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An SCC-DFTB/MD Study of the Adsorption of Zwitterionic Glycine on a Geminal Hydroxylated Silica Surface in an Explicit Water Environment

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ABSTRACT: Theoretical work on amino acid monomers interacting with a silica surface is very important in the field of biomaterials. However, the adsorption of an amino acid monomer on the geminal silanols of silica surfaces has rarely been studied. In this work, we study zwitterionic glycine adsorption on an edingtonite surface covered by geminal silanols using molecular dynamics simulations based on the density functional tight-binding method. By introducing 140 water molecules into the systems, we directly considered the solvent effect. We found that both the amino (NH_3^+) and the carboxylic (COO^-) groups of glycine can directly form hydrogen bonds with geminal silanols. However, unlike the COO^- group, the NH_3^+ group cannot be persistently sustained on the surface. Therefore, the dominant configuration is the COO^- group pointing toward the surface. Our study not only provides a molecular level understanding of the interactions between inorganic materials and biochemical molecules but also demonstrates a feasible theoretical method on a quantum level for studying these interactions in biomaterial engineering.
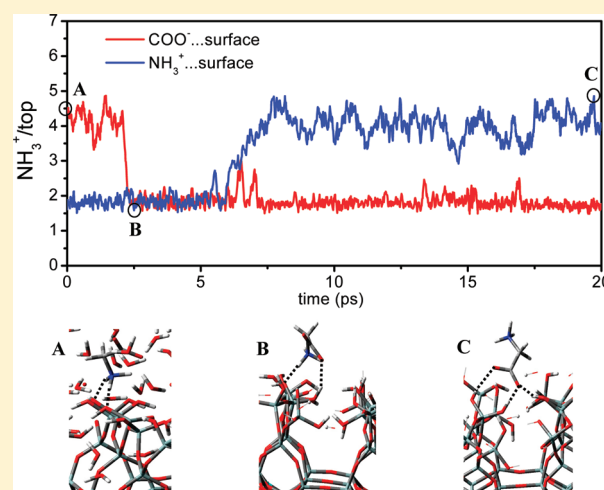
1. INTRODUCTION

In recent years, the interactions between biochemical molecules and inorganic materials have been the subject of intensive studies. They are very interesting cross-disciplinary issues related to early prebiotic chemistry,[1−3] biomedical implants,[4−6] biosensors,[7−11] catalysts,[12] and surface modification.[13] These studies have high scientific value and have attracted wide interest. For example, they can help to test the catalytic role of the peptide bond formation of the crust on an inorganic mineral surface.[3,14] Moreover, finding effective positions for the sterilization of enzymes on a ceramic material[15,16] could facilitate the fabrication of excellent bacteria filters for modern life. Therefore, understanding how an amino acid monomer interacts with an inorganic surface is urgently needed and very significant.

Because of silica's excellent stability and its great abundance on the Earth, the silica surface[17] has become a popular research system. Guided by experimental measurements, such as NMR,[18] IR,[19] and ATR-IR spectroscopy,[20] some theoretical studies have been conducted to explore the interactions of the amino acid backbone with silica surfaces.[21−32] However, the conclusions reached by these studies are often inconsistent with each other. Nonella et al.[21] studied the alanine−silica interaction by means of first-principles molecular dynamics (MD) simulations. They pointed out that the surface−amino group interaction is stronger than the interaction between the surface and the carboxylic (COO^-) group. However, both interactions are indirect, as they occur through bridging water molecules. Meng et al.[22] conducted an experimental study of glycine (GLY) adsorption on silica. From an aqueous solution of variable concentrations and pH values, they found that, at low concentrations (such as 0.01 M), GLY is most likely adsorbed on silica surface sites through its amino (NH_3^+) group. The surface adsorption sites may be silanolate groups ($\cong Si-O^-$). On the other hand, with the support of experimental evidence, Lomenech et al.[23] found that neutral GLY in a vacuum is adsorbed on the neutral silica surface through its carboxyl (COOH) group. The reaction heat is approximately 45 kJ/mol, calculated at the B3LYP/6-31++G** level using a cluster model approach. Similarly, by using density functional theory (DFT) periodic ab initio MD calculations, Costa et al.[24] found that zwitterionic glycine (zGLY) binds directly with the COO^- group, rather than the NH_3^+ group, to a surface silanol. Obviously, there is, as yet, no consensus on how amino acids interact with silica surfaces, either directly or indirectly, through the COO^- or NH_3^+ group.

