A theoretical and experimental study of the possible phenytriethoxysilane species found on treated silica

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Abstract

A modified extended Hückel molecular orbital (EHMO) method, which includes core–core repulsion terms, was used to study the silane adsorption on SiO_2 surfaces. The SiO_2 treated at 300°C was chemically modified with an alcoxysilane, phenyltriethoxysilane (PTES). Therefore, we study the possible adsorption of PTES on two planes (with isolated and geminal silanols) and the possible species formed once the reaction with a SiO_2 surface is finished. Starting from this analysis, it is possible to evaluate the PTES selectivity to the different anchoring points on the SiO_2 surface. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Phenytriethoxysilane; Silica; Modified extended Hückel method

1. Introduction

At the present time and due to the great industrial interest of metallocene as polymerization catalysts, different methods of metallocenes immobilization on solid supports are studied. SiO_2 is the most common support used in olefin polymerization catalysts. The presence of OH in SiO_2 allows the deposition of different species. A new path to make heterogeneous polymerization catalysts is based on a previous chemical treatment with molecules able to alter the SiO_2 surface. The metallocene is deposited on this modified support. The treatments studied use

methylaluminoxane MAO [1], amines [2] or alcoxysilane [3]. In the present work, an alcoxysilane $PhSi(OEt)_3$ (phenyltriethoxysilane: PTES) has been modeled.

The purpose of this paper is to study qualitatively which PTES species are probable on SiO_2 when the support is treated at 300°C. We compare these results with experimental findings of our laboratory on PTES/silica interaction.

2. The extended Hückel molecular orbital (EHMO) method

Molecular orbital calculations were carried out with a semi-empirical procedure (EHMO), which gives an approach to the electronic struc-

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ture. EHMO has been used to study electronic energy changes. It is useful to obtain qualitative trends in adsorption processes, mainly of SiO_2 modifiers and their subsequent fixation on the SiO_2 surface, although quantitative results cannot be considered [4].

The program used (ICONC) was developed by Kamber et al. [5]. It contains repulsive terms to the total energy. The inclusion of these terms is an improvement because they are not explicit in the original EHMO. The repulsive coulombic energy is considered in a pairwise term. The total energy of adsorbed species was calculated as the difference between the electronic energy of the system when the adsorbed molecule is not far away from he surface of a SiO_2 cluster, and the energy of a molecule lying far away from the solid surface. The atomic parameters are listed in Table 1.

The total energy (E_t) of our adsorbate/substrate system is expressed as:

$$E_t = \sum n_i E_i + 1/2 \sum_i \sum_{I \neq j} E_{rep(i,j)}.$$

In this equation, the first term is the valence electrons contribution (n_i) and the second term is the pairwise interatomic repulsion. The valence level i has an energy E_i with occupancy n_i. The repulsion energy of a nucleus i in the presence of a fixed atom j is taken into account as an electrostatic term. The summation is extended to all available atom pairs (E_{rep}). The EHMO theory is based on a physical model for the molecular and solid electronic charge density distribution function. This is partitioned into a perfectly following atom part and a non-

perfectly following bond charge part. For a given molecule, the energy can be evaluated as the integral of the electrostatic force acting on the nuclei. This is a function of the charge distribution. The perfect following bond charge considers two-body repulsion energy, E_r, which is easy to calculate. Each pair repulsion energy includes a nuclear repulsion term and an electron nuclear attraction integral, too. Classical formulae are considered to evaluate these terms. The electron densities are approximated by spherical distributions. The non-perfectly following bond charge density takes accounts of an attractive energy (E_{npf}). This component must be approximated. The approximation is needed because the non-perfectly following density distribution function is unavailable. E_{npf} is well described by the molecular orbital energy stabilization using a model Hamiltonian. The diagonal elements of this Hamiltonian are taken as the negative valence orbital ionization potentials (IPs), the off-diagonal elements on the same center are zero and the off-diagonal elements on different centers are the average of the corresponding diagonal elements multiplied by $2.25 S_{ij} \exp(-0.13R)$. In this equation, S_{ij} is the corresponding valence orbital overlap integral and R is the internuclear distance, The multiplicative factor is a real improvement, comparing it with the original extended Hückel method. The practical effect of the exponential term is to decrease the interactive energy as R increases. Therefore, the equation describes better the real behavior, leading to a sharper increase in the potential curve between atoms. There is a well-known problem of the long-tailed diatomic dissociation curve produced by standard EHMOs [6a,6b]. The usage of this multiplicative factor remedies partly this problem.

