Applied Surface Science 466 (2019) 607–614

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Interaction between polysaccharide monomer and $SiO_2/Al_2O_3/CaCO_3$ surfaces: A DFT theoretical study

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ARTICLE INFO

Keywords:
Polysaccharides monomer-$Al_2O_3/CaCO_3/SiO_2$ surfaces interaction
DFT calculation
Interaction mechanism

ABSTRACT

In the present study, the interaction between a model polysaccharides monomer β-D-glucopyranose with different mineral solid surfaces, including hydroxylated (0 0 1) surface of SiO_2, (0 0 0 1) surface of Al_2O_3 and (1 0 4) surface of $CaCO_3$, were explored by theoretical calculations based on Density Functional Theory (DFT) under periodic boundary conditions. The adsorption geometry of the β-D-glucopyranose monomer (GM) at different solid surface and the interaction energies were analyzed in detail, and the interaction mechanism was determined via electron density differences iso-surface, Mulliken charge, as well as projected density states (PDOS) analysis. Very strong interaction was found between GM and Al_2O_3 (0 0 0 1) surface, which was mainly attributed to the formation of bridging Al—O bonds and H-bonds. There was the bonding between H-1*s* and O-2*p* orbitals for the formed hydrogen bonds and hybridization between O-*p* states and Al-*d* states for the bridging Al—O bonds. The interaction between GM and $CaCO_3$ (1 0 4) surface was mainly attributed to the electrostatic interaction and hydrogen bonded interaction, and was fairly strong, too. But there was only hydrogen bonds between GM and SiO_2 surface, which was relative weak. In all the three adsorbed systems, significant charge redistribution was observed which contributed to the interaction between them, though little electron transferred between them. The finding is very meaningful for providing theoretical direction in proceeding sufficient application of diverse kind of natural sugar-based functional substances in many fields.

1. Introduction

As for the increasing social concern about the serious environmental problems, environmental friendly technologies and products have gained more and more attention, and the application of the green functional substances derived from natural raw materials is on rise [1] in various industrial process. Polysaccharides and modified chemicals based on sugar are widely concerned because of their non-toxic and non-hazardous nature which have broad applications in many industrial processes, ranging from enhanced oil recovery [2–5], dispersion [6], ceramic industry [7,8] to biomineralization [9,10], mineral scaling [11] and so on. In these applications, the adsorption of these functional substances upon mineral surfaces is a key scientific question, which has aroused researchers' interest [12–14]. For example, in Enhanced Oil Recovery (EOR) process, the adsorption loss often occurs due to the interaction between polysaccharides polymer or sugar based surfactants and the mineral surfaces such as SiO_2 and $CaCO_3$, which needs to be controlled [15,16]. While in some other cases, the strong adsorption of polysaccharides upon the mineral surfaces is favorable. For instance, polysaccharides could control the biomineralization process which attributes to the strong interaction with $CaCO_3$ surfaces [9,10,17,18] and be proposed for the aqueous gelcasting of ceramic and Al_2O_3 powers in ceramic industry [7,8].

The adsorption of substances on solid rock surface is a complex process, which is affected by the environment such as pH, salinity as well as additives [13,14]. Thus, it is meaningful and helpful to elucidate how the functional molecules interact with the mineral surfaces exactly from microscopic view for better understand the corresponding adsorption behavior, while it is difficult to be analyzed at atomic scale by experimental techniques.

Molecular dynamic simulations have been recognized as a powerful method to study the adsorption behaviors of small molecules or macromolecules at mineral surfaces, as well as the interaction between them [19–22]. But some detailed information at atomic scale is ignored in these calculations, such as the change in the surface properties after adsorption, the electronic structure and the charge transfer and so on. Theoretical calculation based on the ab initio method, Density Functional Theory (DFT) have proved to be an appropriate method to unravel the interaction mechanism of organic and inorganic molecules with solid surfaces, as they could give out the more specific details

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https://doi.org/10.1016/j.apsusc.2018.10.085
Received 21 July 2018; Received in revised form 22 September 2018; Accepted 9 October 2018

about the adsorption geometry, identify charge transfer and electronic effects at the atomic scale [23–32].

