

# **A Density Functional Study of the Hydrophobicity of Silicalite**

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A Major Qualifying Project Report

Submitted to the faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the Degree of  
Bachelor of Science  
In

Chemical Engineering

28 April, 2010

APPROVED

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## **Abstract**

Factors that influence water adsorption in silicalite were studied. It was found that the energy of adsorption becomes less stable as water molecules are loaded in the silicalite structure. A structure with one water molecule was found to have an energy of -14.42KJ/mol while one with three molecules was - 8.6 KJ/mol. It was also demonstrated that water prefers to diffuse through the larger 10 ring channels as opposed to the small 4 ring channels.

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## Introduction

Silicalite is one of the most studied zeolites that has both hydrophobic and organophilic selectivity (Ramachandran, Chempath and J.). Hydrophobic in this case does not mean water repelling but that the water-water interaction (Labar, Fuchs and Adamo) is much larger than the water-zeolite interaction. It has been widely used to clean up water contaminated with organic compounds. Understanding the behavior of water in hydrophobic micropores is important in a wide variety of fields, ranging from biological membrane transport to applications in carbon nanotubes.

Silicalite is a pure silica MFI structure (Ramachandran, Chempath and J.). Ideally, silicalite would be electrically neutral if it was only composed of silicon and oxygen atoms. It is widely regarded as a hydrophobic structure. Earlier studies showed that silicalite readily adsorbs organic molecules over water. These studies as well as later studies have shown that silicalite actually adsorbs a small amount of water. This should not be the case if silicalite is electrically neutral. Studies have demonstrated that silicalite, also contains aluminum which causes a charge imbalance and therefore favoring water adsorption. The degree of aluminum substitution and its corresponding effect on water loading in the silicalite structure has been an area of interest (Yazaydin).

Molecular simulations performed have shown that a perfect silicalite structure is hydrophobic and does not adsorb water at low pressures (Ramachandran, Chempath and J.). When pressure is increased, the pores become saturated with water molecules at some intermediate pressure. The presence of hydrophilic defects, like the aluminum substitution mentioned previously lead to adsorption of small amounts of water at low pressures. Previous studies have demonstrated that the silicalite structure can adsorb up to 8-9 water molecules in its structure (Fleys).

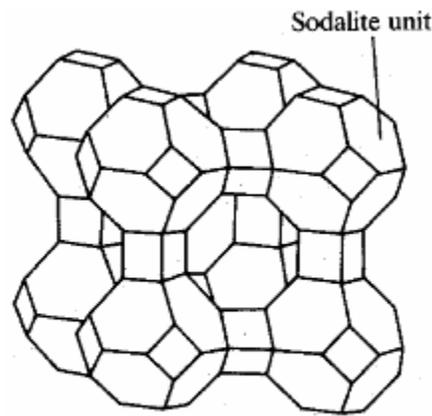
The objective of this research project is to investigate the factors that affect the hydrophobicity of silicalite using density functional theory (DFT). To the best of my knowledge most molecular simulation

studies have been performed using molecular dynamics and Monte Carlo methods. DFT uses a different approach from these two methods as will be discussed in the background section.

## Background

### Zeolites

Zeolites are hydrated micro-porous, crystalline, aluminosilicate minerals. They are usually filled with water in their pores. Zeolites are referred to as aluminosilicate because their structures are mainly composed of silicon, aluminum and oxygen atoms. They are also known as molecular sieves because they have regular openings that let small molecules through and trap the larger ones. Their crystalline and micro-porous nature as well as well-defined pore dimensions gives them properties like high thermal stability ion exchange, sorption capacity. As a result, they are able to exchange ions with some compounds, which make them extremely useful as detergent additives, where they exchange sodium cations found in their structure, with calcium cations found in water. They are also selective adsorbers, making them favorable as molecular sieves.



Zeolite A

Figure 1: Example of Zeolite (Zeolite A) (Dyer)

Zeolites are both naturally-occurring as well as synthetic. Natural zeolites are secondary minerals<sup>1</sup> and can be defined as crystalline, hydrated alumino-silicates of alkali and alkaline-earth cations that consist of periodic three dimensional crystal structures of (Si, Al)O<sub>4</sub> tetrahedra, which are linked together by the sharing of oxygen atoms (Dyer). Their structures have channels and pores that are usually filled with water. At 250°C, the water evaporates in a process known as dehydration. This water can be regained if they are cooled to room temperature (rehydration). There are 50 natural zeolites whose structures have been determined. Such zeolites include clinoptilolite used in the agricultural industry and chabazite in the waste water industry (Ibrahim).

R. M. Barrer demonstrated that zeolites can be synthesized by mimicking the geothermal conditions under which zeolites form in nature (Knott, Neal and S.). Through simple hydrothermal reactions, he was able to demonstrate this process. Synthetic zeolites have an advantage over their natural counterparts because the latter contain many impurities making them ineffective and they also have insufficient quantities in their deposits. Since then over 100 species have been synthesized in the laboratory which have no natural counterparts.

They have a 3-D framework consisting of cross-linked TO<sub>4</sub> tetrahedra where T is Al or Si. Each T atom occupies four connected vertices of a three dimensional network and the oxygen occupy two connected positions between the four connected vertices. The O-T-O bond is close to the ideal tetrahedra bond angle of 109.5°. The T-O-T bond angle is much more flexible and is usually around 140° to 165° (zeolite wolf wiki). The aluminosilicate based zeolites are represented by the formula (M<sub>1/n</sub>AlO<sub>2</sub>xSiO<sub>2</sub>yH<sub>2</sub>O) in which M represents a cation of valence n and x ≥ 1. No Al-O-Al bonds are permitted in a zeolite

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<sup>1</sup> Secondary minerals are minerals altered to a new form after undergoing a chemical change.

according to Loewenstein's rule. The latter states that the ratio of silicon-to-aluminum must be greater or equal to one due to local charge restrictions.

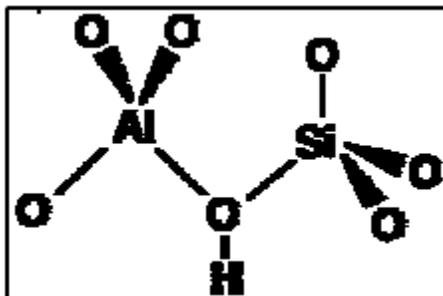


Figure 2: Aluminosilicate Tetrahedra (Dyer)

Zeolite structures contain two types of building units, primary and secondary building units. The  $TO_4$  tetrahedra are often referred to as primary building units (PBU) of zeolite structures. The PBUs are linked together to form a three-dimensional framework and nearly all oxygen ions are shared by two tetrahedra. This makes the silicon to oxygen ratio 1:2. If all the tetrahedra were centered around silicon then the structure would be electrically neutral. However in some structures the quadrivalent Si is replaced with the trivalent Al giving rise to a deficiency of positive charge, and this is balanced by monovalent or divalent cations like  $H^+$ ,  $Na^+$ ,  $K^+$  and  $Ca^{2+}$  located outside the tetrahedra, in the channels and pores. The primary building units are linked up to form secondary building units (SBU). The secondary building units consist of n-ring structures which can contain as many as 20 tetrahedra and as little as 4. They may be assembled in many ways to produce various types of frameworks. Examples of SBUs are shown below.