According to the experimental results of Zhuravlev et al.,[33,34] a silica surface is saturated with silanol groups at a typical density of about 4.6 OH/nm^2, corresponding to a density of isolated, vicinal, and geminal silanols of 1.2, 2.8, and 0.6 OH/nm^2, respectively. By far, the majority of studies has focused on the terminal silanols (the isolated and vicinal ones). Few studies have been concerned about the geminal silanol surface.[24] This may be due to the fact that terminal silanols constitute the majority morphology of an amorphous silicon surface. However, the adsorption of an amino acid onto the geminal silanols can still occur and may be very important. As previously proposed, the local interaction[35] may play a key role in the hydrogen bond interactions between an amino acid and a silica surface. For example, Costa et al.[22] found that only geminal silanols stabilize the zGLY, and terminal silanols do not. Geminal silanols are more reactive than terminal silanols in forming hydrogen bonds with the zGLY. Moreover, in silicosis therapy, it has been found that there are a large number of unsaturated residual bonds and different bonding states of the hydroxyl groups on the nanosilica surface, making the silica with high surface reactivity and thus with physical toxicity.[36,37] For this reason, studies have also been conducted on how to use ^{29}Si NMR spectroscopy to identify geminal and terminal silanols.[38] Therefore, it is necessary to study the interaction between the geminal silanols and biological molecules.

Most MD simulations have been performed in a microsolvated regime, but not in a bulk water environment. Despite the fact that microsolvation with four water molecules has been theoretically and experimentally[39] proven to be sufficient to stabilize the zGLY from being a neutral GLY, the number of solvent molecules may influence the conformation of an amino acid's adsorption onto the surface. As reported by Gambino et al.,[25] the conformation of the lysine side chain changes from the nonlinear to the linear model when more than 10 water molecules act as solvents. Recently, we studied the effect of water molecules on a silica surface by comparing the results with models of a silica surface in an environment of 144 water molecules and in a vacuum, respectively.[40] We explored the influence of solvents on an amino acid by putting a zGLY molecule into the simulation box in the presence of 310 water molecules.[40] We found that, at room temperature, due to their small sizes, water molecules could sustainably and continuously form hydrogen bonds with the surface and the amino acid's COO^- and NH_3^+ terminals. The water molecules play an important role in preventing severe deformation of the surface, enabling a dual nature state of the zGLY. On the surface, the adsorption energy of a water molecule is about −40 kJ/mol, whereas that of a zGLY is about −49.3 kJ/mol. The ability of the COO^- terminal of a zGLY to adsorb a water molecule is stronger than the NH_3^+ terminal.

With the knowledge of the effects and characteristics of a water molecular environment on a silica surface and an amino acid, in this study, we study the adsorption of a zGLY on a geminal hydroxylated silica surface by introducing an explicit water environment. We attempted to reveal how the zGLY behaves on a geminal silanol surface. We established four initial models in which the COO^- and NH_3^+ of the zGLY, respectively, were vertically adsorbed on the top and hollow sites of a surface covered by geminal silanols. All of the simulations were performed in the presence of 140 water molecules. Starting from these initial configurations, we searched for the most stable adsorption configurations using MD simulations. Further details and the MD simulation results are provided in section 4.

2. COMPUTATIONAL DETAILS

In our previous study,[41] we have further validated the reliability of the self-consistent charge density functional based tight-binding (SCC-DFTB) method[42−46] in describing amino acids—surface interaction and achieved reliable adsorption energies (ΔE_{ads}) and hydrogen bond lengths between the amino acid and silanols. By using the SCC-DFTB approach, we were able to handle periodic surfaces containing several hundred atoms, which allowed us to conduct MD simulations at the quantum mechanical (QM) level for up to tens of picoseconds. As this method is at the QM level, the description of the interactions among the water molecules, zGLY, and surface is basically reliable. Because these interactions may lead to charge transfers to some extent, any classical molecular mechanics (MM) method will encounter difficulties and might very likely result in artifacts.