In the present work, to explore the interaction mechanism between polysaccharides or sugar based surfactants and the mineral surfaces essentially, a model polysaccharides monomer β-D-glucopyranose was selected in the calculations, which represented the constituent repeating unit of polysaccharides. The interaction mechanism between the β-D-glucopyranose monomer (GM) and SiO_2 (0 0 1), Al_2O_3 (0 0 0 1), $CaCO_3$ (1 0 4) surfaces at atomic scale was determined using DFT calculations. The adsorption geometry, interaction energy, charge transfer as well as the projected density states were analyzed. The results of this study provide important theoretical knowledge which is very helpful for better understand about the adsorption behavior of the polysaccharides and sugar based additives at the solid surfaces at the atomic level, which is one of the key issues in their efficient usage in various applications.

2. Modeling and DFT computational details

The primitive unit cells of SiO_2, Al_2O_3 and $CaCO_3$ were optimized using first principle Density Functional Theory (DFT) implemented in Dmol^3 code (Dmol^3 is available as part of Material Studio) [33,34]. The generalized gradient approximation (GGA) for Perdew – Burke – Ernzerhof (PBE) exchange–correlation was used in the calculations [35–37]. To describe the interaction more appropriately, the DFT-D2 [38] approach of Grimme was used to account for the London dispersion force [39], which has been shown to perform well for the adsorption properties of molecules on these three solid surfaces [31,40–48]. The all-electron Konhn-Sham wave functions and DNP numerical basis set with a polarization *d* function and a polarization *p* function on hydrogen were used. The atom-centered grids were used for the numerical integration with a real-space cutoff of 4.2 Å. The k-space integrations were performed using a Monkhorst–Pack [49] grid and the k-point mesh was 3 × 3 × 4 for the optimization of SiO_2, Al_2O_3 and $CaCO_3$ unit cells. The self-consistent-field (SCF) convergence criterion was set as 10^{-5} ev, and the convergence criteria were 5.44 $\times 10^{-4}$ eV for energy, 0.004 Ha/Å for force, 0.005 Å for maximum displacement.

Once the optimized unit cells of SiO_2, Al_2O_3 and $CaCO_3$ were obtained, the periodic supercells: (4 × 4 × 1) for Al_2O_3 and (4 × 4 × 2) for SiO_2 with a vacuum thickness of 17 Å were constructed for GM adsorption. The chemical structure of β-D-glucopyranose was shown in Fig. 1. The (0 0 1) surface of SiO_2, (0 0 0 1) surface of Al_2O_3 and (1 0 4) surface of $CaCO_3$ were considered in the calculations. When optimization, half of the “sublayers” atoms were fixed and the constructed initial adsorption models of GM on SiO_2, Al_2O_3 and $CaCO_3$ surfaces were shown in Fig. 2. The optimization of GM was performed in a (19 Å × 19 Å × 27 Å) cell which had the same size with SiO_2 and Al_2O_3 systems, and in a (25 Å × 21 Å × 31 Å) cell which was same as the $CaCO_3$ adsorbed system. All the calculations were performed with PBE/DNP and Γ-point, which were shown to be sufficient to achieve convergence for the adsorption energies [41].

The interaction strength between GM and the solid surfaces could be represented by the interaction energy (ΔE_{int}), which was defined as following:

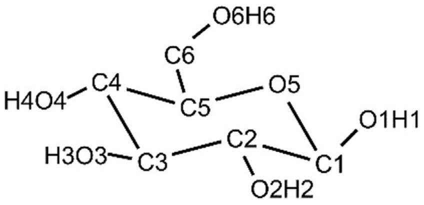

Fig. 1. Chemical structure of β-D-glucopyranose in the DFT calculations.

$$\Delta E_{\text{int}} = E_{\text{GM + slab}} - (E_{\text{GM}} + E_{\text{slab}})$$

where $E_{\text{GM + slab}}$, E_{GM} and E_{slab} represented the energy of β-D-glucopyranose adsorbed on the mineral surfaces, the energy of β-D-glucopyranose in the same cell with the adsorbed systems, the energy of the bare surfaces, respectively. Usually, the more negative was the interaction energy, the stronger was the interaction strength between the adsorbate and the surface [50]. Finally, to further consider the effect of water, the COSMO solvation model [51–53] was taken to optimize the adsorption of GM at the mineral surfaces.