Higher levels of theory (HF or DFT) produce better bond energies than EHMO but they should be performed on smaller surface models, so several problems arise. The most obvious one is the truncation. Dangling bonds are found at the borders of the clusters. The atoms in the periphery of the cluster are more poorly described

Table 1
Atomic parameters

Atom	Orbital	Orbital exponents	Ionization potentials (eV)
H	1s	1.000	− 13.60
C	2s	1.154	− 19.65
	2p	1.451	− 11.13
O	2s	2.163	− 31.60
	2p	2.750	− 16.78
Si	3s	1.60	− 20.44
	3p	1.60	− 12.41

than that of the active site. In a HF-SCF procedure, time is spent calculating the distribution of electronic density of the contours and therefore, the description of the active site is poorer. We can improve the results when dangling bonds are saturated. A distribution of point charges can also be considered for remote atoms. Due to these problems, we prefer to use a big cluster and a semi-empirical method, not so powerful in terms of energy descriptions, as EHMO. The results, we repeat, are only valid in relative or qualitative terms, not quantitative. We are using the ASED or ICONC methods, which compute the electronic structure ''like'' the traditional EHM, but have distance dependence for the H_{ij} matrix elements. Besides, it includes explicit repulsive (coulombic) terms to the energy [9] so the obtained bond distances are better. See, e.g. Refs. 6a 6b 7 8. However, the energies are not correct in an absolute sense. They can be used only in ''relative'' terms, but this is really important in the design of a catalyst. Recently, we explored Ziegler Natta systems with the ICONC method. The predictions were in good agreement with the experimental results [10–12].

The geometry optimization was done at 0.1 Å step and due to the approximate nature of extended Hückel-like methods, the convergence criterion to the energy was set at 0.01 eV.

The semi-empirical molecular orbital calculations were performed in the cluster approximation. Therefore, the adsorption site and its neighborhood were modeled by a portion of an infinite solid. The section of the cluster results in the appearance of the so-called dangling bonds in the borders. Bagus et al. [13] reported that while the electron structure converges slowly in the bulk as the cluster size is higher, the chemisorption properties are predicted in a satisfactory way.

3. The surface and adsorption sites models

The SiO_2 surface model was built on the assumption that the amorphous silica surface can be assimilated into (100) and (111) planes, which contain geminal and isolated silanols, respectively (β-cristobalita) [14]. Therefore, we studied the PTES fixation on two planes in separated form to avoid the problem of the important contribution of (100)–(111) border-line. In this way, the random modeling of hydroxyls on amorphous silica is not considered. The SiO_2 surface model is not a very big cluster, since the important interactions produced between the modifier and the surface are short-range interactions.

3.1. SiO_2 geminal (100)

Sixty-three atoms were used to model the (100) plane of the silica, nine Si, 18 O and 36 H were placed (Fig. 1). In this cluster, dangling bonds were saturated with hydrogen atoms [15]. In agreement with the literature, 15% of OH total of the SiO_2 surface is geminal [15] but we used complete planes to avoid the borderline problem.

3.2. SiO_2 isolated (111)

Sixty-eight atoms were used to form the OH isolated cluster, constituted by 14 Si, 22 O and 32 H (Fig. 2). The proposed model presents the isolated silanols of the (111) plane-forming hexagons [15].