We used the SCC-DFTB method[42−46] and the supercell model for our MD simulations. Following previous studies,[47−51] we chose the appropriate Slater—Koster potential to deal with all of the atoms. On the basis of the forces calculated using the SCC-DFTB method, we carried out MD simulations using the Gromacs package (version 3.3.3).[52,53] We used the canonical ensemble provided by the Nose—Hoover thermostat in a constant particle number, constant volume, and constant temperature regime (NVT). The thermostat was set to T = 300 K with a time step of 1 fs for the integration of the equations of motion.

3. STRUCTURAL MODEL

In this study, we adopted the edingtonite surface slab model,[54,55] generated by cleaving an edingtonite crystal along the [010] direction in its supercell. The surface Si—O bonds were broken, with the Si side being removed. The two O atoms that originally bonded with the removed Si were saturated with two hydrogen atoms to form a geminal silanol surface (i.e., a (100) surface) for simulating the interaction with the zGLY. The other side of the surface was covered by hydrophobic Si—H groups to simulate the bulk environment. This surface structure was placed in an orthogonal supercell. The lattice constants a and b in the Cartesian x and y directions were both 20.9 Å. The lattice constant c in the Cartesian z direction was set as 32.2 Å. These distances are much greater than the 10 Å of overlap integral cutoff in the SCC-DFTB method, and this ensures that the distance between the zGLY monomers is large enough to avoid any noticeable direct quantum mechanical overlap. The slab thickness was about 13.6 Å, leaving sufficient empty space for storing water molecules and to allow the zGLY to interact with the surface. In this study, the rest space of the box was filled by 140 water molecules, which randomly distribute and maintain the density of the solution as about 1.0 g/cm^3.

As shown in Figure 1, the geminal silanol surface (i.e., the (100) surface) had a total of 36 silanol groups. Because of the high symmetry of the edingtonite crystal, there were two topologically distinct regions at the surface, which are marked as the "top" and "hollow" sites in Figure 1. In the following, we regard them as the initial sites for the surface adsorption of the zGLY. We aim at finding the favorable adsorption site and stable orientation of the zGLY on the surface by performing MD simulations.

4. RESULTS AND DISCUSSION

We studied zGLY—surface interactions at the top and hollow sites of the surface in the presence of 140 H$_2$O molecules.
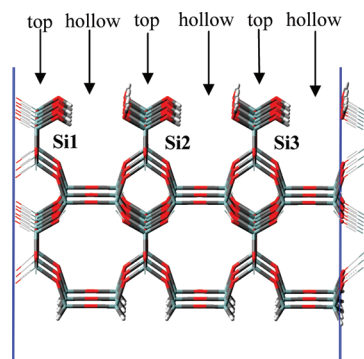
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top hollow top hollow top hollow

Figure 1. Ideal structure of a geminal hydroxylated edingtonite surface with the periodic boundary condition (PBC) of $a = b = 20.9$ Å, $c = 32.2$ Å, and $\alpha = \beta = \gamma = 90°$.

We then analyzed the structures, total energies (E_{tot}), partial charges, and mechanism of these interactions.

4.1. Geometry Results. We first performed static SCC-DFTB structural optimization using a conjugate gradient algorithm for the initial configurations to be used in the followed MD simulations. Because of computational resource limits, we only optimized the configuration that uses 3−6 water molecules around the backbone of the zGLY to prevent the zGLY from converting into a neutral GLY. In our followed MD simulations, the rest of the 140 H_2O molecules were inserted into the simulation box. Figure 2a,d,g,j shows the four initial MD configurations, corresponding to the COO^- or NH_3^+ groups of the zGLY orienting toward the surface, respectively, at the top or hollow site of the surface. We amplified the adsorption parts in the figure and denoted their hydrogen bond lengths in the bottom right corner. During the conjugate gradient optimization, the COO^- or NH_3^+ group formed 2−3 hydrogen bonds with the geminal silanols. Each carboxylic O atom was coordinated with up to three silanols, at an average distance ($O \cdots HO-Si$) of around 1.78 Å. Each amino H atom was only coordinated with one silanol ligand, with an average bond length ($H \cdots OH-Si$) of about 1.72 Å.