3. Results and discussion

3.1. DFT calculations

3.1.1. Geometry optimization of SiO_2/Al_2O_3/$CaCO_3$ unit structure

Our optimized primitive unit cells were characterized by the parameters: a = b = 4.868 Å, c = 5.404 Å for SiO_2; a = b = 4.800 Å, c = 13.010 Å for Al_2O_3, a = b = 5.023 Å, c = 17.409 Å for $CaCO_3$, closely coincided with the experimental values [54–56] and the previously published DFT calculated results [56–59] (see Table 1). Likewise, it could be seen from Table 1 that the bond length of Si-O of SiO_2, Al—O of Al_2O_3 and C—O of $CaCO_3$ calculated here generally agreed with the experimental and DFT calculated values.

3.1.2. Interaction energies between GM and SiO_2/Al_2O_3/$CaCO_3$ surfaces

In the calculations, two different adsorption geometries: a parallel geometry where GM was lying on SiO_2, Al_2O_3 and $CaCO_3$ surfaces and a vertical geometry where GM was almost perpendicular to the surfaces were considered, as shown in Fig. 2. The calculated interaction energies between GM and SiO_2 (0 0 1), Al_2O_3 (0 0 0 1), $CaCO_3$ (1 0 4) surfaces were shown in Table 2. It was found that the interaction between GM and Al_2O_3, $CaCO_3$ surfaces was quite strong while it was rather weak with SiO_2 surface.

3.1.3. Interaction geometries between GM and SiO_2/Al_2O_3/$CaCO_3$ surfaces

To determine the interaction mechanism between GM and SiO_2, Al_2O_3, $CaCO_3$ surfaces, the optimized configurations were analyzed. By analysis of the parallel adsorption geometry at SiO_2 (0 0 1) surface, we observed only small elongations in the O5—C1, O5—C5 and O1—H1 bonds and the C1—O5—C5 and C1—O1—H1 angles (Table 3, the atom label was shown in Fig. 1) compared to the structural data of the free β-D-glucopyranose molecule, which may be attributed to the hydrogen-bonded interactions with SiO_2 (0 0 1) surface. As was shown in Fig. 3, two hydrogen bonds were formed between GM and SiO_2 surface in parallel and vertical geometry. The corresponding hydrogen bond length and angle were listed in Table 4. In the hydrogen bond studies, the hydrogen bonds were classified into three types based on a distance for H⋯Y and an angle for X—H⋯Y [60], such as strong (1.2 Å < H⋯Y < 1.5 Å, 170° < X-H⋯Y < 180°), moderate (1.5 Å < H⋯Y < 2.2 Å, X-H⋯Y > 130°) and weak (H⋯Y > 3.2 Å, X-H⋯Y > 90°) hydrogen bonds [61]. From Table 4, we observed the strength of the most hydrogen bonds formed between GM and SiO_2 surface was moderate. This suggested that hydrogen-bonded interactions contributed significantly to the adsorption of GM at SiO_2 (0 0 1) surface, which could explain why the interaction between GM and SiO_2 surface was relative weak.

The adsorption configuration of GM at Al_2O_3 (0 0 0 1) surface was displayed in Fig. 4, wherein GM interacted with Al and O atoms of Al_2O_3 surface via its O atom and H atom, respectively. Before GM adsorption, all the Al atoms were flat at Al_2O_3 surface (Fig. 2c and d). But when interacted with O atoms of GM, Al atoms were raised and the Al—O bond length at Al_2O_3 surface increased from 1.705 Å to 1.733 Å. In the parallel adsorbed configuration (Fig. 4a), we have observed elongations in O5—C1, O5—C5 and O3—C3 bonds as well as decrease in C5—O5—C1 and C3—O3—H3 angles (Table 5), compared to the