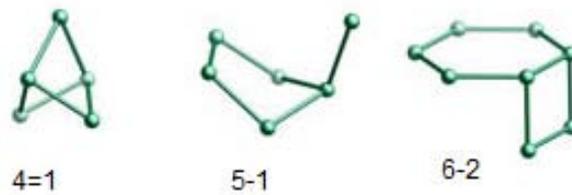


Figure 3: Secondary Building Units (Baerlocher and B.)

Zeolites have many properties due to their crystalline structures, type, size and form of their inner cavities and pores. These properties include cation exchange capacity, acid stability, adsorption properties and wet attrition resistance. These properties make zeolites especially desirable in the environmental protection sector for controlling air and water pollution.

Cation exchange capacity is a measure of the number of counter ions present per unit weight or volume of the zeolite and represents the number of cations available for exchange (Semmens, 1984). It is a function of the degree of Aluminum substitution for Si in the zeolite framework structure. The greater the substitution, the greater the deficiency of charge and therefore the greater the number of alkali or alkaline earth cations required for electrical neutrality.

The dehydration process leaves the zeolites with channels and pores of a particular shape and size. Molecules with a certain diameter can enter the cavities and channels within the structure. However, a molecule that is larger in diameter would not be able to diffuse through; this gives zeolites their molecular sieving property. Factors that affect the rate of adsorption include the Si/Al ratio in the structure, pore volume and size, type of adsorption sites and shape of cages and channels. Selective adsorption gives zeolites many commercial applications including the purification of acid natural gas streams, drying and separation of air to produce oxygen and nitrogen.

## Silicalite

Silicalite is a pure silica MFI type of zeolite (Smit and Siepmann). MFI zeolite membranes (silicalite-1 and ZSM-5) have been the most studied material for gas separations and catalytic reactors. Silicalite is widely used to clean-up water contaminated with organic compounds. Due to the problems associated with activated carbon, hydrophobic zeolites like silicalite are being used in solvent emission control systems (Hunger, M. and J.).



Figure 4: Silicalite Crystalline Structure

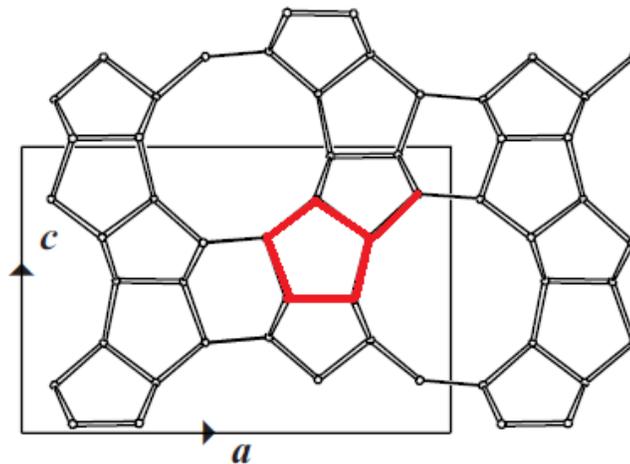


Figure 5: MFI Structure (Baerlocher and B.)

This zeolite belongs to a family known as the pentasil zeolites. This is because its secondary building unit is built from five-membered oxygen rings. A unit cell of silicalite contains 96 tetrahedral units. One unit cell is composed of two straight channels and four sinusoidal channel intersections. The structure consists of sinusoidal channels in the a-direction, with a circular cross-section which are interconnected with straight channels in the b-direction of elliptic cross-section. The structure of the MFI membrane enables it to be both shape and size selective. Silicalite has properties which include hydrophobic properties, higher thermal stability and higher chemical stability . (Motuzas et. al)

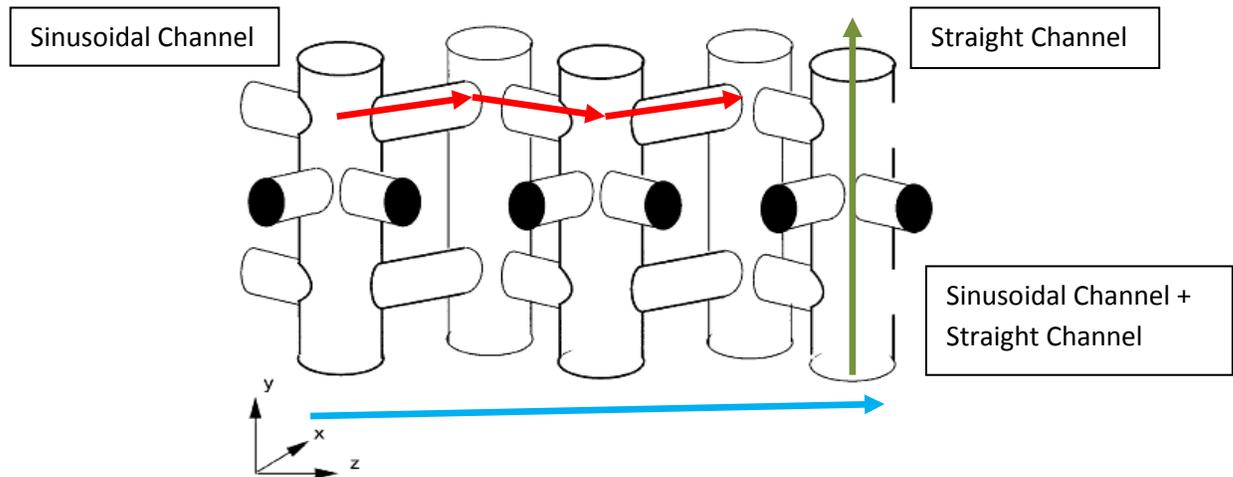


Figure 6: Channels in Silicalite (Ramachandran, Chempath and J.)