Next, we studied the above four systems using an SCC-DFTB/MD simulation for 20 ps. We did not use any constraints on the dynamics of the particles. Hereafter, we use COO^-/hollow, COO^-/top, NH_3^+/hollow, and NH_3^+/top to denote these four systems. As shown in Table 1, in the final 5 ps, the root-mean-square deviations (rmsd) of the temperature was 8.10−8.44 K and the rmsd of the E_{tot} was 121−126 kJ/mol. Hence, we assumed that the system had reached equilibrium at this time.

To clearly identify the orientation of the zGLY on the surface, we examined the time evolution of the distance between the COO^- and the silanol ($D_{COO^- \cdots HO-Si}$) and the distance between the NH_3^+ and the silanol ($D_{NH_3^+ \cdots OH-Si}$). Following the literature,[23] we denoted the $D_{COO^- \cdots HO-Si}$ as the minimum distance between the O of COO^- and the H of the silanols at each moment and $D_{NH_3^+ \cdots OH-Si}$ as the minimum distance between the H of the NH_3^+ and the O of the silanols at each moment. The results relating to these distances are shown as red and blue curves, respectively, in Figure 3a−d. Obviously, except for the obvious instability in the beginning period, the red curves ($D_{COO^- \cdots HO-Si}$) of the four systems basically fluctuated around 2.00 Å, indicating that the COO^- had been stably interacting with the surface silanols to form hydrogen bonds. Using the

Gromacs analysis tool, we found that 1−3 hydrogen bonds appeared between the COO^- and the surface. As illustrated in Figure 2b,e,h, respectively, one, two, and three hydrogen bonds were formed between the COO^- and the silanols. On the other hand, the $D_{NH_3^+ \cdots OH-Si}$ curves varied in larger ranges of 2.64−6.35, 1.62−6.31, 1.48−4.33, and 1.58−4.85 Å for the COO^-/hollow, COO^-/top, NH_3^+/hollow, and NH_3^+/top systems, respectively. It is clear that, in comparison with the COO^-, the NH_3^+ cannot be stably adsorbed on the geminal silanols. In Figure 3, we use hollow circles to mark the minimum value and maximum value of $D_{NH_3^+ \cdots OH-Si}$; the corresponding snapshots are displayed in Figure 2.

With the help of the configurations in Figure 2 and the $D_{NH_3^+ \cdots OH-Si}/D_{COO^- \cdots HO-Si}$ curves in Figure 3, we can infer the adsorption conformation of the zGLY on the surface changing over the time. For example, in the COO^-/hollow system, the peak value of $D_{NH_3^+ \cdots OH-Si}$ appeared as 6.35 Å at 9.280 ps; at the same time, the $D_{COO^- \cdots HO-Si}$ was 2.00 Å. Because the molecular width of zGLY is 4.51 Å, it may be considered that, at this time, the zGLY was perpendicular to the surface. In fact, as shown in Figure 2b, the zGLY is indeed vertical to the surface. That is to say, the NH_3^+ group pointed away from the surface, while the COO^- group formed a hydrogen bond with the surface with a length of 2.00 Å, thus confirming our inference. As another example, the minimum $D_{NH_3^+ \cdots OH-Si}$ of the COO^-/hollow system, with a value of 2.64 Å, occurred at 12.28 ps. Therefore, we can conclude that, at this time, the zGLY had to be parallel to the surface. The structure in Figure 2c confirms that the zGLY was parallel to the surface and that the hydrogen bond length between the COO^- and the surface was 2.09 Å. Accordingly, we obtain the following: (1) If the NH_3^+ is kept away from the surface at a $D_{NH_3^+ \cdots OH-Si}$ of over 6.00 Å (see Figure 2b,f), the zGLY will be perpendicular to the surface. (2) If the $D_{NH_3^+ \cdots OH-Si}$ is kept in the range of 3.00−5.00 Å (see Figure 2i,l), the zGLY will tilt at the surface. (3) If the $D_{NH_3^+ \cdots OH-Si}$ is less than 3.00 Å, the zGLY will basically be parallel to the surface (see Figure 2c,e,h,k). In short, during the entire simulation time, the COO^- formed at least one hydrogen bond with the geminal silanols, while the NH_3^+ frequently changed its orientation. For the NH_3^+/hollow and NH_3^+/top systems, after the MD simulation began, the hydrogen bonds formed between the NH_3^+ and the surface quickly broke (see Figure 3d) and the zGLY flipped, adjusted to a parallel orientation, and finally formed hydrogen bonds with the surface through the COO^-.

