_i$  is the difference in loading for each species, and  $\Delta h_i$  is the heat of adsorption for each species. The loading at specific conditions is calculated using competitive adsorption isotherms, and the heats of adsorption are obtained directly from the molecular simulations. In a power plant, this thermal energy is supplied by diverting steam from the power cycle. Diverting steam effectively imposes a parasitic load on the power plant, which we compute as the product of the thermal energy requirement, the Carnot efficiency ( $\eta$ ) of the extracted steam, and the typical efficiency of a turbine (75%).<sup>17</sup> The compressor work,  $W_{\text{comp}}$ , is obtained from a multi-stage intercooled compressor model with real gas properties using NIST REFPROP<sup>18</sup> for fluid property data. We assume a staged compression, intercooled to 40°C, with a maximum pressure ratio of 2.5 and an isentropic efficiency of 85% below the supercritical point and 90% above it. Finally, the parasitic energy,  $E_{\text{eq}}$ , imposed on the power plant of the CCS process, is given by:

$$E_{\text{eq}} = 0.75 \eta_{T_{\text{final}}} Q + W_{\text{comp}}$$

By calculating the parasitic energy for a given adsorbent over a wide range of possible desorption temperatures and pressures, we find the optimal process conditions for each adsorbent that minimizes the parasitic energy. Using a similar analysis, a state of the art amine capture process would have a parasitic energy of 1060 kJ/kg CO<sub>2</sub>. A more rigorous engineering analysis of an amine process retrofitted to a coal-fired power plant which includes pressure drop through equipment, losses in heat exchangers, and other energy losses, shows a parasitic load of 1327 kJ/kg CO<sub>2</sub>, about 25% higher.<sup>4</sup> Therefore, we seek materials that exhibit a parasitic energy significantly lower than 1060 kJ/kg CO<sub>2</sub> with the

expectation that, similar to the amine process, a more detailed analysis of a process attached to a power plant will increase this number. We also emphasize that for the present analysis we treat the flue gas as a binary gas mixture of 14% CO<sub>2</sub> and 86% N<sub>2</sub>. This assumption allows us to focus first on the energy consumption of these materials. Only if the energy consumption looks sufficiently attractive relative to other processes, additional criteria such as sensitivity to other flue gas components (e.g., H<sub>2</sub>O, SO<sub>x</sub>, NO<sub>x</sub>), as well as cost, attrition, stability, and availability can be examined.

As we have sought to determine the minimum parasitic energy of a material, the most important data are the (mixture) adsorption isotherms. As the experimental adsorption isotherms are known for only very few materials, we rely on molecular simulation to predict these isotherms for the different materials. Conventional grand canonical Monte Carlo (GCMC) simulations allow us to predict a complete isotherm on the basis of the crystal structure of the material.<sup>19,20</sup> These simulations, however, require on the order of days of CPU time, which is prohibitively slow to screen hundreds of thousands of materials. To obtain adsorption isotherms in a high-throughput manner, we have developed an efficient algorithm that allows us to obtain a complete isotherm in a few seconds on a graphical processing unit (GPU). Our method relies on the observation that pure component adsorption isotherms in these materials can be accurately described using dual- or single-site Langmuir isotherms.<sup>21</sup>

$$q_i = \sum_{j=1}^N \frac{K_{i,j} P_i}{1 + \frac{K_{i,j} P_i}{q_{sat,i,j}}}$$

In the equations above,  $q_i$  is the loading at the partial pressure  $P_i$  of the components  $i$ ,  $K_{i,j}$  is the Henry coefficient, and  $q_{sat,i,j}$  is the saturation loading of the component  $i$  at identified adsorption site  $j$ . In our model, only the single-site ( $N$  equal to 1) isotherm was adopted for

$N_2$  while either single- or dual-site ( $N$  equal to 2) isotherms were applied for  $CO_2$ . The temperature dependence of the Henry coefficients follows directly from the heats of adsorption, both of which were obtained from molecular simulations. The total saturation loading of pure component gas was calculated using a correlation of guest molecule density in the framework to pore diameter. For  $CO_2$  adsorption, the use of dual-site isotherms is required for structures that contain particularly strong adsorption sites; this behavior arises because  $CO_2$  first adsorbs at these sites, and only once all these positions are saturated does  $CO_2$  adsorb in the rest of the material. Figures 2a and 2d illustrate the difference between materials best described by single site and dual site isotherms, respectively. The long tail of the histogram in the lowest energy region is the signature of the presence of these strong adsorption sites. If such a signature exists, we use a dual-site description; otherwise, the isotherms are described using a single site. Figure 2e shows a typical case of such a dual site isotherm for pure  $CO_2$ . One observes a plateau in the isotherm at low pressure, which results from the saturation of the strong adsorption sites by  $CO_2$ . Each strong adsorption site can generally accommodate only one  $CO_2$  molecule, so the saturation loading for these sites is just the sum of the number of unique sites. We have developed an automated algorithm to identify the presence of these sites during molecular simulation and accordingly divide the structure into two regions, computing their own associated adsorption Henry coefficients, heats of adsorption, and saturation loadings. Figures 2b and 2e demonstrate that our model is able to predict the correct temperature dependence of the pure component isotherms.

The most commonly used method to predict mixture adsorption isotherms is ideal adsorbed solution theory (IAST).<sup>22</sup> However, as carbon capture of flue gases occurs at relatively low pressure, competitive Langmuir isotherms give an equally good description. It is important for dual-site Langmuir isotherms to take the saturation value for  $N_2$  to be the same as  $CO_2$  outside of the strong adsorption region, which is required for consistency with the assumptions of the competitive adsorption isotherm.<sup>23</sup> To test the reliability of the

competitive Langmuir model to predict the mixture isotherms on the basis of the pure components, we used the GCMC simulated mixture adsorption isotherms as “experimental data” to test whether the Langmuir model correctly predicts these mixture isotherms given the predicted pure component isotherms. We have tested over 50 different structures and for all systems, the competitive model accurately reproduces the mixture isotherms over a large range of pressures, including the partial pressures relevant for flue gas separations. Figures 2c and 2f demonstrate the performance of the competitive isotherm model with the corresponding GCMC simulations (see SI for the other structures).

Figure 3a shows the optimized parasitic energy as a function of the CO<sub>2</sub> Henry coefficient for all known zeolite structures. For these materials we observe a monotonically decreasing parasitic energy as a function of the Henry coefficient. To investigate the lowest parasitic energy that can be obtained using these materials, we perform calculations on a database of over one hundred and thirty-five thousand predicted zeolite structures.<sup>13</sup> These calculations identify predicted structures with parasitic energy that are lower than can be obtained for the known structures. Figure 3b shows some of the structures that have near-optimal parasitic energy.

