



## Configurational study of amino-functionalized silica surfaces: A density functional theory modeling



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### ARTICLE INFO

#### Article history:

Received 3 January 2015

Received in revised form 18 February 2015

Accepted 26 March 2015

Available online 3 April 2015

#### Keywords:

Amino-functionalized silica

APTES

Hydrolyzed forms

DFT

NBO

AIM

### ABSTRACT

Despite extensive studies of the amino-functionalized silica surfaces, a comprehensive investigation of the effects of configuration and hydrolysis of 3-aminopropyltriethoxysilan (APTES) molecules attached on silica has not been studied yet. Therefore, the methods of quantum mechanics were used for the study of configuration and hydrolysis forms of APTES molecules attached on the surface. For this purpose, five different categories based on the number of hydrolyzed ethoxy groups including 16 configurations were designed and analyzed by the density functional theory (DFT) method. The steric hindrance as an effective factor on the stability order was extracted from structural analysis. Other impressive parameters such as the effects of hydrogen bond and electron delocalization energy were obtained by using the atoms in molecules (AIM) and natural bond orbitals (NBO) theories.

Consequently, it was found that the stability of configurations was attributed to steric effects, hydrogen bond numbers and electron delocalization energy. The maximum stability was achieved when at least two of these parameters cooperate with each other.

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### 1. Introduction

Nanoparticles have been intensively researched during the last few decades. Due to their high surface to volume ratio, the nanoparticles have unique properties than bulk materials [1]. Silica nanoparticles (NPs) is perhaps one of the most studied materials in nanoscience. This is due to the remarkable properties such as high chemical and thermal stability and its possibility to be modified by a wide range of functional groups [2]. Modification of silica surfaces with variety of functional groups such as thiol [3], amine [4,5], phenyl [6] was performed with different kinds of organosilanes. APTES is most frequently used as organosilane agent for preparation of amino-functionalized silica surfaces [7]. Aminosilylated surfaces are widely used in biochemistry [8], catalyst technology [9], analytical chemistry [10] and industries [11]. Functionalized surfaces can be prepared in the gas or liquid phases [12]. But, the modification of silica surfaces with different types of organosilanes

is frequently achieved in liquid phase that includes the sol–gel, aqueous and organic solvent methods [11]. APTES forms an internal zwitterion in water while anhydrous organic solvent produces a uniform monolayer of APTES on the surface [13]. The presence of small amount of water in anhydrous organic solvent, for example toluene, has an important effect on the mechanism of molecular layer formation and structure of the deposited layer of organosilanes [14]. Silanization that is most frequently used to attach APTES molecules on different silica surfaces begins with the hydrolysis of ethoxy groups in APTES. This step catalyzes by the presence of water molecules and leads to the formation of silanols. The condensation of APTES silanols with silanol groups present on silica surface (surface silanols) results in the formation of a monolayer of APTES via siloxane bonds (Si–O–Si). In addition, there are other possible ways for interaction of APTES with surface silanols and/or adjacent APTES via hydrogen bonding or electrostatic attraction. These interactions reduce the number of available silanol groups on silica surface and APTES for more formation of siloxane bond [15,16].

The attached APTES layer on silica surfaces have been characterized by many techniques including Fourier transform infrared spectroscopy (FTIR) [17], thermogravimetric analysis (TGA) [18], CHN elemental analysis [4], and ellipsometry [19]. But, these methods are unable to determine the numbers of hydrolyzed ethoxy

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groups on the silica surfaces. Therefore, use of the quantum mechanics methods can be useful for this purpose. Application of computational chemistry cover an extremely wide range from predicting the structure, configuration stability, spectra (IR, NMR or UV–vis) and reactivity of complicated molecules to understanding the catalytic property of materials [20]. Quantum mechanics calculations such as ab-initio [21], DFT [22] and combination methods [23] were used as an extensive branch of computational chemistry for determination of stability and surface adsorption on silica surfaces [24]. Unfortunately, high accuracy quantum mechanical methods cannot be used for the large molecules. The ONIOM method which is originally developed by Morokuma and coworkers [25] is among the modern proposals devoted to tackle large molecular systems with quantum mechanical methods.

In the present work, for the first time a theoretical calculation on possible configurations of amino-functionalized silica surfaces were performed by ONIOM method. For this purpose, a silica surface was designed and silanol density for this surface was considered as 6 OH per nm<sup>2</sup>. Two APTES molecules were anchored on it in the energetically favorable configuration. Additionally four water molecules were placed on the top of surface for designing the hydrolyzed configurations. Based on the number and position of hydrolyzed ethoxy groups, 16 different configurations were constructed and optimized in the best available and applicable level of theory. Finally, for better understanding of effective factors on the stability order of configurations, the natural bond orbital (NBO) [26] and atoms in molecules (AIM) [27] were performed on the system.

## 2. Materials and methods

The first step in our calculation was the design of the silica surface. It was modeled similar to other works [28,29]. Based on Niinisto et al. study [30], the number of hydroxyl groups on the surface (silanol groups) were dedicated to 6 groups. To make simpler, in our calculation a mono layer surface was selected and the inner sheets were replaced by frozen methyl groups to keep crystalline surface structure (Fig. 1). This structure was optimized at the B3LYP/SDD level of theory and was considered as the initial construction for further calculations.