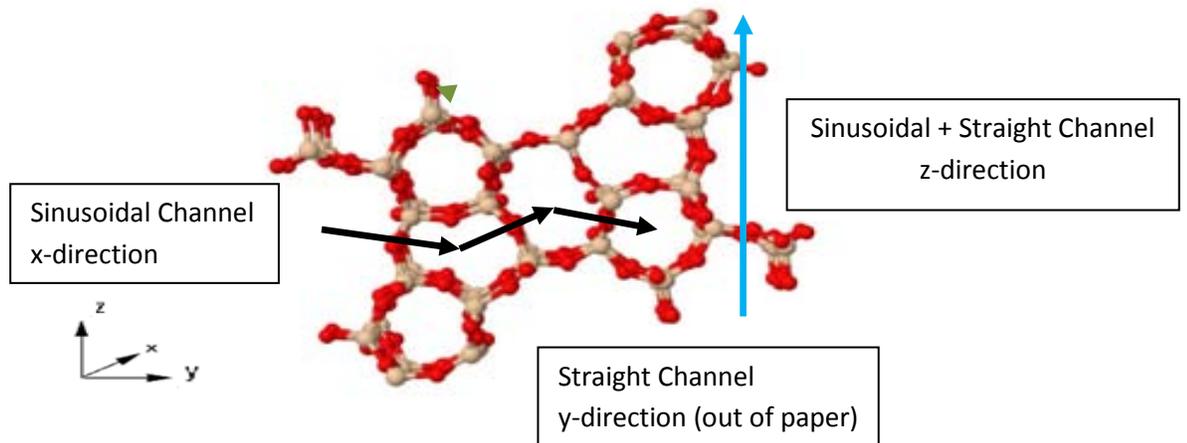


Figure 7: Channels in Silicalite

It is generally accepted that silicalite is a hydrophobic material. In several experiments silicalite was shown to preferentially adsorb organics from water. An important characteristic of zeolites is the Si/Al ratio (Dyer). The presence of aluminum creates a charge imbalance. The increase of the Si/Al ratio results in a more neutral framework, resulting in higher thermal stability and hydrophobicity. This accounts for why the purely siliceous compound, silicalite-1 is hydrophobic and has no ion exchange or catalytic properties. Theoretically, there are no aluminum atoms in the silicalite structure; therefore there are no cations to compensate for the extra charge. However defects in the structure of silicalite allow a certain amount of water to be adsorbed. There are two common types of defects (Yazaydin). A zeolite may have extra framework cations, which account for the non-neutrality of the silicalite framework due to presence of aluminum sites which substitute the missing silicon atoms (Yazaydin). Moreover, they may have a Si-OH group. The second defect may either occur on the surface of a zeolite where the Si-O-Si network is terminated and an oxygen atom cannot be bonded to a silicon atom or within the zeolite where a silicon atom is missing. In the latter case four Si-OH groups are formed per each missing silicon atom and this structure is called a silanol nest.

## Water in Silicalite

A lot of research has been carried out to investigate the hydrophobic nature of silicalite. Different factors that influence the loading of water on the structure have been proposed. As mentioned previously, one main factor is the ratio of silicon to aluminum. Other reasons are the presence of silanol sites and an increase in external pressure. Ramachandran et. al carried out Monte-Carlo simulations of water in silicalite. They were able to demonstrate that for truly hydrophobic micropores, water was not adsorbed at low pressures (Ramachandran, Chempath and J.). However, as pressure was increased, the loading of water molecules on the zeolite increased. They also added silanol defects on to the structure, which led to water loading even at low pressures.

A study by Fleys was done to compare the behavior of water in hydrophobic nanopores (Fleys). Fleys used silicalite-1 and dealuminated zeolite Y for his comparison. He investigated the factors that affected self-diffusion which are temperature, the shape and size of the cavities and the effect of loading water molecules. The study was carried out using molecular dynamic simulations. Fleys demonstrated that diffusion increases with increasing temperature (between 250K and 600K). There was more diffusion in the y-axis, which had the straight channels. The z-axis which had a combination of both the straight channels and sinusoidal channels had the least diffusion. The self-diffusion coefficient was shown to decrease as the loading increased. Previous studies showed that the silicalite structure can adsorb up to eight water molecules.

Yazaydin used Fleys' findings lay the groundwork to investigate the influence of defects on the silicalite structure. As mentioned before, an ideal silicalite-1 structure would be composed of only silicon and oxygen, making it electrically neutral. However, silicalite structures contain other atoms which are referred to as defects. These include aluminum substitution of silicon, which causes introduction of cations into the structure and silanol, which is brought about by the breaking up of the tetrahedral and

addition of hydrogen to the oxygen atoms. Both these defects bring about a deficiency in charge which is thought to affect the loading of water onto the silicalite structure. Yazaydin utilized molecular dynamic simulations in his study. Silanol nests were found to tremendously increase the adsorption of water. The cations also increased the amount of water adsorbed.

From a computational viewpoint, zeolites are particularly challenging systems since chemical reactions occur inside the material. Moreover, they are big enough to require large computers and large simulations when modeling them. Although molecular simulations have emerged as a powerful tool to shed light on some processes like diffusion and adsorption taking place in zeolites, available inter- and intramolecular potentials are not always able to reproduce key differences in adsorption properties of similar compounds. It has been shown that the use of different classical force fields could lead to rather different results. The reasons behind these differences are yet to be determined. A forcefield is a set of equations with parameters describing the interactions between atoms. A forcefield has both intermolecular and intramolecular components. Due to the discrepancies in parameters, the simulations not only fail to agree with each other but also with experimental results.

In this study, a different approach was taken using the density functional theory that does not require forcefield parameters (Labar, Fuchs and Adamo); it utilizes the geometry of the structure. Initially, molecular dynamics was the method used to model silicalite. However, the forcefield parameters obtained from previous literary work, to simulate the interaction with the water molecule, did not agree with this model (Labar, Fuchs and Adamo). Due to this, molecular dynamics was only used in optimization of the lattice structure. DFT was then adopted as the method to model the interactions between silicalite and water.

## Quantum Mechanics

Quantum mechanics is a set of principles describing the known behavior of energy and matter that predominate at the atomic and subatomic scales. Classical or Newtonian mechanics deals with the macroscopic world. Essentially both quantum and classical mechanics seek to explain the state of a dynamic system after a change is applied to it (Tang).

According to classical mechanics the state of an object at time  $t$  is specified in terms of its position  $x(t)$  and velocity  $v_x(t)$ , which is the change in position with respect to time. All other dynamic properties like linear momentum,  $p_x(t)=mv_x$ , kinetic energy  $T=(mv_x^2)/2$  and potential energy  $V(x)$  depend on only  $x$  and  $v_x$ . The key concept of Newtonian mechanics is Newton's second law of motion that states that the force acting on an object,  $F_x$ , is directly proportional to the acceleration  $a_x=d^2x/dt^2$  (Tang).

$$F_x = ma_x = m \frac{d^2 x}{dt^2}$$

There are a number of fundamental difficulties which arise when trying to use classical mechanics on an atomic or subatomic scale (Tang). For example, measurements on atomic and subatomic particles carried out on a quantum level give results that are statistical averages over an ensemble of a large number of similarly prepared particles, not precise results on any particle. According to quantum mechanics, the state of a system on an atomic or subatomic scale is not characterized by a set of dynamic variables. Instead, it is completely specified by a state function. A state function is a function of chosen variables (canonic variables) of the system under study. For example, consider a particle constrained to move in a linear space along the  $x$ -axis. The state function which is arbitrarily given the symbol  $\Psi$  is a function of  $x$ . its state is specified as  $\Psi(x)$ . How the state of the particle changes with time is specified by  $\Psi(x,t)$  rather than  $v(x)$ . How  $\Psi(x)$  changes explicitly with time is referred to as a wave

function, because it often has properties similar to those of a wave, even though it is supposed to describe the state of a particle.

## Density Functional Theory

Density Functional Theory (DFT) is a computational method that derives properties of the molecule based on the determination of the electron density of the molecule. Electron density is a physical characteristic of all molecules (Gotwals and Sendlinger). Although DFT is relatively new, it addresses one of the major criticisms of the ab initio method. Ab initio is a computational method that is based on quantum chemistry (Levine). Ab Initio's major criticism is that the energy of the molecule depends on the wavefunction, which is a mathematical construct and not physically observable. Even with these drawbacks, the wavefunction has been a good predictor of the energy of a molecule.

In its simplest form the theory is represented by the following equation (Gotwals and Sendlinger).

$$E_{DFT}[\rho] = T[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho]$$

Where E is the energy, T is the kinetic energy of the electrons,  $E_{ne}$  is the nuclear-electron attraction (Columbic) energy, J is the electron-electron repulsive (Columbic) energy, and  $E_{xc}$  is the electron-electron exchange-correlation energy. Each of the terms in this equation is a functional of the electron density. The next task then becomes to find an appropriate functional for each of the terms. The first three terms (T,  $E_{ne}$  and J) can be determined from either ab initio or semi-empirical methods. The electron exchange-correlation energy is the term that causes most of the concern.