The parasitic energy as a function of the Henry coefficient shows three regimes. The mixture isotherms in these regimes are shown schematically in Figure 4. Adsorption of CO<sub>2</sub> takes place at flue gas conditions (1 atm and 40°C). The subsequent desorption is achieved by decreasing the (partial) pressure and/or increasing the temperature. The difference in CO<sub>2</sub> concentration between adsorption and desorption defines the working capacity of a material and gives the amount of CO<sub>2</sub> that is removed in an adsorption cycle. For materials with a small Henry coefficient (see Figure 4a), the performance is poor because the working capacity is small, yet the entire system needs to be heated to the desorption conditions, giving a high parasitic energy. In addition, the adsorption of CO<sub>2</sub> is of the same order of magnitude



as  $N_2$  in these materials and hence the selectivity of such a material is unusably low. Materials with a larger Henry coefficient have a significantly larger working capacity and correspondingly lower parasitic energy. This trend continues until the Henry coefficient of the material is so large that at flue gas conditions the pressure is too high for the  $CO_2$  adsorption to be in the linear regime. Figure 4b shows that at these conditions the  $CO_2$  loading at the adsorbed state is not fully determined by the Henry coefficient anymore, and that materials with the same Henry coefficient have different working capacities depending on the pore volume. Figure 4c illustrates that at even larger Henry coefficients the adsorption of  $CO_2$  becomes so strong that it becomes increasingly difficult to regenerate the material. Another important observation is that we have a broad optimum. The reason for this broad minimum is that the Henry coefficient shows a strong correlation with the heat of adsorption, and the heat of adsorption has two opposing contributions to the parasitic energy. As the temperature dependence of the Henry coefficient is proportional to the heat of adsorption, a higher heat of adsorption increases the working capacity. While this reduces the parasitic energy, it is offset by the requirement to supply more energy to desorb  $CO_2$ , which again increases the parasitic energy.

Our screening shows a large set of zeolite structures that have a parasitic energy well below the current technology (1060 kJ/kg  $CO_2$ ). Inspection of these optimal structures highlights their diversity: we find one-, two-, or three-dimensional channel structures, cage-like topologies, and more complex geometries. To illustrate this point we show in Figure 3b a diverse sample of structures<sup>24</sup> contained in the optimal zeolites. It is interesting to compare these with the optimal known zeolite structures in Figure 3a. Several of the known zeolite structures have a sufficiently low parasitic energy, however, most of these known structures are one-dimensional channels, which may suffer from severe diffusion limitations.<sup>14</sup> By contrast, many of the predicted zeolite structures have side pockets where  $CO_2$  strongly adsorbs, along channels with larger diameters. Transport of  $CO_2$  to and from the sites of

adsorption occurs via the larger channels, so diffusion is not expected to be a limiting factor here. Interestingly, none of the known zeolites has this characteristic feature, and we consider this observation to be a significant finding.

A common feature of most optimal materials is a set of local regions of the structure that bind CO<sub>2</sub> preferentially, leading to dual-site adsorption behavior. Figure 5 shows the parasitic energy as a function of the binding energy of a CO<sub>2</sub> molecule at each of those local regions. To this figure we added those materials that have (near) optimal Henry coefficients, but without such dual-site behavior, which includes some of the known zeolite structures. We observe a similar correlation as for the Henry coefficient, since the binding energy dominates the Henry coefficient for structures with these preferential sites. The binding energy needs to be optimal: too low and the material adsorbs too little CO<sub>2</sub>, too high and the material becomes too difficult to regenerate. Figure 5 further shows that the parasitic energy is influenced by the density of strong adsorption sites in the material; the optimal materials exhibiting the largest number of strong adsorption sites per unit volume. This observation is important as it rationalizes why these materials exhibit a lower limit for the parasitic energy. The existence of a strong adsorption site requires a minimum amount of zeolite material, which, combined with the size of a CO<sub>2</sub> molecule, gives an upper limit to the total number of such local regions that can exist per unit volume.

An important practical question is whether we can synthesize these optimal materials. As the synthesis conditions of the known zeolites favor the formation of low-density structures,<sup>25</sup> one expects that among the predicted structures these low-density structures are the most likely ones to be synthesized. As highlighted in Figure 3a, this subset has many structures with optimal performance indeed. Recent developments<sup>26</sup> in novel structure directing agents may make it possible to synthesize some of these predicted optimal low-density structures.

An alternative strategy to create optimal Henry coefficients is to synthesize zeolites with different Al:Si ratios. In aluminosilicate zeolites, cations are present in the pores to compensate for the charge imbalance introduced by the  $\text{Al}^{3+}$  that replaces a  $\text{Si}^{4+}$ . Figure 6 shows the effect of cations on the parasitic energy for the known zeolites for different Al:Si ratio. Cations create adsorption sites for  $\text{CO}_2$  but also reduce the pore volume. The net result on the parasitic energy of these two effects depends on the particular structure. The addition of cations to low Henry coefficient structures causes a decrease in the parasitic energy due to the increased number of adsorption sites; however, continued addition of cations eventually increases the parasitic energy as the pore volume decreases. By contrast, addition of cations to near-optimal Henry coefficient structures increases the parasitic energy since the decrease in pore volume dominates. It is important to stress that every structure has its own optimal Al:Si ratio. Comparison with the parasitic energy for the all-silica structures shows that the addition of cations does not yield a material that has a lower parasitic energy for the same Henry coefficient. This observation is consistent with the notion that one has to create an adsorption site with exactly the right adsorption strength and that there is a limit to the maximum number of adsorption sites per unit volume.

Figure 7a shows the parasitic energy for ZIFs. For these materials, the overall parasitic energy is higher than for zeolites. As we have focused on the simplest linker (imidazole), the selectivity towards  $\text{CO}_2$  is rather low: linkers with higher selectivity will increase the Henry coefficient to a more optimal value and reduce the parasitic energy. Figure 7b gives a set of optimal ZIF structures. These structures look very different from the optimal zeolite structures; optimal ZIFs are those in which there are channels where  $\text{CO}_2$  can access the non-hydrogen atoms of the structure.

There are important experimental consequences to our results. Our metric provides a direct insight into the overall performance of a material in an actual carbon capture process.

In this context, it is instructive to compare our metric with the recently proposed alternative metric based on the adsorption breakthrough time.<sup>15</sup> Materials with the higher Henry coefficient, for a given saturation loading, will give the longer breakthrough time. However, as this study shows, materials with extremely high Henry coefficients perform poorly because the regeneration step cannot be ignored in a carbon capture process. This illustrates the limitation of focussing on a single material property rather than the entire process. In this respect our all-silica zeolite curve can be used as a benchmark for other materials.

Our screening establishes a theoretical limit for the minimal parasitic energy that can be achieved for this class of materials. Such a target will be useful to focus experimental efforts to synthesize such materials. To facilitate this synthesis effort, all of these structures, together with all physical properties that lead to the increase in performance, are available online.<sup>27</sup>

## Methods

Since for most of the materials experimental data do not exist, we use molecular simulations to predict the adsorption isotherms. As input, these simulations require the crystal structure of the materials and a force field describing the interactions. In addition, by accelerating computationally expensive steps in molecular simulation using GPUs, we enable screening of materials in a high-throughput manner.