3.3. The PTES model

The modifier [PhSi(EtO)$_3$] was modeled considering one of the three ethoxy groups such as hydroxyl (OH). This model was chosen by tak-

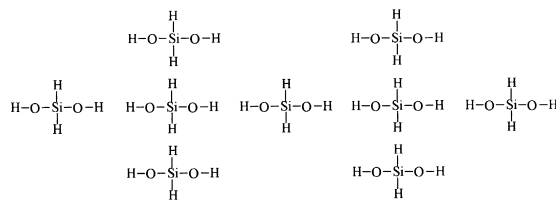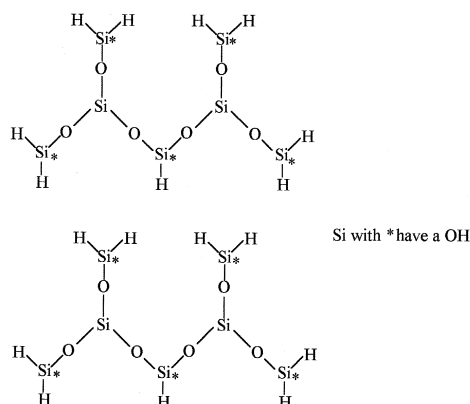Fig. 1. Model of geminal SiO_2 (100). Top view.

Fig. 2. Model of isolated SiO_2 (111). Top view.

Table 2
Bond distances in the molecule of modifier

Type of bond	Distance (Å)
Si−O	1.54
Si−C	2.52
O−H	0.96
C−H	1.10
C_{ar}−H	1.08
O−C	1.48

ing into account that silicon has a tetrahedral spatial structure, and two of the ethoxy groups will be downward. The remaining phenyl group (Ph) and the last ethoxy group will be far away from the surface. So, the most important interaction would take place between two silane ethoxy groups and silica surface. We propose a representative model of reality changing an ethoxy group by an OH. Fig. 3 shows the spatial structure of the proposed model for the silane molecule.

The silane model has 30 atoms, one Si, three O, 10 C and 16 H and has the formula, $PhSi(OEt)_2OH$. The spatial structure proposed is the one of minimum energy. The final bond distances in the silane molecule are shown in Table 2. Bond angles were respected (Table 3).

4. Experimental

The treated silica used was characterized by means of the following techniques: Brunauer–Emmet–Teller (BET) area, scanning electronic microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The OH surface
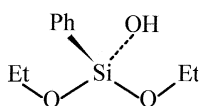
concentration before and after the thermal pretreatment of silica was obtained with the nBuLi titration method.

4.1. BET area

Before the BET area determination, the sample was thermally treated at 300°C in high vacuum (10^{-4} Torr). The pore diameter was obtained using the complete N_2 adsorption isotherm data.

4.2. FTIR

The analysis was done with KBr as mixer, using a Nicolet 530 FTIR.

4.3. Method of nBuLi for OH determination

Using inert atmosphere (N_2), a known quantity of nBuLi is added to a known weight of silica to achieve the complete titration of surface OH. An excess of nBuLi is added to determine later the remaining Li. The reaction takes place overnight at room temperature, in inert atmosphere. After filtering and four washings with toluene, bidistilled water is added to

Fig. 3. Model of PTES. Lateral view.

Table 3
Final angles of bonds in the molecule of modifier

Type of bond	Angle of bond (°)
C−O−Si/H−O−Si	120
O−Si−O/O−Si−C	109
C−C−C (aliphatic)/H−C−H/H−C−C	109
C−C−C (aromatic)/H−C−C	120

the toluene used in the washings to produce the hydrolysis of non-reactive nBuLi, so Li is now in the aqueous phase. Finally, the organic phase is separated and bidistilled water is added to achieve a known volume of solution to be analyzed by atomic absorption. The determination of Li was done with an AAS Ins. Lab. 551 [16].