A functional is defined as a function of a function. In this case the function is the electron density, which is a function of three variables -x, -y and -z position of electrons. The energy of the molecule is a functional of electron density. The determination of electron density is independent of the number of electrons. Another advantage of DFT is that density depends on the x-y-z coordinates of the individual

electron (Gotwals and Sendlinger). DFT scales as ( $N^3$ ) unlike ab initio methods which scales ( $N^4$ ), where N is the number of electrons in the system. This makes DFT calculations much faster and accurate.

$$\text{Electron density} = \rho(x, y, z)$$

$$\text{Energy of molecule} = f[\rho(x, y, z)]$$

Llewellyn Thomas and Enrico Fermi were able to come up with a relationship between the electron density of a molecule and the wavefunction of a molecule with multiple electrons. The Thomas-Fermi model was the origin of the density functional theory. However, the method became more concrete using the two Hohenberg-Kohn theorems (H-K). The first theorem helps reduce the many-body problem of the electrons by using functional of electron density as mentioned previously (Kohn). The second theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional. This theory was in turn adapted by Kohn and Sham into a practical version of the density functional theory. The KS, theory describes the mathematics of electron densities and their subsequent correlations to molecular energies.

There are roughly three types of density exchange correlation-functionals (Gotwals and Sendlinger). The Local density approximation is not too popular or useful as it assumes that for a molecule with many electrons, the energy of the system only depends on the local density, or density at a given point uniform throughout the molecule. This approximation does, however, work well with electronic band structures of solids, which describes the range of energies in which electrons are permitted or not permitted (forbidden). Outside of this application, however, local density approximations are typically not very accurate. The second method is the gradient-corrected method that tries to account for the non-uniformity of the electron density. The last method is comprised of hybrid methods. Hybrid methods attempt to incorporate some of the more useful features from ab initio methods (specifically Hartree-Fock methods).

One of the advantages to the density functional theory is high computational accuracy without unreasonable computing time. However, the main challenge is in determining the most appropriate method for a particular application.

## Methodology

As stated earlier, one of the goals of this study was to make a comparison of the results previous simulations performed by other authors. This comparison focused on the behavior of water in silicalite using molecular dynamic methods to density functional theory. The software package used was CP2K which is freely available on the internet (CP2K Developers Home Page). This chapter presents the different approaches used to investigate the adsorption of water in silicalite as well as how this information was implemented in CP2K to produce the desired results.

## System Set-up

In order to determine the energy of adsorption involved with loading of water molecules into the silicalite structure, a simulation with an empty silicalite structure was initially run. A water molecule was then simulated. Water molecules were then added to the silicalite structure. They were placed in different positions in the pores, including the sinusoidal channels and straight channels to investigate the positions the water molecules preferred to occupy. The most preferred position in this case would be the one with the most negative energy of adsorption (most exothermic). The effect of water molecules loadings was also investigated. The silicalite structure was loaded with up to 3 water molecules. As demonstrated by Fleys and other previous studies, silicalite can only hold up to 8 – 9 water molecules (Fleys).

## CP2K

Density Functional Theory has become an efficient tool for electronic structure calculations. Most applied methods use either Gaussian-type functions or plane waves (Grotendorst). Plane waves provide an orthogonal basis set and are independent of atomic positions making the force calculation very simple. However, there are strong variations in the wave function close to the nuclei, requiring a large number of plane waves. There exist pseudo potentials (simple functions to replace complicated wave function expressions to model core electrons) to help alleviate this problem, but the number of plane

waves still remains huge. Gaussian-type functions are localized at the atomic centers, making them more efficient in this respect as they provide a more compact description of the atomic charge, eliminating the need for pseudo potentials.

CP2K utilizes the quickstep code which provides fast and accurate density functional calculations using a mixed Gaussian and plane waves approach (Grotendorst). Gaussian orbitals are used to represent the wave functions. The plane waves are used to represent the electron density. Quickstep tries to combine the merits of both Gaussian and the plane waves methods.

The energy functional for a molecular or a crystalline system in the framework of the Gaussian and plane waves method using the Kohn-Sham formulation of the density functional theory is defined as follows (Grotendorst) (Mundy, Rousseau and Curioni):

$$\begin{aligned}
 E[n] &= E^T[n] + E^V[n] + E^H[n] + E^{xc}[n] + E^{II} \\
 &= \sum_{\mu\nu} P_{\mu\nu} \left\langle \varphi_{\mu}(r) \left| -\frac{1}{2} \nabla^2 \right| \varphi_{\nu}(r) \right\rangle + \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_{\mu}(r) | V_{loc}^{PP}(r) | \varphi_{\nu}(r) \rangle \\
 &+ \sum_{\mu\nu} P_{\mu\nu} \langle \varphi_{\mu}(r) | V_{nl}^{PP}(r, r') | \varphi_{\nu}(r') \rangle + 2\pi\Omega \sum_G \frac{\tilde{n}^*(G)\tilde{n}(G)}{G^2} + \int \tilde{n}(r) \varepsilon_{XC}[\tilde{n}] dr \\
 &+ \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}
 \end{aligned}$$

Where  $E^T[n]$  is the kinetic energy,  $E^V[n]$  is the electronic interaction with the ionic cores,  $E^H[n]$  is the Hartree (Coulomb) energy and  $E^{xc}[n]$  is the exchange-correlation energy. The interaction energies of the ionic cores with the charges  $Z_i$  and positions  $R_i$  is denoted by  $E^{II}$ . The electronic interaction with the ionic cores is described by norm-conserving pseudo potentials with a potential split in a local part  $V_{loc}^{PP}(r)$  and a fully non-local part  $V_{nl}^{PP}(r, r')$ .

The electron density

$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_{\mu\nu}(\mathbf{r}) \varphi_{\nu}$$

is expanded in a set of contracted Gaussian functions

$$\varphi_{\mu}(\mathbf{r}) = \sum_i d_{i\mu} g_i(\mathbf{r})$$

Where  $P_{\mu\nu}$  is a density matrix element,  $g_i(\mathbf{r})$  is a primitive Gaussian function, and  $d_{i\mu}$  is the corresponding contraction coefficient.

### Potentials

The GPW method works like plane waves methods with atomic pseudo potentials. It uses the pseudo potentials of Goedecker, Teter, and Hutter (GTH) (Grotendorst). CP2K provides a database with many GTH pseudo potentials optimized for different exchange-correlation potentials. Perdew, Burke and Ernzerhof (PBE) parameter sets were used for the exchange-correlation potentials. (Grotendorst)

### Basis Sets

The Kohn-Sham orbitals are expanded in Gaussian orbital functions in the framework of the GPW method, therefore an appropriate set of Gaussian functions was defined as a basis set for each quickstep calculation. DZVP (double zeta valence with polarization) basis set was used for this study.

### Wave function Optimization

The total ground state energy of a system for a given atomic configuration is minimized by an iterative self-consistent field (SCF) procedure. It uses the method of orbital transformations utilizing only the occupied states. This provides an efficient algorithm for wave function optimization that scales as the number of occupied states squared multiplied by the number of basis functions.