**Crystal Structures:** For the all-silica zeolite structures, we used the experimental zeolite crystal structures<sup>28</sup> and the database with predicted, fully optimized zeolite crystal structures.<sup>13,25</sup> This database was constructed by searching the chemical space of possible SiO<sub>2</sub> structures that are zeolite-like. This was done by examining all 230 space groups and a wide range of unit cell dimensions and silicon densities. Symmetry operations acting upon crystallographically unique atoms were used to generate the full unit cell structure. A Monte Carlo procedure was used to sample this vast space of possibilities giving 2.6 million topologically distinct zeolite-like structures. The structures identified by the Monte Carlo sampling procedure were optimized by detailed interatomic potentials.<sup>29,30</sup> Depending on the force field 330,000-590,000 of these structures are within this thermodynamically accessible band of energies +30kJ/mol-Si above  $\alpha$ -quartz. The structures in this database have topological, geometrical, and diffraction characteristics that are similar to those of known zeolites.<sup>25</sup>

In most zeolites the Si can be exchanged with Al, which creates a charge deficit that is compensated by cations (e.g., Na<sup>+</sup>, H<sup>+</sup>, Ca<sup>2+</sup>). Only for a limited number of structures location of these Al sites are known.<sup>20,31</sup> A reasonable starting point<sup>20</sup> is to assume a random distribution of Al over the T-sites such that Loewenstein's rule<sup>32</sup> is obeyed, which implies a maximum Al/Si ratio of one. For this ratio and for Al/Si equal to zero we have one unique structure. For the other Al/Si ratios there are many different possible distributions of the Al atoms over the T sites. For these ratios we generated at least ten different distributions and the cations were subsequently added at the minimum energy positions.<sup>33</sup> Each distribution can have a slightly different adsorption isotherm and we averaged the parasitic energy.<sup>31</sup> In addition, we compared the results for systems in which the cations were fixed at the minimum energy configurations, with simulations in which the cations were free to move. For structures with a low Henry coefficient, we found a lower parasitic energy if the cations were allowed to move. However, for those structures with optimal Henry coefficients, the differences between these two systems were very small.

Zeolitic imidazolate frameworks (ZIFs) are a class of metal-organic frameworks that have a pore topology that is isomorphic with the zeolite structures.<sup>12,34</sup> In ZIFs the transition metal atoms (M) replace the Si atoms and imidazolates (IM) replace bridging oxides in zeolites. Given that the M–IM–M angle is similar to the Si–O–Si angle, ZIFs form 3D networks with topologies that are very similar to zeolites. In our screening study we applied this analogy to the zeolite database to generate ZIFs. In the reported zinc and IM-based ZIFs with IZA zeolite topologies<sup>34</sup> the distance between zinc atoms and the center of IM rings is about 1.95 times larger than the Si–O distance in zeolites. A ZIF structure was generated by scaling the unit cell of the corresponding zeolite structure by the same factor and exchanging each oxygen atom with an IM group and each Si atom with a Zn atom. We have validated the resulting ZIF geometries by comparing geometries of two structures for which the experimental geometries are known: ZIF-3 (DFT) and ZIF-10 (MER). The observed differences in the geometries do not translate into significant differences in the parasitic energy.

**Model and Simulation details:** Calero and co-workers<sup>35,36</sup> have developed a force field that accurately reproduces the experimental isotherms in zeolites. For ZIFs, parameters for the framework atoms were taken from the DREIDING force field<sup>37</sup> and parameters for CO<sub>2</sub> and N<sub>2</sub> were taken from the TraPPE force field.<sup>38</sup> Framework-molecule interaction parameters were calculated using the Lorentz-Berthelot mixing rules. Partial charges for ZIF framework atoms were computed using the connectivity based approach of Zhong and Xu.<sup>39</sup> Adsorption isotherms were calculated using grand canonical Monte Carlo simulations (GCMC).<sup>19</sup> The experimental equations of state are used to convert the chemical potentials into (partial) pressures.

**GPU Calculations:** To screen a large number of zeolite and ZIF structures we developed a graphics processing unit (GPU) code to accelerate the molecular simulations. We focus on computing the Henry coefficients and the heats of adsorption. The algorithm is divided into three different routines: (1) energy grid construction, (2) pocket blocking, and (3) Widom test particle insertion.

(1) *Energy grid construction:* To save computational time we construct a grid, giving the energies of the atoms at the grid positions in the unit cell of a framework.<sup>20</sup> The energy grid has a mesh size of 0.1 Å and the interaction between the gas molecule and all of the framework atoms is modeled by the Lennard-Jones potential and the Coulomb potential, with Ewald summations used to approximate the latter. Each of the grid points maps to a single CUDA (Compute Unified Device Architecture) thread and the pairwise potentials are computed in parallel across different CUDA blocks.<sup>40</sup> The positions of the framework atoms are put inside the fast constant memory in the

GPU to expedite calculations. At the end of the routine, the array that contains the energy values is transferred from the GPU to the CPU as an input to the pocket blocking routine.

- (2) *Pocket blocking*: In a GCMC simulation, one can insert molecules in pockets that are inaccessible from the outside.<sup>41</sup> The void space analysis algorithm<sup>42</sup> is used to detect and block these inaccessible pockets.<sup>43</sup> We use the values from the energy grid to determine the accessibility of a particular configuration/point in the unit cell using the (multicore) CPU, as this routine does not map well to the GPU architecture. The discrete energy grid is mapped to a binary grid of accessible/ inaccessible points based on a certain threshold value that is chosen to be large enough such that on an experimental time scale, the pocket is considered inaccessible. Finally, we utilize a parallel flood fill algorithm to segment the grid into connected, accessible regions. These regions are then classified as either channels or inaccessible pockets, and we set all grid points inside pockets to a very high-energy value.
- (3) *Widom test particle insertion*: utilizing this revised energy grid, we can calculate both the Henry coefficients and the heats of adsorption using Widom insertion moves.<sup>19</sup> We randomly insert a guest molecule inside the simulation box and calculate both the Boltzmann factor and the energy values for the particular guest molecule configuration. We can use interpolating functions to estimate the energy values at points that are not directly on the grid. In the GPU architecture, each CUDA thread can conduct independent Widom insertion.

Overall, most of the computational wall time is spent in the GPU energy grid construction routine. In this routine, there is roughly a factor of 50 in performance improvement going to the GPU (Tesla C2050 Fermi) from the CPU (single core of a 2.4 GHz Intel 5530 Xeon).

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**Additional information**

The authors declare no competing financial interests. Supplementary information accompanies this paper on [www.nature.com/naturematerials](http://www.nature.com/naturematerials). Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to B.S.

**Figure 1: Hybrid pressure and temperature swing adsorption.** In the adsorption step (1) the flue gas is brought into contact with the solid adsorbent. The material selectively adsorbs CO<sub>2</sub> and (nearly) pure N<sub>2</sub> leaves the adsorber. When the adsorber is saturated, it is regenerated (2) by heating the system and/or applying a vacuum. The purge (3) and cooling or repressurization step (4) brings the system in its original state (1). The amount of CO<sub>2</sub> that is removed from the flue gas in a single cycle defines the working capacity of a material. The regenerated CO<sub>2</sub> is subsequently pressurized to 150 bar for geological storage.

