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Strained ring motif at silica surfaces: A quantum mechanical study of their reactivity towards protic molecules

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ABSTRACT

The ring opening reactions of $(SiO)_n$ ring motifs ($n = 2$, 3 and 4) at the silica surfaces by the interaction with H_2O (forming two SiOH silanol groups) and HCOOH (forming a SiOH group and a Si—O—C(=O)—H surface mixed anhydride group) has been studied by means of quantum chemical methods. Results are based on a cluster approach adopting the B3LYP-D2/6-311++G(d,p) level of calculations for computing the energetics of reaction. All reactions envisage an activated complex in which the nucleophilic part of the molecules (O atom for H_2O and the carbonyl O atom for HCOOH) attacks the Si atoms of the $(SiO)_n$ moiety followed by a proton transfer from the molecules towards an O atom of the ring. Opening of the most strained two-membered $(SiO)_2$ ring by the considered molecules is highly exoergic. For the medium strained three-membered $(SiO)_3$ ring, two different Si atoms can react, one exposed to the exterior part of the surface and the other buried in the inner region of the surface. Reaction with the outer Si atom is exoergic, whereas that with the inner Si atom is endoergic, indicating the role of possible constraints enforced on the reaction products by the silica surroundings. Opening the regular four-membered $(SiO)_4$ ring is an endoergic process for the both probe molecules. Calculations also show that the energy barriers for reactions with HCOOH are lower than with H_2O because the transition state structures involving HCOOH exhibited a 6-membered ring, far less strained than the 4-membered ring found with H_2O. A further reason is the more acidic character of the HCOOH compared to H_2O, favoring the proton release towards the silica surface oxygen. Furthermore, it was shown that the energy barriers of the ring opening reactions with H_2O is significantly lowered by the presence of an additional H_2O molecule acting through the proton relay mechanism. Reaction energies, in contrast, are less favorable with HCOOH than with H_2O, thus indicating that the formation of SiOH groups is favored with respect to the Si—O—C(=O)—H moiety. Finally, population analysis indicate that the electrophilic character of the C atom in the Si—O—C(=O)—H moiety is higher than for the isolated HCOOH, thereby making it more prone to undergo nucleophilic attack bringing an easier formation of amides.

1. Introduction

Silica-based materials are among the most abundant and important inorganic materials on the Earth's crust, and are involved in many different areas such as heterogeneous catalysis, chromatography, biomaterials or drug delivery [1]. Pure silica (SiO_2) consists of a network of $[SiO_4]$ tetrahedrons (central Si atom surrounded by O vertex atoms) that are connected through the corners. The different ways in which the $[SiO_4]$ building blocks are interconnected give rise to the different silica polymorphs. Moreover, the Si—O—Si angle that connects two tetrahedra has a very low deformation energy, which allows for the occurrence of either crystalline silica materials or amorphous/glassy materials.

Bare silica surfaces are characterized to present siloxane (Si—O—Si) and silanol (Si—OH) groups. These are chemical functionalities that impart the hydrophobic and hydrophilic character to the silica surface. That is, whereas the presence of silanols allows for the adsorption of polar molecules through hydrogen bond, siloxanes are generally involved in the adsorption of apolar molecules via weak dispersive forces. Thus, the nature, density and distribution of these surface functionalities determine the physico-chemical properties of silica surfaces, and in particular the adsorptive features [2]. Various sites involving different types of silanols were identified. Isolated silanols (I) are single or terminal Si—OH groups, whose interaction with the neighboring closest