4.4. Impregnation with PTES

We deposited the PTES modifier on the treated silica by means of a gas–solid reaction in controlled atmosphere, using a system with the possibility to put in contact SiO_2 with the silane in gas phase. Liquid silane was kept at the desired reaction temperature and a flux of N_2 permits us to contact a desired weight of silica (placed in the outlet of gas) with the gaseous silane. The temperature of the system was 150°C. This temperature was selected considering the boiling point of $Ph(OEt)_3Si$ (170°C). The contact time between the solid and the flux of inert plus gaseous silano was 3 h. Later, a steam of N_2 was passed through the silica for 2 h to achieve the total removal of the non-reactive PTES molecules. The final solid was clear yellow. The carbon content was measured by a C and N analyzer, following standard procedures.

5. Results and discussion

5.1. Experimental results

The pretreatment decreases the OH content from 4.33×10^{14} to 3.67×10^{14} mol OH/cm^2. The initial BET area was 306.5 m^2/g. The initial pore diameter was 22 nm, the pore volume was 1.53 cm^3/g, and the average particle size of irregular shapes was 50 μm.

The treated silica has a BET area of 352 m^2/g, a pore diameter of 25 nm and a pore volume of 1.67 cm^3/g. The OH concentration was evaluated by the nBuLi method and the result was 3.67×10^{14} OH/cm^2. The FTIR

spectrum of this treated SiO_2 shows an important decrease of adsorbed water in 3300 up to 3800 cm^{-1}, especially the one centered in 3370 cm^{-1}. Bands at 3746.1 and 3657.1 cm^{-1}, assignable to isolated silanol and geminal groups, are important in this region. The C percentage obtained of the silane deposition on the SiO_2 was 3.25% C.

5.2. The PTES adsorption

We analyzed different adsorptions of the modifier on silica. The fixation reaction of silane over SiO_2 is only possible through silanols groups. In the case of a surface able to form siloxanes by dehydration, it is considered as another point for the fixation on the silica surface. Therefore, we consider four situations:

A — PTES on isolated silanols;
B — PTES on siloxane, formed by the dehydration of two isolated silanols;
C — PTES on geminal silanols; and
D — PTES on siloxane, formed by the dehydration of two geminal silanols.

In the first and third cases proposed, we are considering that the reaction will be between the EtO^- of the silane molecule and the H of the silanols. In cases B and D, the reaction with a siloxane ($\equiv Si-O-Si\equiv$) would produce a surface $\equiv Si-O-Si(OEt)OHPh$ group and a $\equiv Si-OEt$ group. The reaction considering the Ph group is sterically hindered for the proposed model of the modifier. We found this by calculation.

There are four possible situations, but two of these are feasible energetically, according to the proposed model and the results obtained by EHMO. These favorable situations are A and C.

The species formed by reaction of PTES with isolated silanols (A) remain anchored on silica surface forming a 180° ($Si-O-Si$) angle (see Fig. 4). In this reaction, an EtOH molecule is also obtained. The alcohol adsorption on SiO_2 was not considered. Electronically, the superpo-

Reaction:

(Sup)-Si-OH + PhSiOH(EtO)₂ → PhSiOH(EtO)-O-Si-(Sup) + EtOH
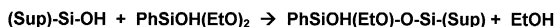
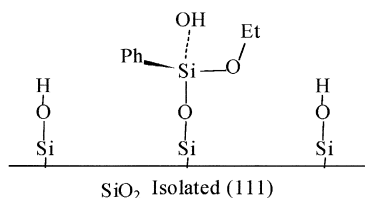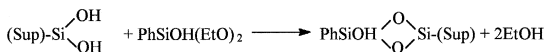**Model of Final Supported Species**

Fig. 4. Lateral view of the PTES species formed on the isolated OH.

sition between pπ filled orbital of oxygen and the dπ of Si of the surface enhances with the angular increase. This situation helps the lineal condition. In the particular case of PTES, the increase of the angle is enhanced by the presence of a phenyl group [6a,6b].

The probable species on SiO_2 geminal (100) (C) is formed by reaction of two geminal silanols groups (of the same Si) with two ethoxy groups of silane. Two EtOH molecules are also formed (Fig. 5). The others species proposed present positive energies, so they are in a very much lower proportion.