**Figure 2: (Mixture) adsorption isotherms.** Probability distribution of the energies of a particle inserted in the pores (top), pure component isotherms for CO<sub>2</sub> and N<sub>2</sub> and pure CO<sub>2</sub> isotherms at different temperatures (middle) and mixture isotherms (bottom) for two materials: the zeolite SIV ((a), (b), (c)) and the predicted zeolite h8286959 ((d), (e), (f)). The symbols are the results from the GCMC simulations and the lines are the results of our methodology utilizing the GPU calculations.

**Figure 3: Parasitic Energy as a function of the Henry coefficient of CO<sub>2</sub> for all silica zeolite structures.** The Henry coefficient can be obtained from the adsorption isotherm; at sufficiently low pressure the Henry coefficient times the pressure gives the number of adsorbed molecules. In figure (a) we compare the International Zeolite Association (IZA) zeolite structures (red squares) with the predicted structures (blue circles). For the predicted zeolite structures, we only plot the set of most dissimilar structures and those materials that have a sufficiently large Henry coefficient ( $> 5 \cdot 10^{-5}$  [mol/(kg Pa)]). The open blue circles are computationally predicted structures near the low-density feasibility line, which are most likely to be synthesizable. The green lines give the parasitic energy of the current MEA technology, and the black line is the minimal parasitic energy observed for a given value of the Henry coefficient in the all-silica structures. In the SI we show the

sensitivity of the parasitic energy on uncertainties in our parameters. All data points can be linked to a structure by accessing [www.carboncapturematerials.org](http://www.carboncapturematerials.org)

Figure (b) gives some examples of the optimal all-silica structures; out of the 50 top performing materials we selected the six most diverse. The figures show the atoms of materials as ball and stick (O, red ; Si, tan). The surface gives the local free energies in the pores of the material, where warmer colors indicate the dominant CO<sub>2</sub> adsorption sites.

**Figure 4: Adsorption isotherms.** The loading in the zeolite is plotted as a function of the partial pressure of CO<sub>2</sub> (green or purple) or N<sub>2</sub> (orange). Adsorption is set by the flue gas conditions (40°C, 1 atm and 14% CO<sub>2</sub> and 86% N<sub>2</sub>). The working capacity follows from the difference in the amount of adsorbed CO<sub>2</sub> at adsorption and desorption conditions. In most of these materials the N<sub>2</sub> adsorption is so small that N<sub>2</sub> adsorption does not contribute much to the parasitic energy, and only for materials where the adsorption of CO<sub>2</sub> is equally small do we consider the contribution of N<sub>2</sub>. At sufficiently low pressure, these adsorption isotherms are linearly related to the pressure, with the proportionality constant defined as the Henry coefficient. (a) A material for which the Henry coefficient is sufficiently low that both the adsorption and desorption are in the Henry regime. A low Henry coefficient (green) gives a relatively small working capacity and purity of the product stream. Increasing the Henry coefficient (purple) gives a significant increase of the working capacity. (b) If the Henry coefficient becomes much larger, the number of adsorbed CO<sub>2</sub> molecules is so large that CO<sub>2</sub>-CO<sub>2</sub> interactions in the materials are important at the partial pressure of CO<sub>2</sub> corresponding with flue gas conditions. Hence, the adsorption cannot be characterized with a Henry coefficient only. (c) For those materials with a very high Henry coefficient, a further increase of the Henry coefficient will have little effect on the uptake value at adsorption as this is now

dominated by the pore volume. For desorption, however, increasing the Henry coefficient will further decrease the working capacity. For (b) and (c), as desorption occurs at higher temperatures, the desorption pressure is still in the Henry regime.

**Figure 5: Optimal materials.** The parasitic energy as a function of the binding energy for a CO<sub>2</sub> molecule. The binding energy is defined as the lowest energy that can be observed in a given structure. If this binding is sufficiently strong, dual-site adsorption behavior will arise. The fraction of each material's volume which is occupied by low-energy strong adsorption sites is displayed as colored solid circles. Structures without these specific features (i.e., single site adsorption behavior) are displayed as open blue circles.

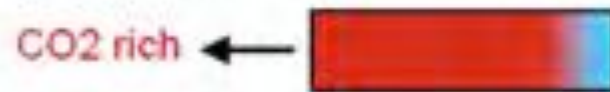
**Figure 6: Parasitic energy for zeolites with cations.** The parasitic energy as a function of the CO<sub>2</sub> Henry coefficient for known zeolite structures with different Al/Si ratios is shown. The all-silica IZA structures are shown as red squares and the corresponding structures with different cation concentrations are labelled as follows: Si:Al=9 (blue circles), Si:Al =3 (green triangles up), and Si:Al =2.3 (orange triangles down)).

**Figure 7: Parasitic energy for ZIFs.** (a) The parasitic energy as a function of the CO<sub>2</sub> Henry coefficient for ZIFs is shown. The green lines give the parasitic energy of the current MEA technology, and the black line is the minimal parasitic energy calculated for a given value of the Henry coefficient in the all-silica structures. (b) Out of the 50 top performing ZIFs, we selected the six most diverse. The figures show the atoms of materials as ball and stick (Zn blue-grey, O blue, H white, and C grey). The surface gives the local free energies in the pores of the material, where zinc (blue) is the dominant CO<sub>2</sub> adsorption site.