Essentially, geometries of the silicalite structure in the  $-x$ ,  $-y$ , and  $-z$  direction are inputted in CP2K. From there, the program carries out calculations where it is able to optimize the geometry of the structure and produce one that is both stable and containing the least energy.

## RESULTS AND DISCUSSION

### Lattice Energy Minimization

Before performing any molecular simulations, it is important to ensure that the structure is stable. This is done by ensuring the lattice energy of the structure is at its minimum. The lattice energy minimization was carried out using DL\_POLY. The unit cell volume of silicalite was varied (by varying the lattice constants) and the corresponding lattice energy recorded. A graph of lattice energy against unit cell volume was plotted as shown in Figure 8. We attempted to model H<sub>2</sub>O in silicalite in DL\_POLY, but finding a suitable potential proved difficult, so we only used CP2K to model H<sub>2</sub>O adsorption.

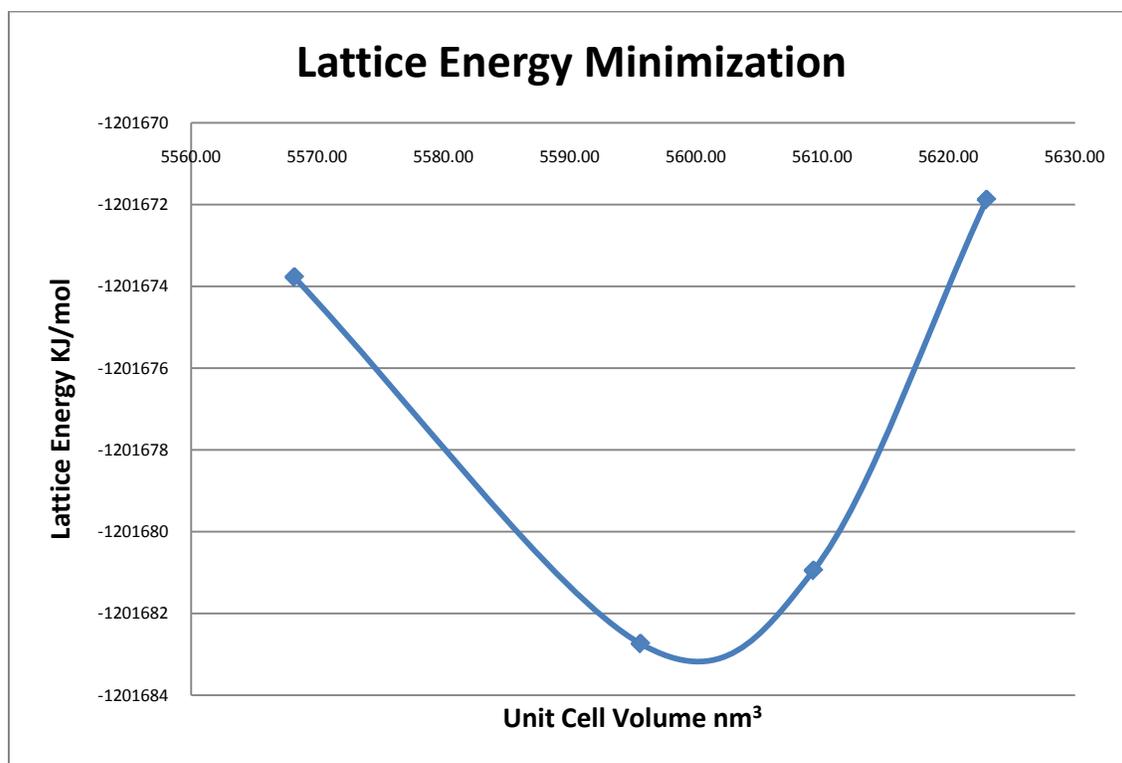


Figure 8: The lattice energy is plotted as a function of unit cell volume. Results were calculated using DL\_POLY

The results yielded a parabolic curve with a minimum point. The unit cell volume at this minimum point was used to obtain the lattice parameters a, b and c.

**Table 1: Unit Cell Dimensions**

Lattice Parameter	Length (Å)
<b>a</b>	20.09Å
<b>b</b>	19.89Å
<b>c</b>	13.37Å

### **Effect of Loading on the Energy of Adsorption**

The silicalite structure was successfully filled with three water molecules to investigate the effect of loading on the energy of adsorption. A graph of the energy of adsorption against the number of water molecules is plotted in Figure 9. Figure 9 shows that the energy of adsorption increases as the number of water molecules increase. The change in energy is greater when the second water molecule compared to when the third is added.

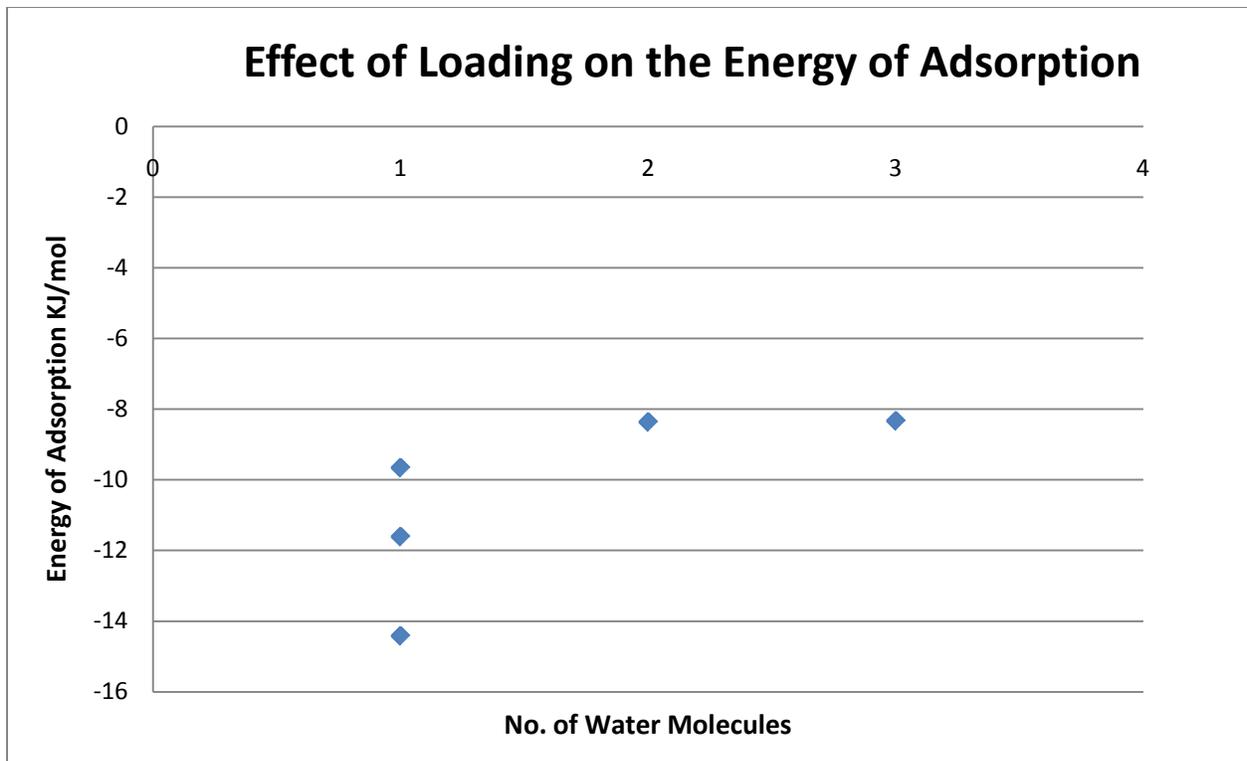


Figure 9: Effect of Water molecule loadings on the Energy of Adsorption

Previous studies using molecular dynamics have shown that silicalite can hold up to 8-9 water molecules in the structure. Moreover, as the loading increases the slope of the line decreases up to a point where it is constant. The results demonstrated in Figure 9 agree with those done by Fleys in his thesis where he investigated the effect of loading on the diffusion coefficient (Fleys). He was able to demonstrate that the diffusion coefficient decreases with successive increase in the number of water molecules.