In both cases (A and C), we want to know the most stable position and to distinguish the more selective site to both types of adsorption. Therefore, we positioned the PTES molecule at different distances from the reaction site. In this

Reaction:
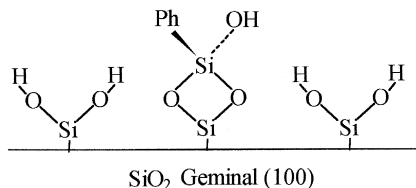

Model of Final Supported Species

Fig. 5. Lateral view of the PTES species formed on the geminal OH.

way, we obtained the energy curves for the two silanol types. In the first situation (A), the molecule of PTES was placed with the O of EtO$^-$ on the H of the isolated silanol (Scheme 1). The energy minimum is at O (ethoxy group)$-$H (silanol group) distance of 2 Å ($E = -0.187$ eV). When the PTES is near to the surface, the repulsion is important. When the distance is greater than the distance in the energy minimum, an increase of the energy system occurs. In the second case (C), the Si of silane was placed on the Si of the SiO_2 lattice, then the distance O (ethoxy group)$-$H (silanol group) was varied (Scheme 2). In this way, the O$-$H distances are the same for both EtO$^-$. In this case, the behavior of the energy curve is not similar to the former case, but the minimum of energy is at 2.7Å in the O (ethoxy group)$-$H (silanol group) ($E = -1.2603$ eV). In both curves, an increase of energy exists when the
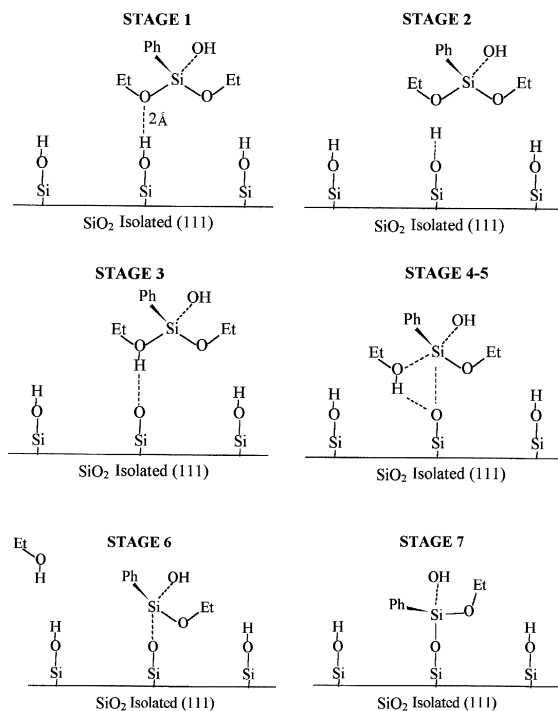
Scheme 1. Adsorption of PTES on isolated silanols in the different stages.
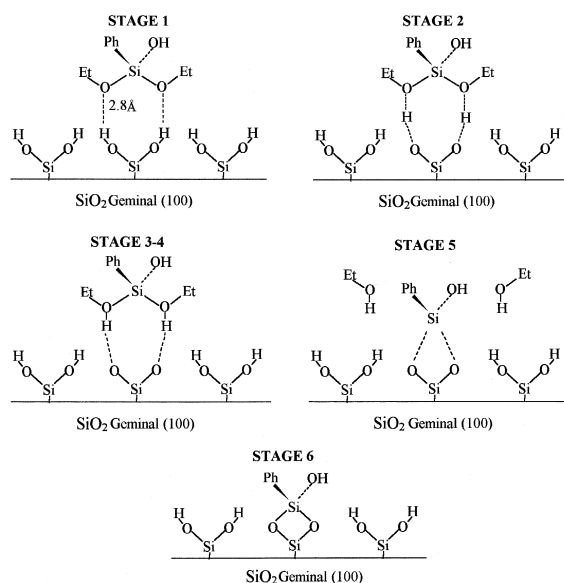
Scheme 2. Adsorption of PTES on geminal silanols in the different stages.