**1 Adsorption**



**2 Heating / Vacuum**



**3 Purge**



**4 Cooling / Repressurization**



**1 Adsorption**



Figure 1

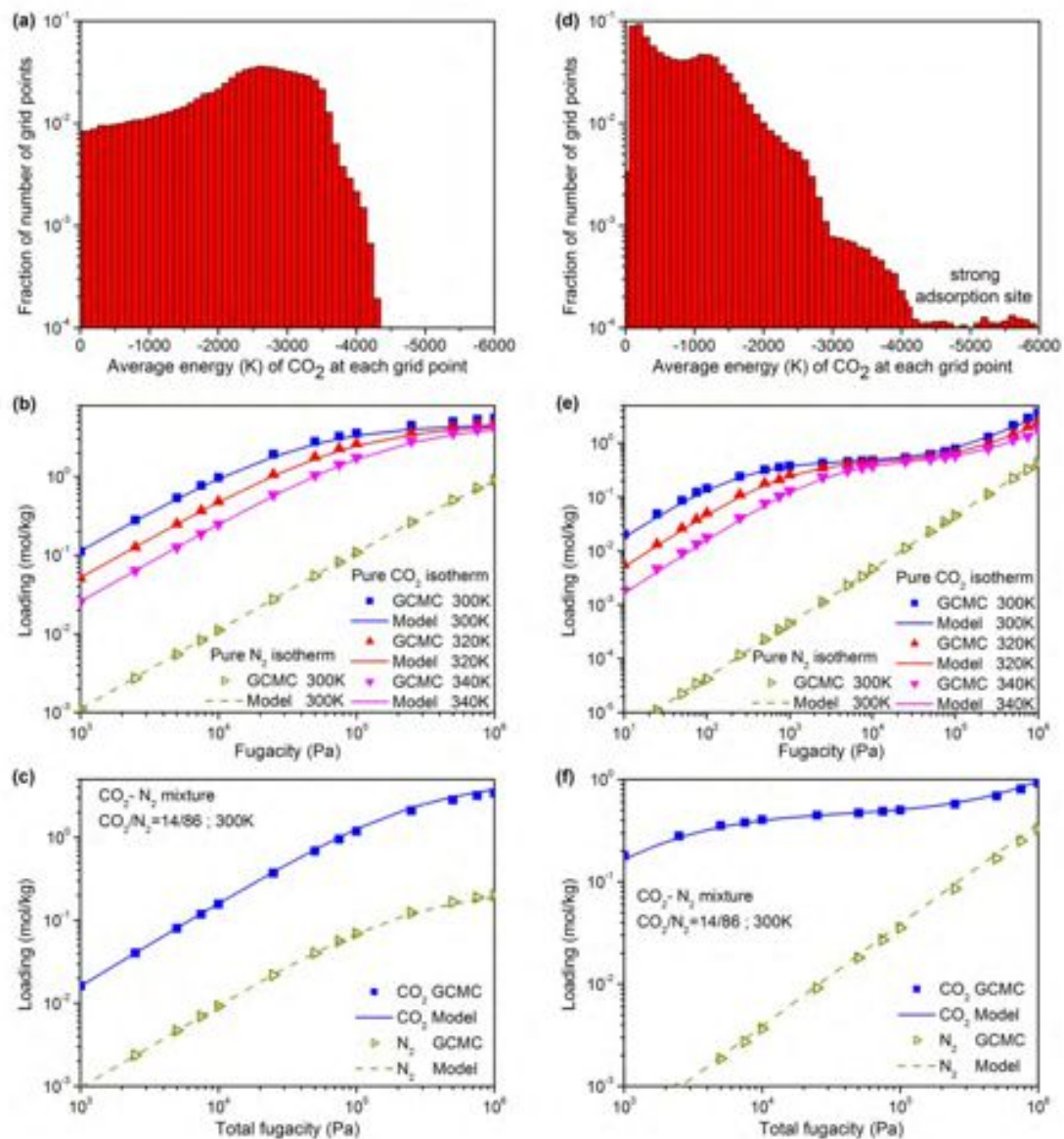


Figure 2



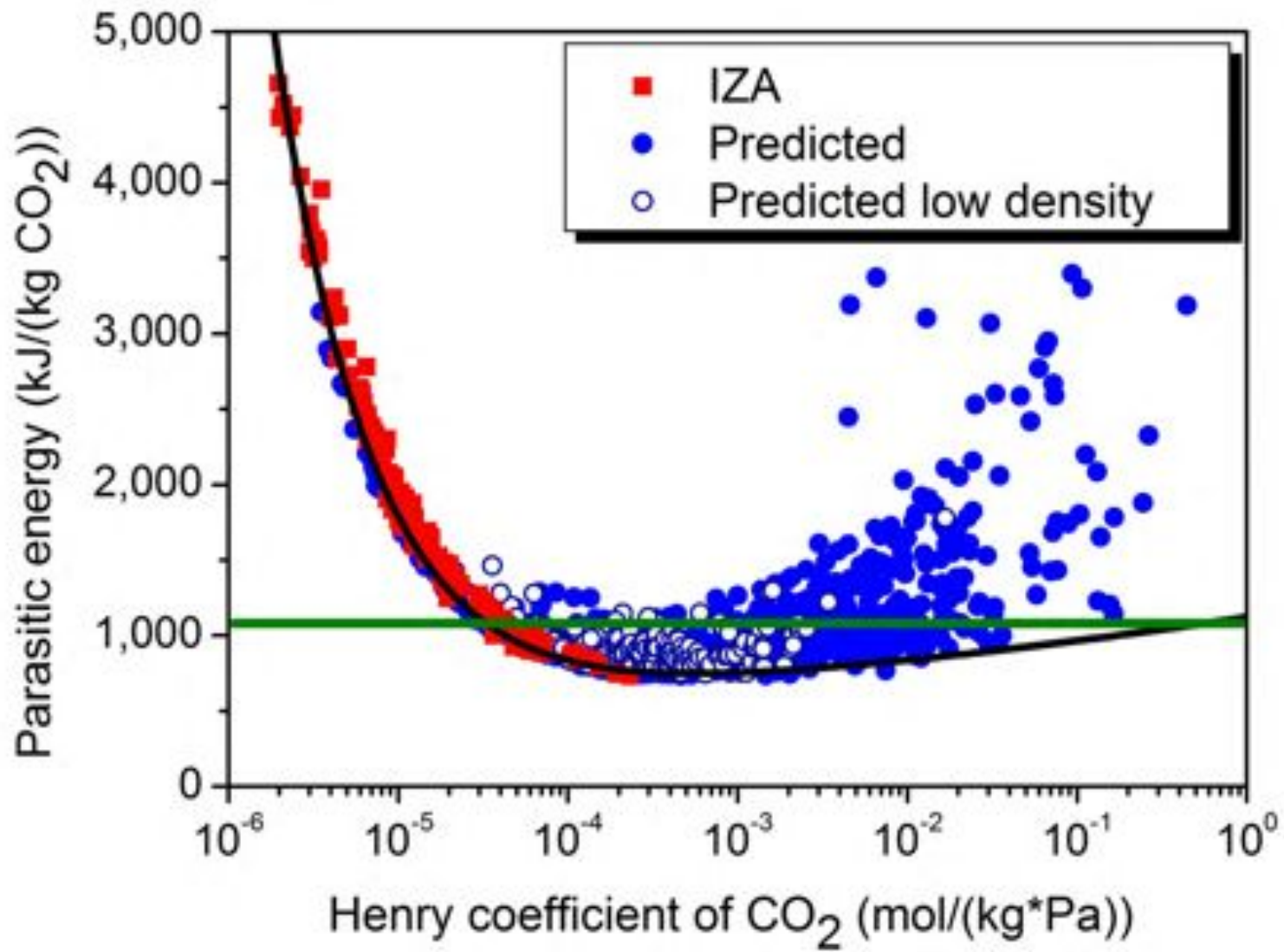


Figure 3a

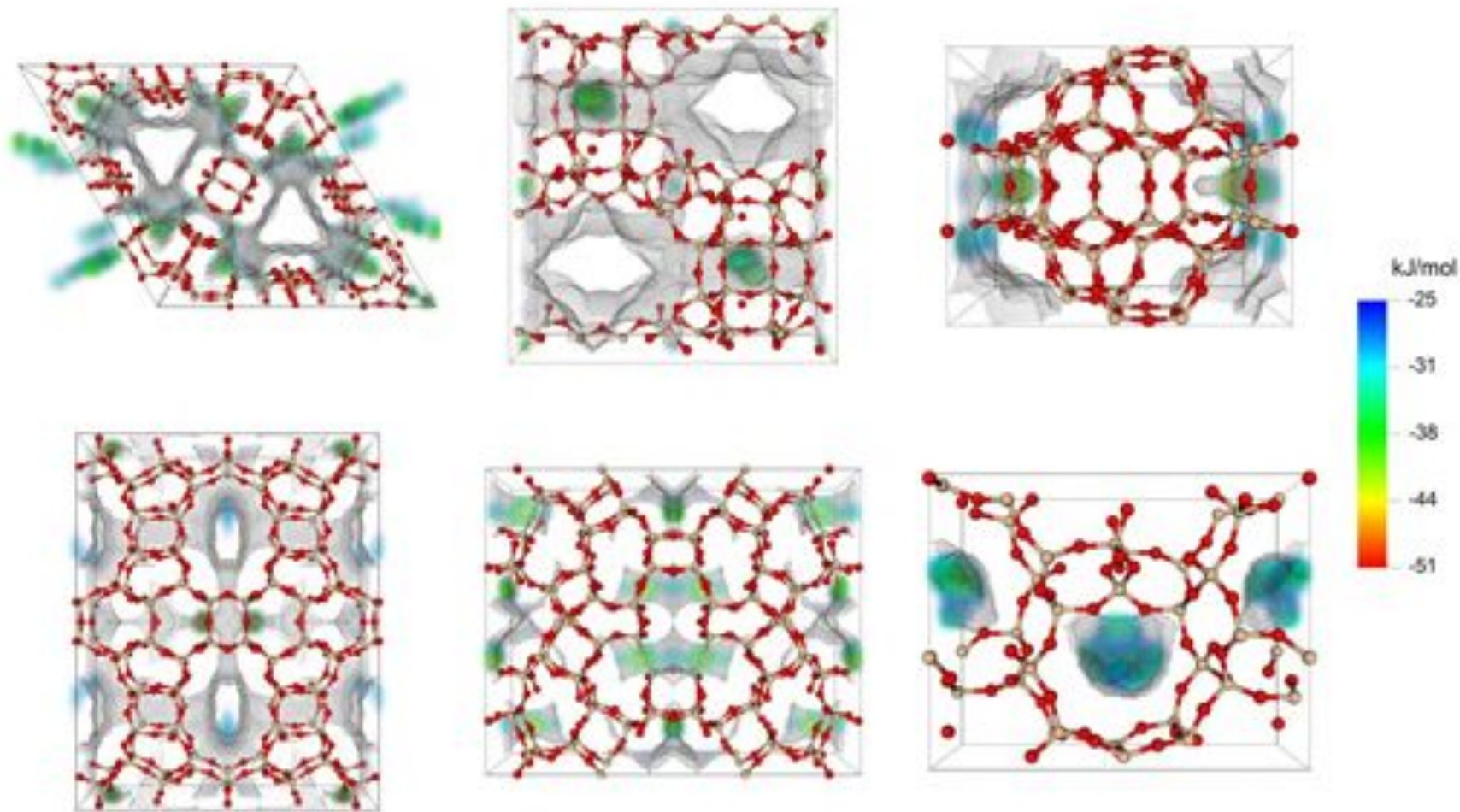