Despite the poor hydrogen-bonding stability, the NH_3^+ group can still directly interact with the surface. This result is different from that reported by Nonella et al.[21] and Costa et al.,[24] who found that the NH_3^+ group does not interact directly with the surface silanols, but through water molecules. It should be noted that, although they used more rigorous first-principles DFT methods, the number of water molecules in the simulation box was small. It infers that the role of the explicit water environment was different from that of microsolvation in amino acid−surface interactions. As shown in Figure 2e,h,k, with the zGLY parallel to the surface, the hydrogen bond lengths between the NH_3^+ and the surface were, respectively, 1.62, 1.48, and 1.58 Å. However, these parallel orientations were only able to last for up to 3 ps. As shown in Figure 3d, in the 2.30−5.36 ps period, the blue curve of the $D_{NH_3^+ \cdots OH-Si}$ oscillated at around 2.00 Å.

On the other hand, no matter which side interacted with the surface, the zGLY would eventually be transformed into the hollow site upon the adsorption at the top site. As confirmed in
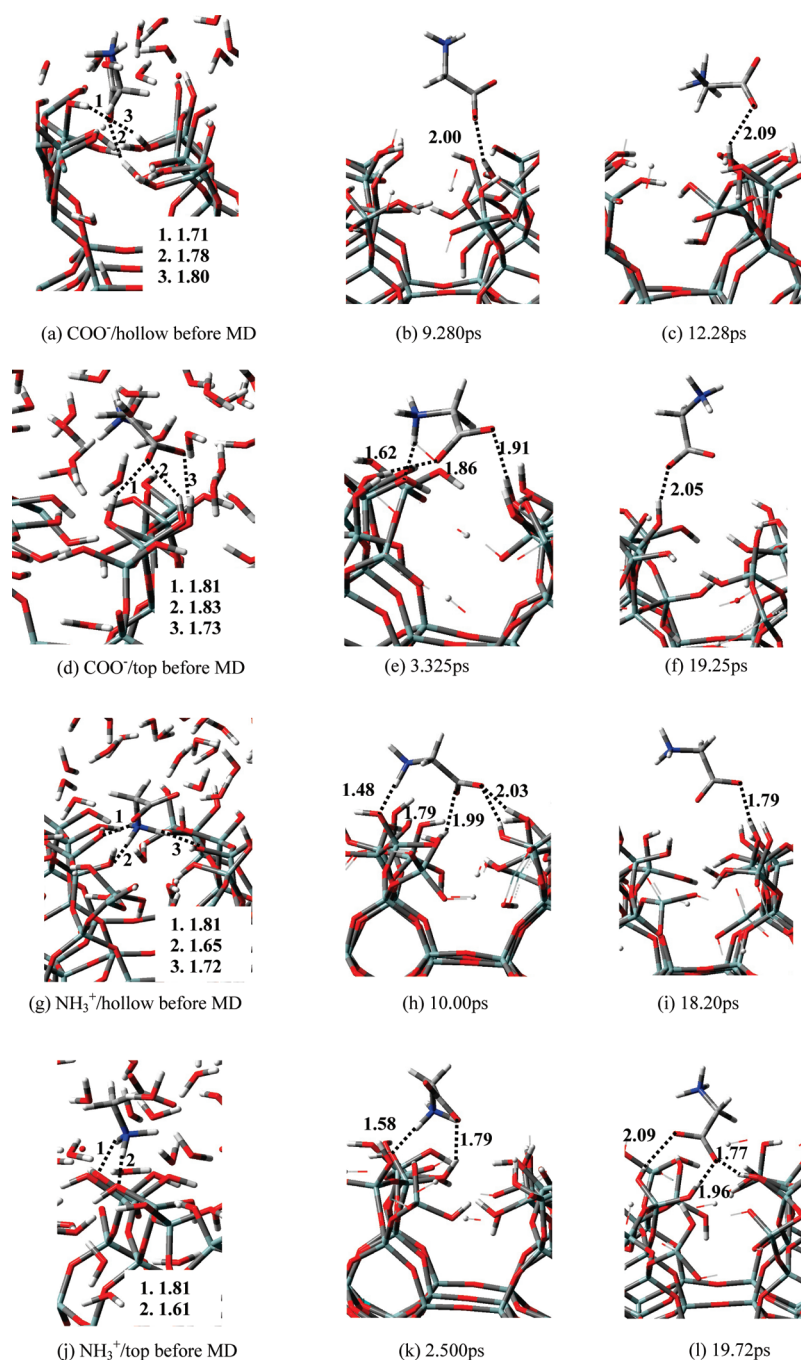
Figure 2. Starting MD configurations and snapshots corresponding to the time with marks of hollow circles in Figure 3. The zGLY—surface interaction is evidenced, and all water molecules are invisible in the figure except for (a), (d), (g), and (j). Unit: Å.