Fig. 7. Energy curve of adsorption of PTES on geminals silanol in function of the distance O−H (O of EtO$^-$ and H of OH).

distance O−H is less than the distance in the energy minimum.

The curve of the Fig. 6 suggests that the adsorption of the PTES molecule on isolated silanol is possible when the distance is at 2 Å or slightly superior. The minimum of energy is small (-0.187 eV) and suggests low adsorption
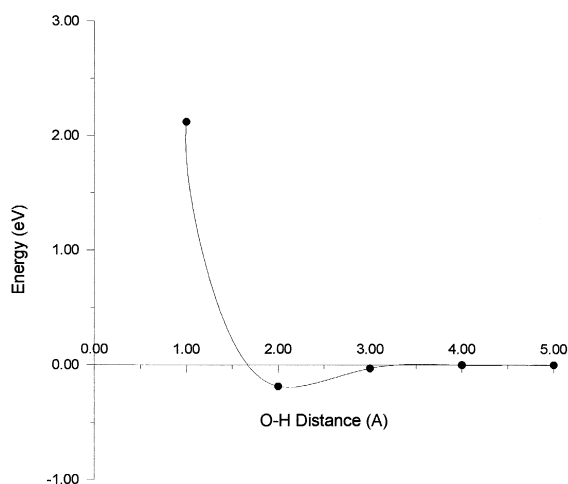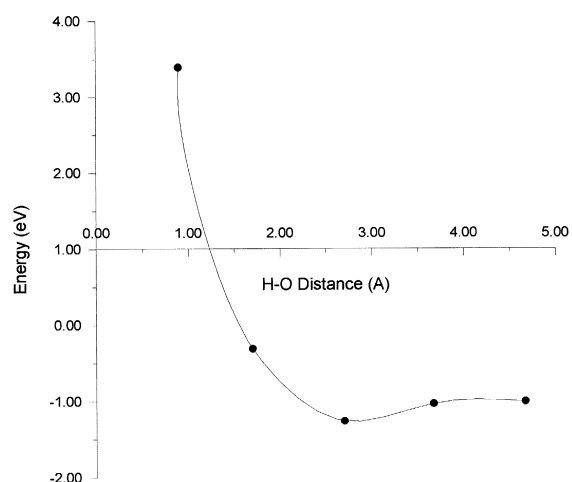
energy of a modifier on this site. In the case of the curve shown in Fig. 7, the adsorption is more favorable because the energy of adsorption is more important at O (ethoxy group)−H (silanol) distances longer than 1.5 Å (1 eV).

In conclusion, the PTES adsorption on geminal silanols is more favorable energetically. Therefore, the adsorption on this site is more probable than on isolated silanols.

5.3. The reaction path

For the energetically possible species, we study a reaction path (Schemes 1 and 2) from the most probable position of adsorption to the final position of the rest of silane on the silica surface. The reaction paths were designed considering that the ethoxy group (EtO$^-$) is a bad salient group. For this reason, the path was designed considering first the stretching of the O−H bonds of silanols to achieve the proper bond angle and distance. Later, we produce the separation of the EtOH molecules.

In the case of adsorption of PTES on isolated silanols, the different stages in the path are:

Stage 1: the silane is at a distance of minimum energy adsorption ($d = 2$ Å);

Fig. 6. Energy curve of adsorption of PTES on isolated silanol in function of the distance O−H (O of EtO$^-$ and H of OH).
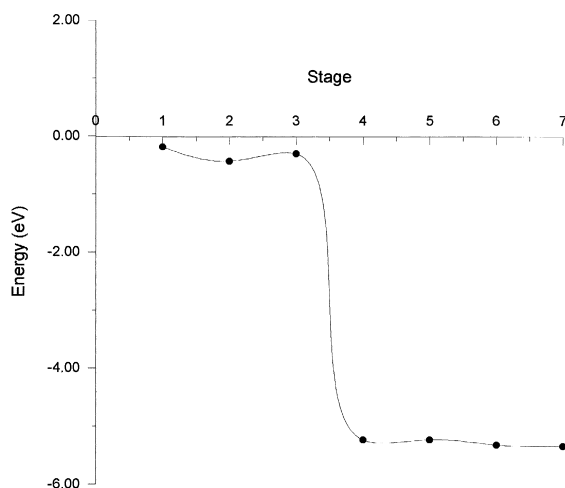
Fig. 8. Energetic curve for the stage in the reaction path of PTES on isolated OH groups on SiO_2 (111).