Figure 3b

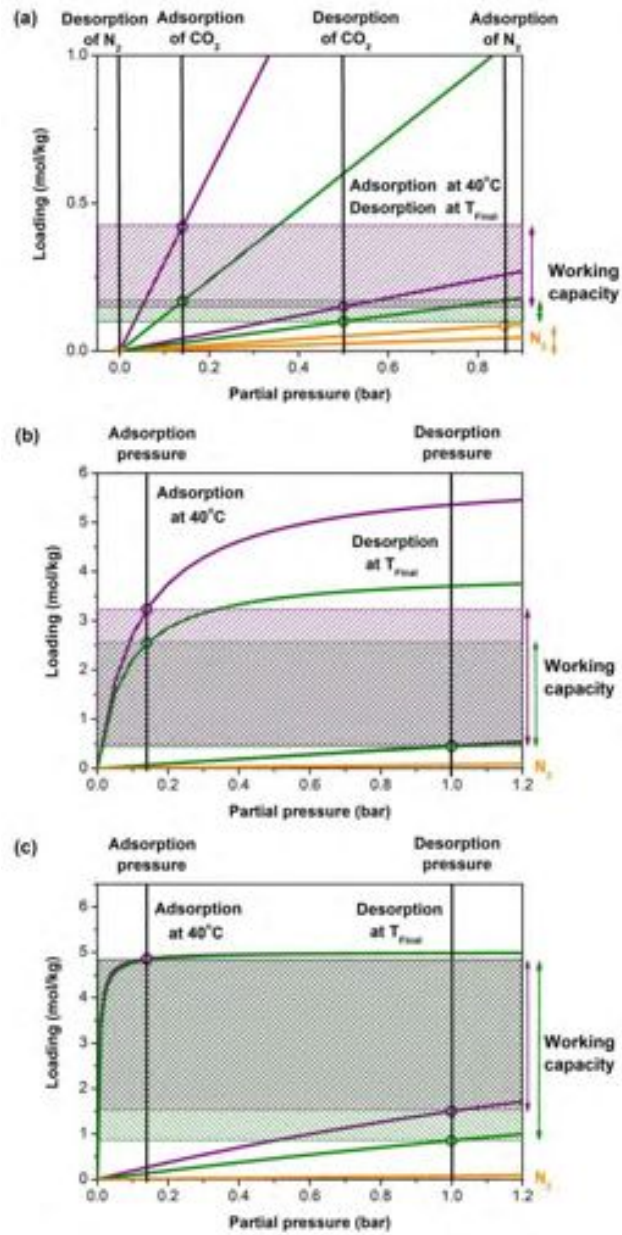


Figure 4

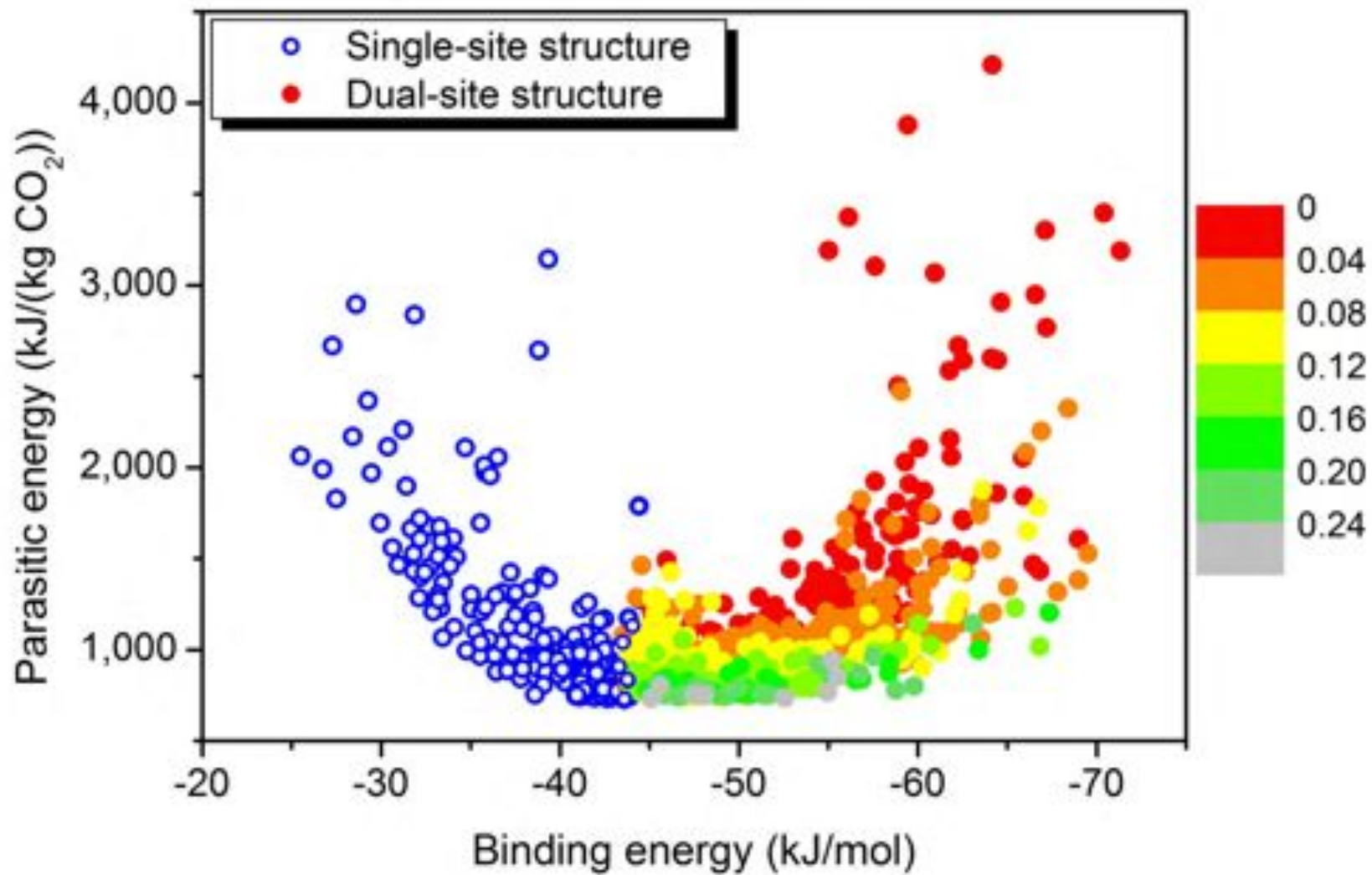


Figure 5