Therefore, the increase in water molecules slows down the rate of diffusion through the structure. The reason proposed is the fact that hydrogen bonds have a stabilizing effect. Consequently, the total entropy and potential energy of the system decreases as the number of water molecules (hydrogen bonds) increase. This is the same phenomenon shown in Figure 9. As the hydrogen bonds increase in the

structure, they are acting as a limiting effect and hence preventing more water from being adsorbed in to the water molecule.

### Effect of Position of Water Molecule on the Energy of Adsorption

The water molecule was placed in different positions to study the effect of its position in the silicalite structure on the energy of adsorption. There were 5 different positions/channels/pores in which the water molecules were placed. For each simulation the distance of the water molecule to the silicalite atoms was taken and recorded. The results obtained are presented in the figures below.

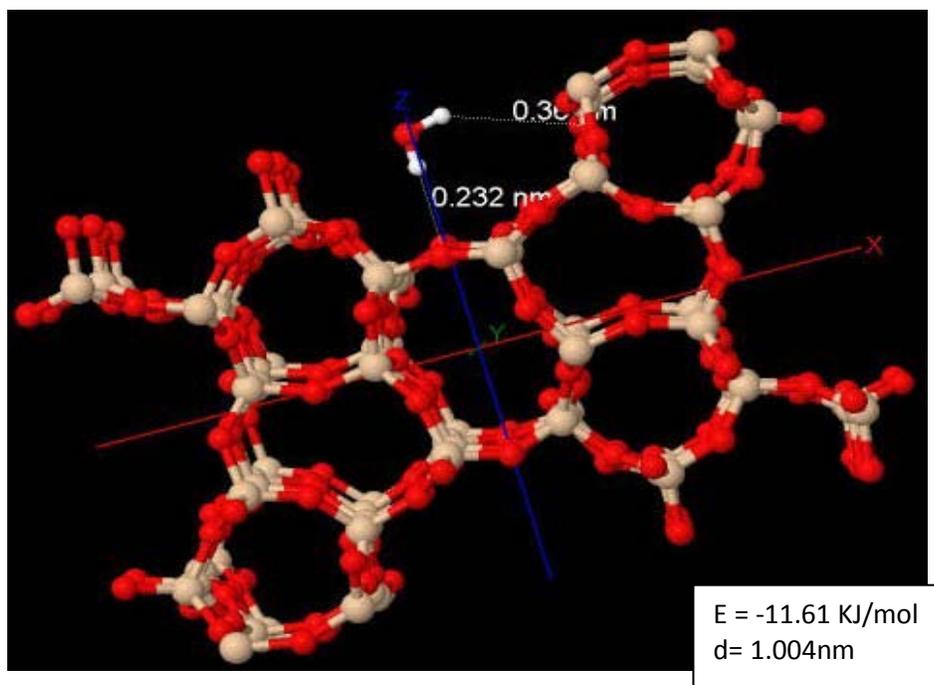


Figure 10: Water molecule located in a pore with a diameter of 1.004nm where E is the energy if adsorption and d the diameter of channel