Stage 2: the silane was maintained in the former position, but both O–H bonds in direction to the O of the ethoxies were varied because both were lost;

Stage 3: stretching of the O–H bond of isolated silanol until the bond distance with the EtO^- group is reached;

Stage 4: the EtOH formed was slightly separated and the rest of the silane was approached to the final position of bond;

Stage 5: a new approach of the rest of silane to the surface and an increased EtOH surface distance in a concerted reaction in the perpendicular plane at the surface coordinates (see Scheme 1);

Stage 6: the silane is at final bond position and EtOH molecules are far away; and

Stage 7: the surface species of silane in the silica, without EtOH.

Analyzing the curve in Fig. 8, we can observe a little increase of the energy when the stretching of the O–H bond of silanols occurs. This difference is 0.24 eV that corresponds to the energy of bridged hydrogen bond formed in the adsorption O–H $\cdots$ O. Data in the literature [14] suggest that this bond presents energy between 15 and 40 kJ/mol (0.15–0.40 eV), depending on its length. These values of energy for bridged hydrogen bond correspond to the case when the three atoms (O–H $\cdots$ O) are in line. The next stage presents high stability energy until the final species of PTES is formed on the isolated silanols. These species are at Si–O distance of 2.87 Å with a relative energy of -5.33 eV.

When the silane is adsorbed on geminal silanols, the stages are:

Stage 1: silane at the more stable position of adsorption ($d = 2.8$ Å);

Stage 2: the silane is in the former position with stretching of the two O–H bonds in direction of the O of the two ethoxy groups;

Stages 3 and 4: stretching of the O–H bonds until bond distance between H of the silanols and O of the ethoxy groups is reached;

Stage 5: the EtOH formed was separated and the rest of silane was located at a position with a Si–O distance of 3.25 Å, found by calculation; and

Stage 6: position of major stability of the species on surface silica (2.8 Å with a relative energy of -8.29 eV).
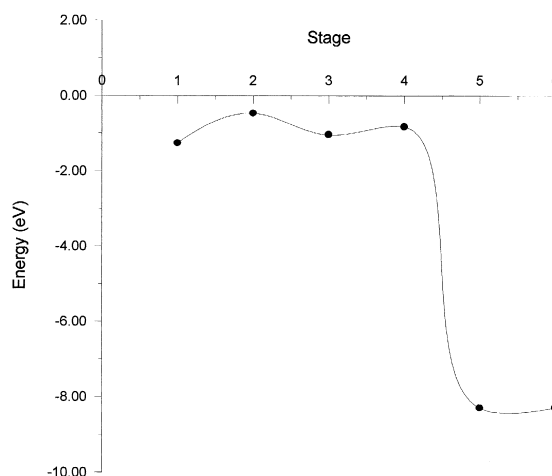

Fig. 9. Energetic curve for the stage in the reaction path of PTES on geminal OH groups on SiO_2 (100).

Analyzing Fig. 9, we see that the formation of the species shown in Fig. 5 is completely stable once the energy barrier is exceeded. The first two are small and correspond to consumption of energy to obtain the ruptures of the O−H bond of the two silanols that will react with the PTES.

A similarity between the energy curves for both reaction paths is the important decrease of the relative energy when the EtOH molecule is far away and the rest of silane is near the position of the minimum energy.