After designing the initial surface, APTES molecules were added on the surface to form the amino-functionalized silica surface. Because of APTES molecule size and its steric hindrance, only two molecules can be attached to 1 nm<sup>2</sup> of the surface. Our initial calculations revealed that the best position for these two molecules was achieved by replacing the H<sub>38</sub> and H<sub>32</sub> (Fig. 1). Since four hydrolysable ethoxy groups were on the surface, four water molecules were placed on it to simulate the hydrolyzed forms. The proposed amino-functionalized silica surface included 153 atoms, which was costly and time-consuming for high-level quantum mechanical calculations. Hence, a two-layer ONIOM method [25] was used for optimization the designed surface. Here 86 atoms include four silanols, two functionalized silanols, two anchored APTES groups and four water molecules were assigned to the high layer, quantum mechanics (QM), and other 67 atoms were belonged to the low layer, molecular mechanic (MM) (Fig. 2). The QM subunit was optimized by the DFT methods via using the B3, Becke three parameters [31], for exchange functional and PW91, Perdew–Wang 91 [32], for non-local correlation corrections with applying the 6–31 g (d) basis sets [33]. But the MM layer uses the universal force field (UFF) [34] for optimization. This initial amino-functionalized silica called as 4-ethoxy that none of ethoxy groups is hydrolyzed.

As can be seen from Fig. 2, water molecules can hydrolyze the attached groups in APTES. Depends on the number of hydrolysable

groups (e.g. OCH<sub>2</sub>CH<sub>3</sub>), there are four hydrolyzed categories. If one of the ethoxy groups is replaced by hydroxyl group, the 3-ethoxy category will be formed. This reaction could be continued until all of the ethoxy groups will be substituted and a fully hydrolyzed surface will be produced. It is clear that the 2-ethoxy, 1-ethoxy and 0-ethoxy categories are generated by progress the reaction (Scheme 1). Each category has different forms depending on the location of the hydrolyzed group. Since in 0-ethoxy and 4-ethoxy categories all and none of ethoxy groups are hydrolyzed respectively, they have only one form. In the 3-ethoxy classification, one group is hydrolyzed and due to four possible hydrolysable positions, it has four different forms. There are similar conditions for 1-ethoxy that one unhydrolyzed ethoxy group could be existed in the four various forms. Between these categories, the 2-ethoxy has most forms, six forms, because of its two ethoxy groups are hydrolyzed simultaneously. Therefore based on our calculations, when the hydrolysis reaction is happened on the surface, 16 possible forms are existed per 1 nm<sup>2</sup>. The other forms (15) were optimized at the same level of theory as 4-ethoxy form.

For increasing the accuracy of energy results, the single point energy calculations were performed at the level of B3PW91/6-311++G (d, p; UFF). Furthermore, the solvent effects was considered by SCRF=CPCM (solvent = hexane) keyword which performs a PCM calculation [35] using the CPCM polarizable conductor calculation model [36]. All calculations were performed by using Gaussian 09 program package [37].

Finally, the nature of effective surface interactions in the most stable configurations was realized with NBO and AIM analyses. For this purpose, the most stable form of each category was selected and additional inspections were done on them. NBO analysis has been used with the purpose of understanding and describing electron delocalization and hydrogen bond (HB). Delocalization of electron density between occupied Lewis type and unoccupied non-Lewis orbitals corresponds to a stabilizing donor–acceptor interaction. The energy of these interactions can be computed by the NBO calculations, which come from the second order perturbation theory. In addition, the type and strength of the hydrogen bonds can be determined from charge transfers (CT) between involved NBO orbitals and their energies. Also AIM theory as a powerful method are applied for investigation the molecule's structure and bonding. This theory is based on topological analysis of the electron charge density ( $\rho$ ). Electron density properties at bond critical point (BCP) are used for description of bond formation in AIM theory. Two most important parameters in this theory are bond critical point charge density ( $\rho_{BCP}$ ) and the Laplacian of charge density ( $\nabla^2\rho_{BCP}$ ), which are used for description of the strength and type of bond. For a localized bond, covalent bond, the  $\rho_{BCP}$  and  $\nabla^2\rho_{BCP}$  have positive and negative values respectively while for a delocalized bond, such as hydrogen bonds, both of them are positive with lower values [38].

The NBO calculations were carried out on the B3PW91/6-311++G (d, p) level of theory in hexane environment by using the NBO package included in Gaussian 09 program [39]. Moreover, the electron density and the type of existing bond on the surface of different forms were investigated by AIM theory by means of AIM All 2010 program package [40]. It is mentioned that the QM level was used for AIM and NBO computations.

## 3. Results and discussion

### 3.1. Structural and energy analysis

As it was mentioned, the starting structure for our purpose was the 4-ethoxy form which its surface was not hydrolyzed (Fig. 3). Due to the positional similarity of 1, 3 and 5 surface silanols and

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