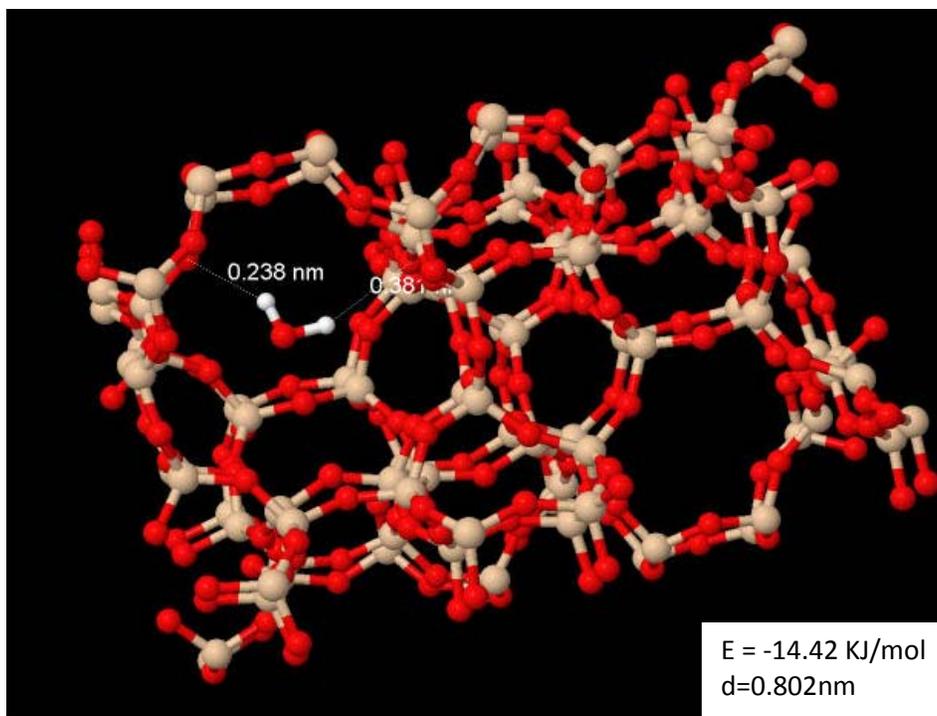


Figure 11: Water molecule located in a pore with a diameter of 0.802nm

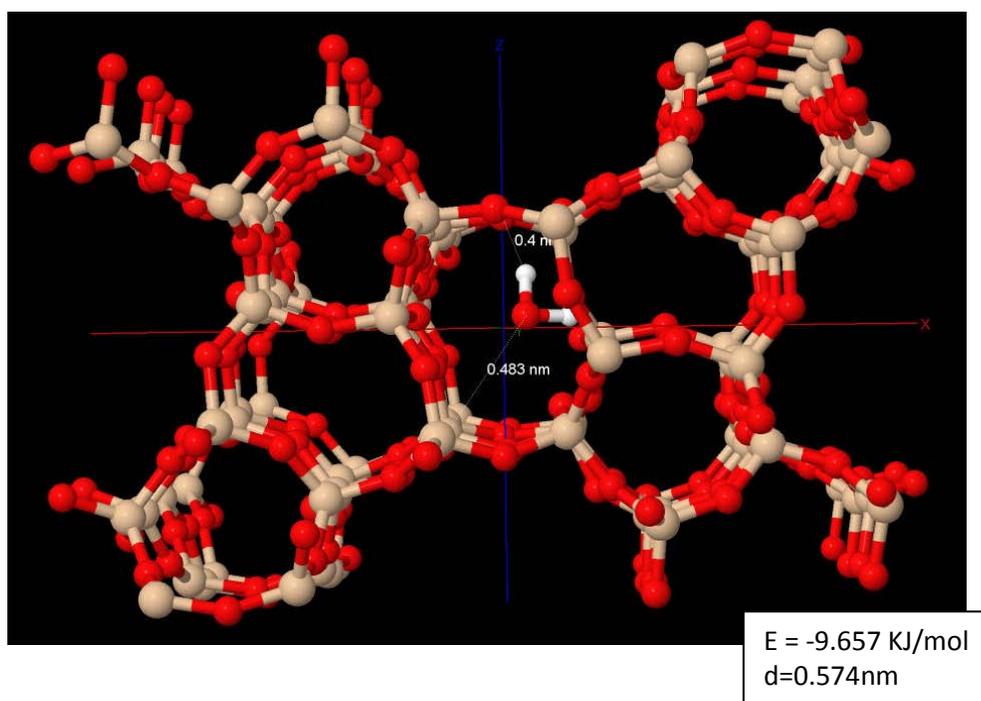


Figure 12: Water molecule located in a pore with a diameter of 0.574nm

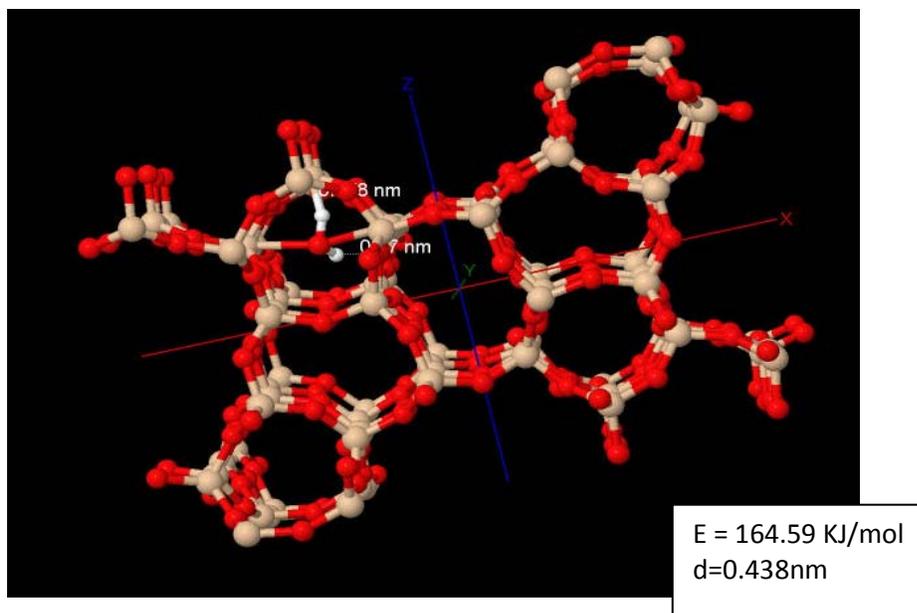


Figure 13: Water molecule located in a pore with a diameter of 0.438nm

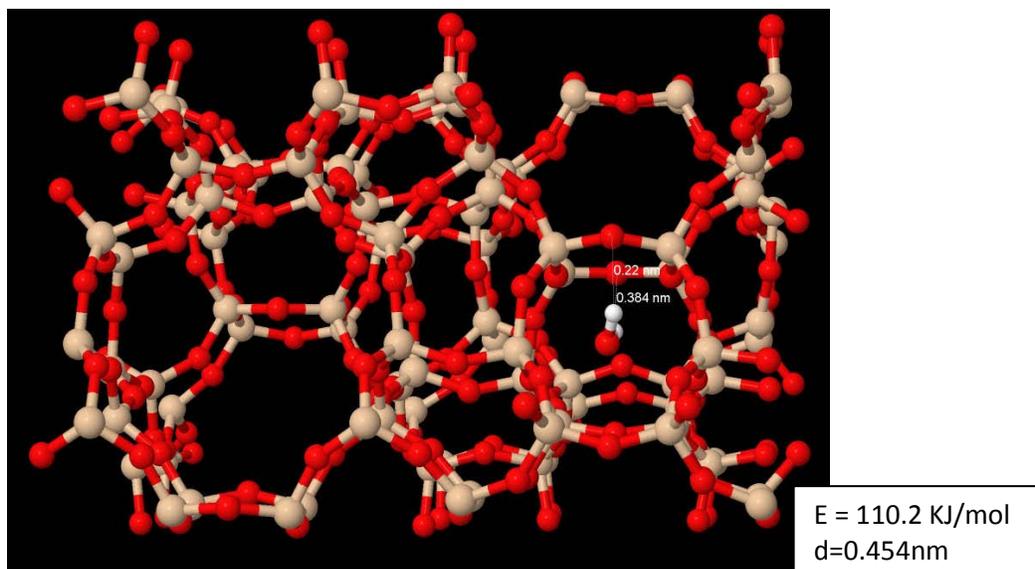


Figure 14: Water molecule located in a pore with a diameter of 0.454nm

The energy of adsorption is exothermic when the water molecules are placed in the large channels. In Figure 10, the water molecule is located in a 10 ring channel with a diameter of 1.004nm. The water molecule in Figure 11 is also located in a 10 ring channel, but has a diameter of 0.802nm. Figure 10 and 11 produced the most stable energy of adsorption. Figure 12 has the water located in a smaller channel with a diameter of 0.574nm and has a less stable energy of adsorption than the previous two; however, the situation is still favorable as the energy of adsorption is exothermic. Figures 13 and 14 have very high positive energy of adsorption values. The water in figure 13 is located in a channel of diameter 0.438nm. From the picture, one can see that the water molecule is interacting strongly with the walls of the channel. This could prevent the stable adsorption of water in this channel. This demonstrates one of the main properties of zeolites, selective adsorption, where some molecules diffuse through some channels by virtue of their size. In this case, the size of the water molecule is too large to diffuse through this channel. Another conclusion that can be drawn is that the size of the channel has a greater effect on adsorption than the direction. In Fleys' thesis he concluded that diffusion is fastest in the y-direction, which has the straight channels and slowest in the x-direction. However, in this case, diffusion in this channel would be unfavorable even though it would occur in the y-direction.

## Conclusions and Recommendations

Density functional theory was the method used to simulate the hydrophobicity of silicalite. Factors that influenced the energy of adsorption were investigated. The influence of loading of water molecules on the silicalite structure as well as the influence of the position of the water molecule in the structure was studied.

Adsorption of water becomes less favorable with increase in water molecule loading. This is because the energy of adsorption becomes less stable. As demonstrated in the results chapter, hydrogen bonds have a stabilizing effect which lead to a decrease in the total energy of the system, making the energy of adsorption increase and become less favorable. Comparison of with results obtained using molecular dynamics agreed with each other and showed a similar trend.

The energy of adsorption is most stable when the water molecule is located in a large channel, specifically the 10 ring channels. As presented in the results chapter, the energy of adsorption in the 10 ring channel was -14.42 KJ/mol as opposed to that in the 4 ring channel with an energy of 164 KJ/mol. The proximity of the water molecule to the walls of the silicalite structure hinders the adsorption of water through the channel. Therefore the closer the water molecule is to the walls, the less favorable it is for adsorption to occur.