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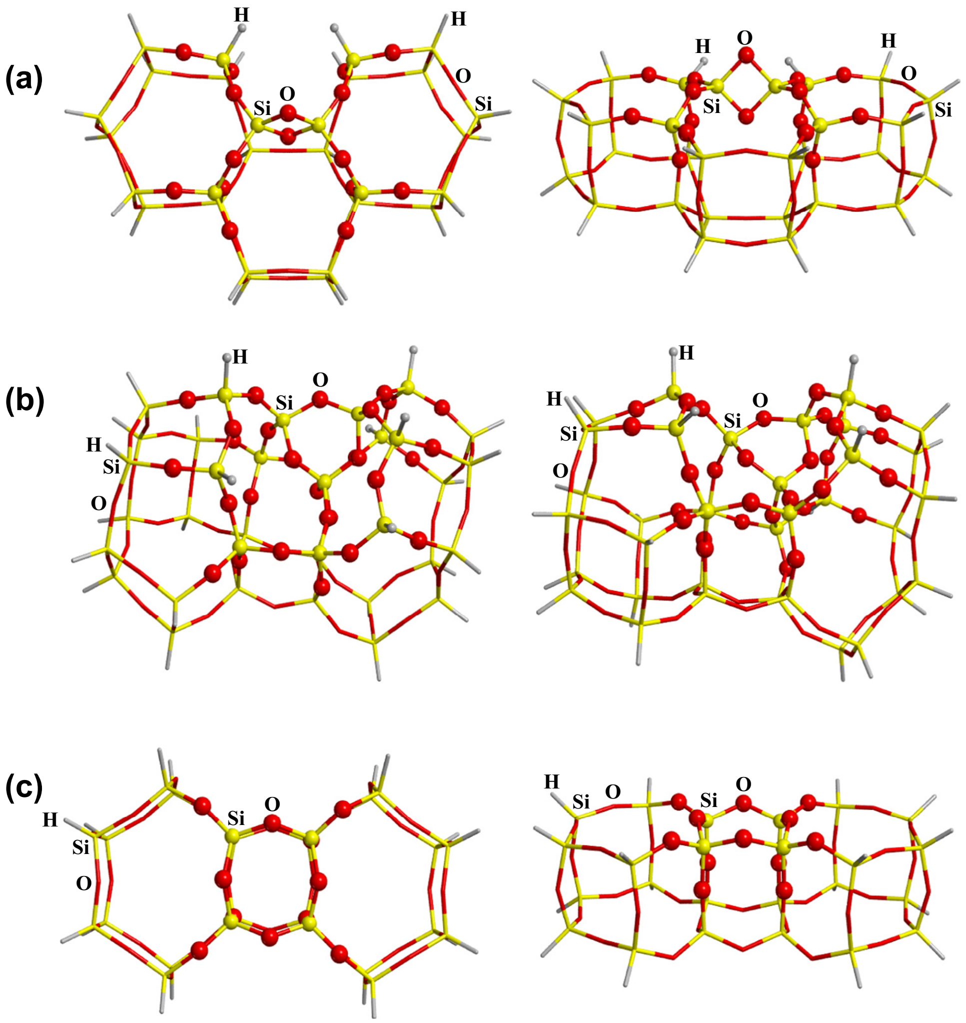

Fig. 1. Clusters adopted to model the all-silica surfaces containing the S2R (a), S3R (b) and S4R (c) rings. Structures shown in the left side are top views; in the right side are lateral views. Atoms shown as balls belong to the high-level zone in the ONIOM2 calculations and are treated at B3LYP/6-311++G(d,p). The real system is treated at the MNDO level.

silanol group is practically null; geminal silanols (G) are those bound to the same Si atom (HO—Si—OH); vicinal silanols (V) involve two hydroxyl groups separated by a siloxane bridge (HO—SiOSi—OH); and interacting silanols (H) are those silanol groups that are mutually H-bonded [3,4].

The concentration of silanols at the surfaces depends on the thermal treatment suffered by the silica sample. When a silica surface is heated, a progressive reaction of pairs of mutually interacting silanols occurs yielding to the formation of siloxane groups via the condensation reaction: Si—OH + Si—OH → Si—O—Si + H_2O. This has dramatic consequences on the hydrophilic/hydrophobic character of the material; that is, a fully hydroxylated silica surface possessing a hydrophilic character can manifest a hydrophobic character if it is outgassed at high temperatures [5]. Condensation of silanols via thermal treatment also induces structural changes at the surfaces. Depending on the kind of the involved pair of silanol groups, the condensation brings about $(SiO)_n$ rings of distinct nuclearity n. Condensation of interacting H pairs may lead to the formation of $(SiO)_3$ and $(SiO)_4$ rings (referred to S3R and S4R, respectively) or higher nuclearity ($n > 4$) rings. When the treatment temperature is higher than 900 K, condensation of vicinal V pairs also takes place forming highly-strained $(SiO)_2$ rings (referred to S2R).

The presence of S2R, S3R and S4R species were experimentally identified by means of spectroscopic techniques. Two infra-red bands at 888–891 and 908–910 cm^{-1} were detected in silica samples activated at high temperatures, which were assigned as the signature of the $(SiO)_2$ ring deformation modes [6–12]. In addition, the contact of the sample with 8–10 Torr of NH_3, H_2O or CH_3OH at room temperature causes these IR features to disappear immediately [7,9,13,14], attributed to the fast opening of the highly-strained S2R moiety. More specific vibrational bands at 605–607 cm^{-1} for S3R and at 131–133 and 490 cm^{-1} for S4R were also identified in Raman spectra [15,16]. Moreover, there is experimental evidence that exposure of S3R to water brings about the disappearance of the ring, due to the appearance of two newly formed silanol groups [16]. However, this is not the case for S4R which remains stable towards the water attack. This seems to indicate that the energy gain provided by the S3R strain relief is sufficient to cause the ring opening, whereas S4R is only slightly strained and consequently stable to water exposure. This is in agreement with the fact that the S4R moiety is very common as a secondary building unit in the framework of many microporous all silica zeolites while the S3R is much more rare [17]. Moreover, these strained moieties will also appear by thermal treatment of zeolites at the external surfaces as well as imperfection in the interior walls of zeolites [18].