Figure 2, the hollow site is more favorable to form hydrogen bonds than the top site.

4.2. Energetic Analysis. Next, to reveal the more favorable side of the zGLY to the surface adsorption based on the calculated E_{tot}, we simulated these four systems again, but with the surface and the zGLY being restricted in the initial coordinates. We calculated harmonic potentials according to the formula $V_{pr}(r_i) = \frac{1}{2}k_{pr}|r_i - R_i|^2$. In the x, y, and z directions, the force constant k_{pr} was set to 1000 kJ/(mol nm^2). All of the water molecules moved freely in the box. We collected the topological data at 10—15 ps. The rmsd of the temperature varied in the range of 6.75—8.71 K, while the rmsd of the

E_{tot} varied in the range of 100—127 kJ/mol. The average E_{tot} values during the last 5 ps were obtained by fitting the binned energy data to Gaussian functions (Gaussian peak position and width), as shown in Figure 4. The absolute peak values were, respectively, −3 529 980, −3 529 910, −3 529 730, and −3 529 760 kJ/mol for the COO$^-$/hollow-pr (pr means position restrained.), COO$^-$/top-pr, NH$_3^+$/hollow-pr, and NH$_3^+$/top-pr systems. Setting the fitted E_{tot} of the COO$^-$/hollow-pr system to zero, we obtained the relative E_{tot} of the other three systems. While not energetically very distinct, a small E_{tot} difference may exist between the systems when the NH$_3^+$ or the COO$^-$ group interacts with the surface. The orientation of

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Table 1. MD Results of Four zGLY—Surface Interacting Systems

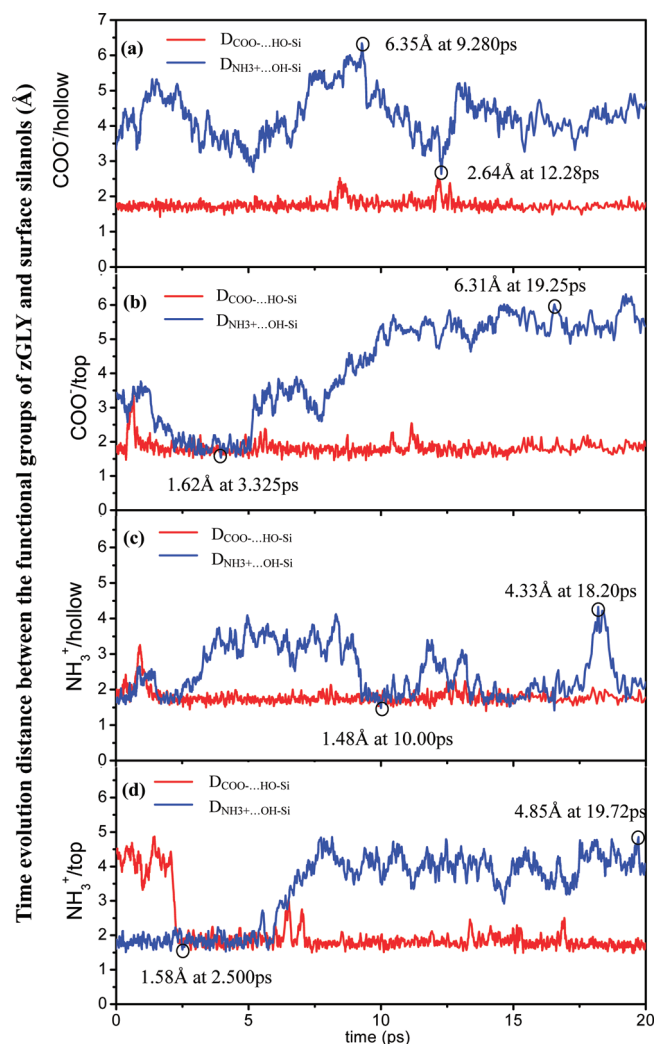| systems	average E_{tot} (kJ/mol)	rmsd E_{tot} (kJ/mol)	rmsd T (K)	charge on surface	charge on water	charge on zGLY
COO^-/hollow	−3 530 070	124	8.10	−0.476	+0.434	+0.0424
COO^-/top	−3 530 030	121	8.44	−0.381	+0.369	+0.0124
NH_3^+/hollow	−3 530 060	126	8.42	−1.09	+1.02	+0.0719
NH_3^+/top	−3 529 950	125	8.39	−0.637	+0.583	+0.0539
COO^-/hollow-pr	−3 529 980	127	8.71			
COO^-/top-pr	−3 529 910	108	6.75			
NH_3^+/hollow-pr	−3 529 730	112	7.23			
NH_3^+/top-pr	−3 529 760	100	6.97			