One of the problems researchers are facing when investigating the hydrophobicity of silicalite is the unavailability of experimental results and the fact that the computational results do not agree with the experimental ones. For future work, molecular simulations could be carried out where defects are added to the structure up to a point where the simulation mimics the experimental results. This will give the researchers a starting point where they can begin to realistically compare both methods and obtain much more accurate and realistic results.

Other things to keep in mind, when comparing results obtained while using different methods like molecular dynamics and Monte Carlo simulations is to ensure that the forcefield parameters be uniform across the board, to ensure the results are more accurate and uniform.

The hydrophobicity of silicalite is a very useful property that has gained popularity especially in the removal of organics from water (Yazaydin); therefore continued research on this phenomenon is very important so as to gain a better understanding of it.

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## Appendices

### Appendix A: Sample Energy of Adsorption Calculations

$$E_{ad} = \frac{E_{silicalite + water} - E_{empty silicalite} - E_{water}}{\text{no. of water molecules in structure}}$$

Where  $E_{ad}$  is the energy of adsorption

$$E_{ad} = \frac{-3506.26 - (-3471.81) - (-2 * 17.22)}{2}$$

$$E_{ad} = -0.00319 \text{ a.u.} * 2526 \frac{\text{KJ}}{\text{mol}} \text{ a.u.}^{-1} = -8.3636 \frac{\text{KJ}}{\text{mol}}$$

Table 2: Summary of Energy of Adsorption Values

	Loaded Silicalite	Empty Silicalite	No. of water molecules	Water	Energy of Adsorption (a.u.)	Energy of Adsorption (KJ/mol)
1	-3489.04	-3471.81	1	-17.2213	-0.00549	-14.4214
2	-3489.04	-3471.81	1	-17.2213	-0.00442	-11.61
3	-3488.99	-3471.81	1	-17.2213	0.041974	110.204
4	-3488.97	-3471.81	1	-17.2213	0.062692	164.5991
5	-3489.03	-3471.81	1	-17.2213	-0.00368	-9.65722
6	-3506.26	-3471.81	2	-34.4426	-0.00319	-8.3636
7	-3523.48	-3471.81	3	-51.664	-0.00317	-8.33132

## Appendix B: Sample CP2K Input File

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    POTENTIAL_FILE_NAME ./GTH_POTENTIALS
    WFN_RESTART_FILE_NAME x-RESTART.wfn
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    CUTOFF 300
  &END MGRID
  &QS
    WF_INTERPOLATION ASPC
#    WF_INTERPOLATION PS
    EXTRAPOLATION_ORDER 3
  &END QS
  &SCF
    EPS_SCF 1.E-6
    SCF_GUESS RESTART
    MAX_SCF 400
  &OT T
    PRECONDITIONER FULL_SINGLE_INVERSE
    MINIMIZER DIIS
    LINESEARCH 3PNT
  &END OT
  &END SCF
  &XC
    &XC_FUNCTIONAL PBE
    &END XC_FUNCTIONAL
  &END XC
  &PRINT
    #&TOPOLOGY_INFO
    # XYZ_INFO T
    #&END TOPOLOGY_INFO
#    &V_HARTREE_CUBE
#    FILENAME ./rut_elpot
#    &END V_HARTREE_CUBE
#    &E_DENSITY_CUBE
#    FILENAME ./rut_density
#    &END E_DENSITY_CUBE
#    &MO_CUBES
#    WRITE_CUBE T
#    NHOMO 2
#    NLUMO 1
#    &END MO_CUBES
  &END PRINT
  &END DFT
  &SUBSYS
    &CELL
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Si 6.5399610886 0.6366638058 11.1648716815  
Si 13.5500439732 19.1012956306 1.9771537317  
Si 3.5058143305 19.1015582869 4.5941274670  
Si 16.5841805872 0.6364766927 8.5478853756

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Si 16.5841612489 9.2325340584 8.5478674733  
Si 3.5058157908 10.5054760445 4.5941013104  
Si 5.6072608036 1.0570674143 0.8616399764  
Si 14.4827446613 18.6809724163 12.2803605790  
Si 4.4383912518 18.6816681064 7.4333640910  
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Si 15.6515866816 8.8126557086 5.7086386433  
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Si 2.4890238009 1.0269780439 0.6294954001  
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Si 1.4538292512 0.7203911896 10.8162219476  
Si 18.636171782 19.0176050658 2.3257757271  
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Si 11.4996345407 0.7200989369 8.8960580573  
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Si 11.4996474764 9.1489131619 8.8960601279  
Si 8.5903545584 10.5890933839 4.2459345441  
Si 4.087302775 1.3626066842 9.4597812570  
Si 16.0027111125 18.3754359856 3.6822422583  
Si 5.9587428875 18.3790440929 2.8876850332  
Si 14.1312687446 1.3590514762 10.2542850584  
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Si 14.1312463859 8.510038814 10.2543159639  
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Si 6.3479938133 12.3410530294 10.9970163085  
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Si 3.6965280379 7.3971029362 4.4261771646

```

Si 5.5038977035 16.3363172372 0.5682752306
Si 14.586143314 3.4017004877 12.5736613501
Si 4.5425296246 3.4016034377 7.1426347228
Si 15.5475057013 16.336405105 5.9994120196
Si 14.5861067913 6.4673147327 12.5737210021
Si 5.503883175 13.270688167 0.5683008637
Si 15.5474822306 13.2705968201 5.9993829998
Si 4.5425132839 6.4673973834 7.1425685499
Si 2.3811327676 16.3387086004 0.2893406748
Si 17.7088679957 3.3992486328 12.8526673686
Si 7.6660370865 3.3995675606 6.8542918198
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Si 6.1479735774 3.3931460705 2.7363157193
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Si 6.1479787856 6.4758476342 2.7363252562
H 9.86 12.7 11.8
H 10.86 12.7 13.0
O 9.86 12.7 12.76
&END COORD
&KIND Si
  BASIS_SET DZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q4
&END KIND
&KIND O
  BASIS_SET DZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q6
&END KIND
&KIND H
  BASIS_SET DZVP-MOLOPT-GTH
  POTENTIAL GTH-PBE-q1
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  BASIS_SET DZVP-MOLOPT-GTH
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#   RANGE 145 192
#   &END FIXED_ATOMS
#   &END CONSTRAINT
&END MOTION
```

## Appendix C: Force field Parameters for Lattice Energy Minimization

```

Si          28.0855      4.000   96   0
O           15.9994     -2.000  192  0
FINISH
VDW   3
    
```

### Intermolecular Buckingham Potentials

$$U(r_{ij}) = A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}$$

Table 3: Buckingham Potentials

Species	A	C
Si-Si	0	0.30017
O-O	0	0.30017
Si-O	149643.89	0.30017

### Three Body Potentials

Screened harmonic

$$U(\theta_{jik}) = \frac{k}{2} (\theta_{jik} - \theta_0)^2 \exp\left[-\left(\frac{r_{ij}}{\rho_1} + \frac{r_{ik}}{\rho_2}\right)\right]$$

Table 4: Screened Harmonic Potentials

Species	k	$\theta_0$	$\rho_1$	$\rho_2$
Si-Si	17.7504	109.4666667	0.32769	2.0