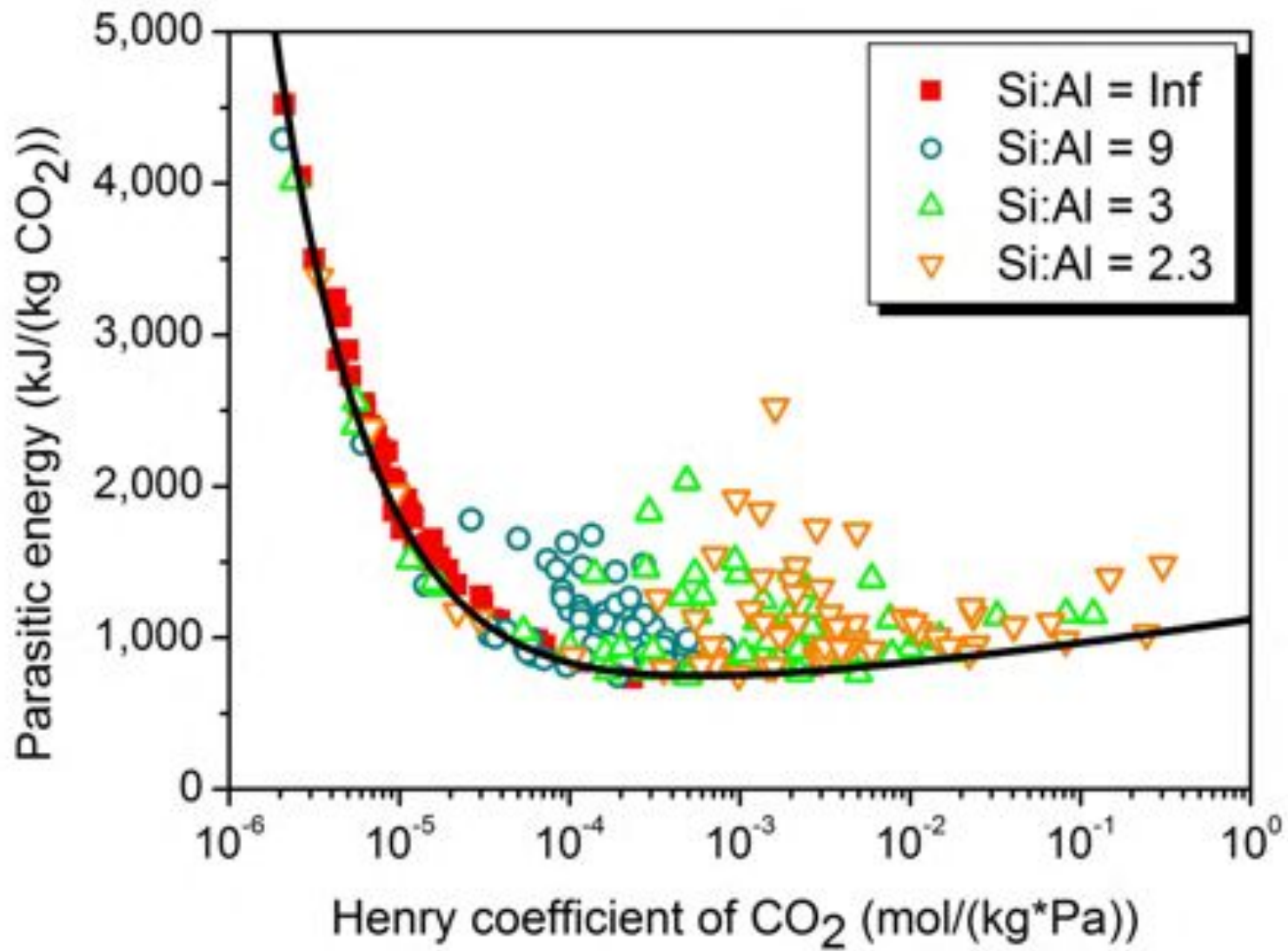


Figure 6

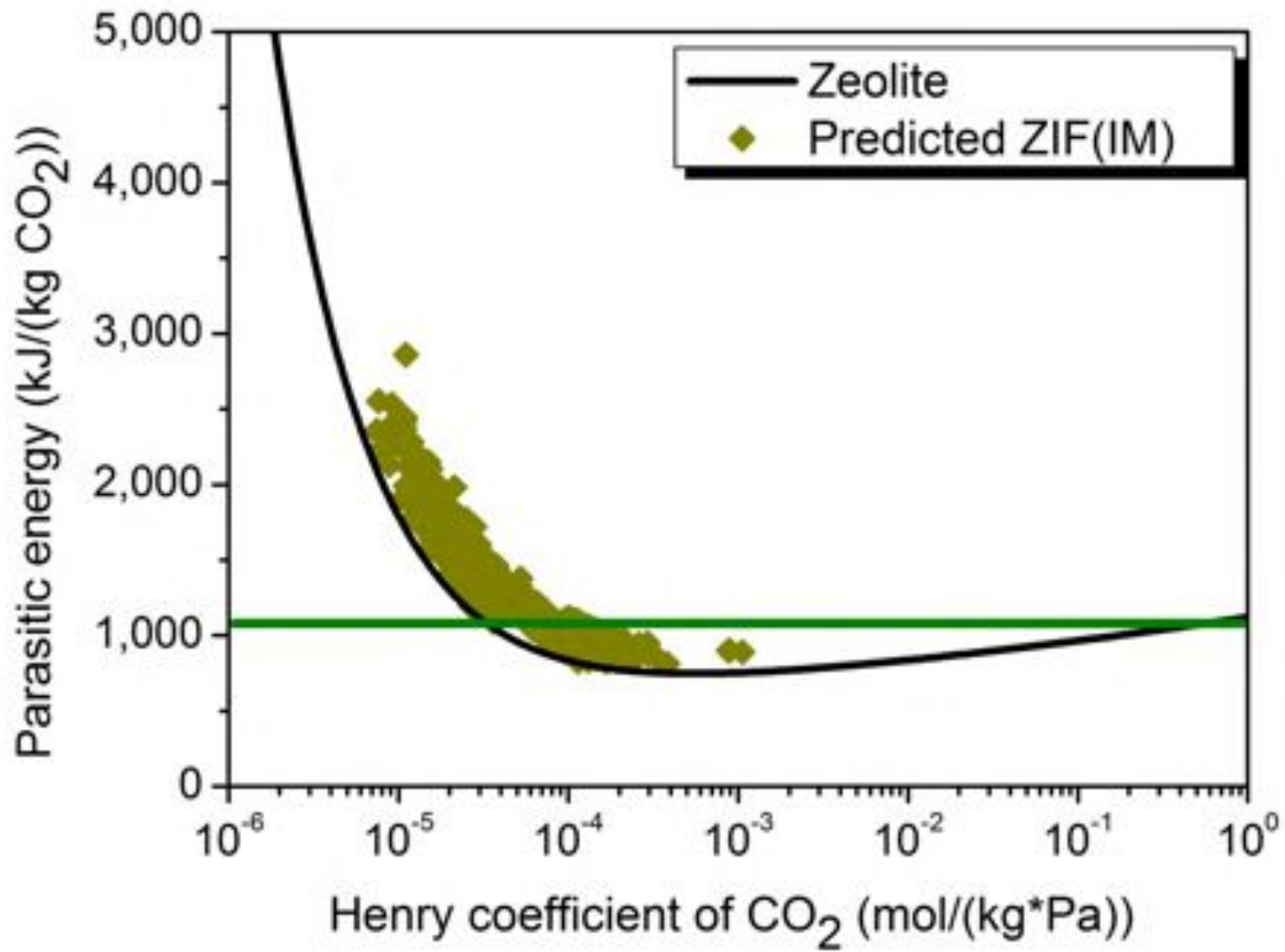


Figure 7a

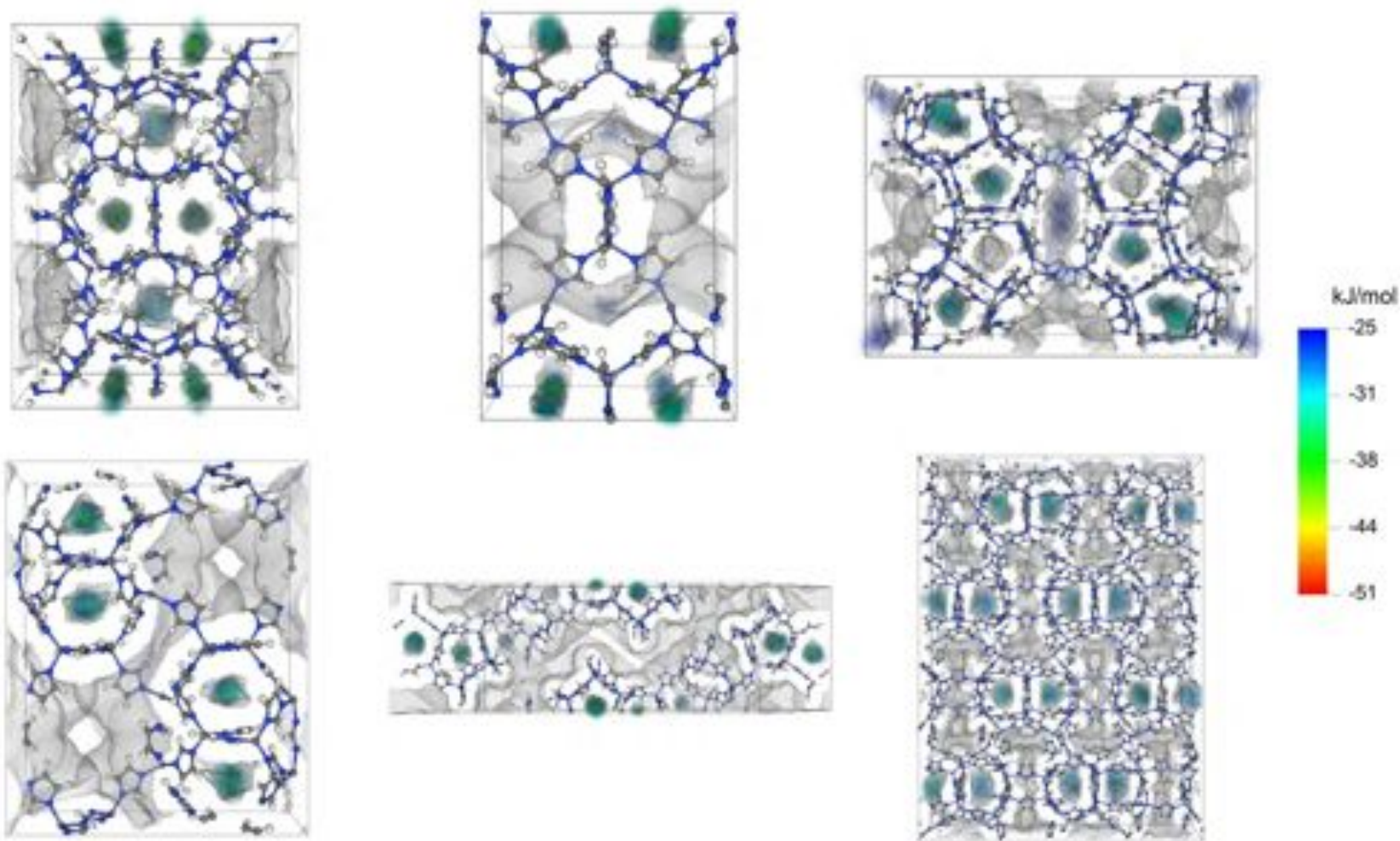


Figure 7b