Figure 3. Time evolution distance between the functional groups of zGLY and surface silanols ($D_{COO^-\cdots HO-Si}$ and $D_{NH_3^+\cdots OH-Si}$) in 20 ps for systems of (a) COO^-/hollow, (b) COO^-/top, (c) NH_3^+/hollow, and (d) NH_3^+/top.

Figure 4. GDF fitting curves for the E_{tot} of COO^-/hollow-pr, COO^-/top-pr, NH_3^+/hollow-pr, and NH_3^+/top-pr systems.

weakest H-bonding interaction between the amino group of glycine and the silica surface using the ONIOM2(B3LYP/6-311++G**:MNDO) level of theory.[56]

In the same way, without any atomic position restrictions, the average E_{tot} at 15−20 ps of the COO^-/hollow, COO^-/top, NH_3^+/hollow, and NH_3^+/top systems were also fitted using Gaussian functions. The results are listed in Table 1. The E_{tot} of the COO^-/hollow, COO^-/top, and NH_3^+/hollow systems exhibited an insignificant difference of only 10−40 kJ/mol, far less than the rmsd of the E_{tot}. Thus, in the MD simulation without the atomic position being restrained, the final positions of the zGLY on the surface were basically the same (i.e., COO^- hydrogen bonding with the surface at the hollow site), as shown in Figure 2. For the NH_3^+/top system, if enough simulation time was given, the final configuration would be consistent with that of the other three systems. In fact, compared with the rmsd of the E_{tot}, the energy difference can be regarded as negligible.

In our work, the desorption state was confirmed when the zGLY was separated from the surface by at least one layer of water molecules, whereas the adsorption state was reached when the COO^- group of the zGLY formed hydrogen bonds with the surface. Putting the zGLY 5.7 Å away from the surface, we ran an MD simulation for 15 ps. In 0−4 ps, the average distance of the zGLY from the surface is 4.4 Å; in 8−14 ps, the COO^- of the zGLY formed hydrogen bonds with an average distance of 1.8 Å. The ΔE_{ads} of the zGLY on the geminal silanols were calculated from the E_{tot} differences of the desorption (0−4 ps) and the adsorption (8−14 ps) states. The result was approximately −150 kJ/mol,

the COO^- toward the surface was energetically more favorable than the NH_3^+ by at least 150 kJ/mol. This was actually slightly larger than the rmsd of the E_{tot} data. Thus, by comparing the E_{tot} of these four isomers, we drew the same conclusion, namely, that the NH_3^+ group does not have a better ability to approach the geminal silanols than the COO^- group. This is in agreement with the conclusion drawn by Rimola et al., who also confirmed the
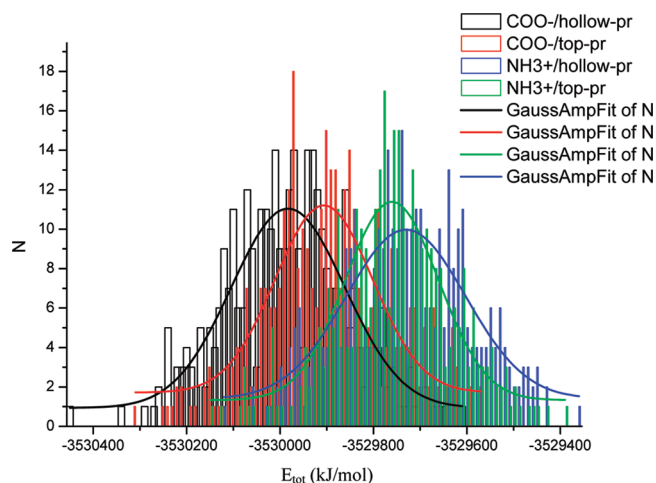
which is close to Costa et al.'s result (-140 kJ/mol).[24] If the mean energy per hydrogen bond is 46 kJ/mol,[22] this adsorption corresponds to the formation of 3−4 hydrogen bonds. This is reasonable because each of the O in the COO^- can form up to three hydrogen bonds with the silanols.

4.3. Charge Transfers and Mechanism of Interaction. Before the MD simulations, the partial Mulliken charges on the silica surface and the 140 H_2O molecules were zero. The GLY was zwitterionic, but the molecule as a whole was neutral. After 20 ps of the MD simulation, the Mulliken charge of the zGLY in all of the systems was slightly positive, with less than $+0.1$ electrons, as shown in Table 1. The surface itself carried a negative charge, which varied from -0.381 to -1.09. To balance the negative charge of the surface, the 140 H_2O molecules took some positive charges. The results show that the simulated interaction involved a considerable charge transfer; therefore, classical MM methods are inappropriate and the SCC-DFTB method is a reasonable simulation tool.

Despite the obvious charge transfer described above, which seems to favor attraction of NH_3^+ by the negative charged substrate, the affinity of the NH_3^+ to the silanols is rather low, as revealed in our MD simulations. This is due to the termination of the surface with silanol where the positively charged H repels any coming NH_3^+. We note that we did not observe any proton release from the silanol or NH_3^+ in our MD simulations, and thus, the low affinity of the NH_3^+ to the silanols cannot be explained using the conventional acid−base (proton) theory.[24] In addition, in our model, the geminal silanols were of high density (8.3 OH/nm^2), thus providing more opportunities for COO^- to be adsorbed. Moreover, we conjecture that each carboxylic O atom can form up to three hydrogen bonds with the silanols but that each amino H atom can only form one hydrogen bond; hence, there is definitely more chance for COO^- attaching onto the silanols than NH_3^+. If the structural morphology of a silica surface can be controlled, geminal silanols are a very promising candidate for fixing the COO^- group of the lateral chain or the backbone of an amino acid. If the surface is dominated by silanolate groups ($\cong Si-O^-$), the acidic NH_3^+ is likely to be selectively attached to the surface.

5. SUMMARY AND CONCLUSIONS

In the presence of 140 water molecules and using an SCC-DFTB/MD simulation, we systematically studied the most favorable adsorption conformation for the zGLY interacting with the geminal silanols of an edingtonite surface. The results show that, at room temperature, during the first 20 ps of an MD simulation, the zGLY remains zwitterionic and can be well "solvated" on the geminal silanols, forming up to four hydrogen bonds mainly through the COO^- group. The NH_3^+ group can directly form a hydrogen bond with the surface, but only in a very unstable way. The orientation of the zGLY on the surface can be vertical or parallel, but is mainly tilted. The ΔE_{ads} of the zGLY adsorption on the geminal silanols is estimated to be -150 kJ/mol. In addition, we found that the hollow site of the surface is very favorable for the adsorption of the zGLY.

The mechanism that explains why COO^- has more adsorption capacity on a silica surface than NH_3^+ is as follows: (1) the H of silanols likes to accept COO^-; (2) the high geminal silanol density of the surface increases the probability that the amino acid will be adsorbed; and (3) the COO^- has more chance of being adsorbed on the surface than the NH_3^+, because each O of

the COO^- can form up to three hydrogen bonds, whereas each H of NH_3^+ can only adsorb one silanol.

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