5.4. Stability of formed species on silica surface

The final distance of the species with respect to the silica surface was found with stretching of the Si−O bonds (Figs. 10 and 11). In Fig. 10, we can see a minimum in 2.87 Å, but the variation of the energy is very small and the formed species on the isolated silanols present a large range of Si−O distance where the species is stable. From the curve, it is possible to see that at a distance of less than 1.5 Å, the species is energetically unstable. The species formed on the geminals silanols presents a similar behavior. The minimum of energy is at 2.8 Å, but the bond can change between 2.71 and 3.10 Å, with a minimum variation of the energy. When the
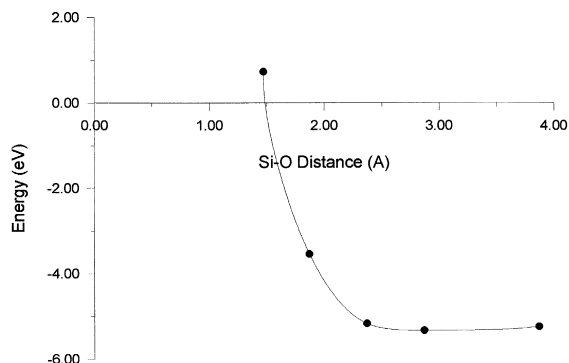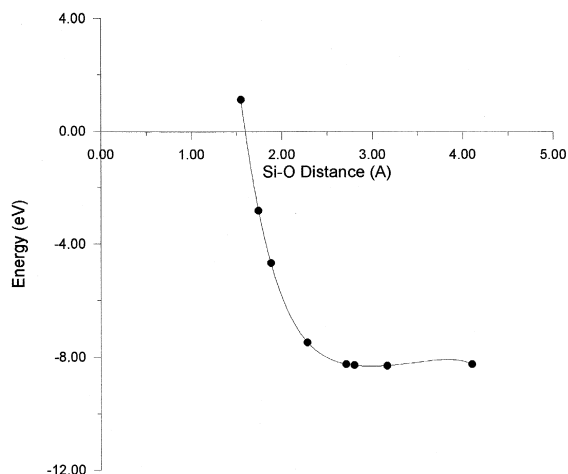

Fig. 11. Energy curve of PTES system on geminal OH as a function of the length of Si−O bond.

Si−O distance is less than 1.7 Å, the system SiO_2–PTES is unstable because the repulsion is increased.

From the results obtained from the semi-empirical study, we can conclude that the gas–solid reaction between the SiO_2 and the modifier PTES occurs mainly on two sites. One of them presents more stability in the adsorption step and in the final fixed species (geminal silanols). The isolated silanols present a stable position but the energy is low. This proves that the reaction would be most feasible over geminal silanol than over isolated silanols. These results suggest that the reaction presents high selectivity.

The results obtained can be used to explain the experimental data obtained in our laboratory that it is usually accepted that 15% of the total OH of the surface silica is geminal silanols. The reaction would take place over one geminal silanol (GEM) out of five (due to sterical hindrance). Knowing surface OH concentration, it is possible to obtain the number of reactive OH in this plane which are able to react with the modifier PTES. Two geminal silanols react with every PTES molecule, and the number of carbon moles in this species is 8 mol C/mol PTES. Analyzing these results, we obtained a

Fig. 10. Energy curve of PTES system on isolated OH as a function of the length of Si−O bond.

value 3.22×10^{-5} mol of silane (equivalent to 0.309% C). This value does not exceed the carbon content; therefore, we suppose that the modifier molecules fixation also occurs in plane (111) AIS. Therefore, 2.41×10^{-4} mol of the silane are fixed on the isolated SiO_2 (considering that the formed species contain 10 mol C/mol PTES) to complete the mass balance of silane. In this case, the relation OH/PTES is 1:1; therefore, we can calculate the percentage of isolated OH reacting with PTES. This value is 12% of the total available isolated groups (taking account of vicinal silanols) and indicates the percentage of isolated silanols that are bonded with silane molecules. Therefore, the results of low C percentage are in agreement with the low adsorption on this isolated silanol because it is less stable energetically, according to the results obtained with theoretical analysis.

It is reported that in a number of cases, alkoxysilanes are more useful than the corresponding chlorosilanes for reacting with silica surfaces. The increased reactivity of alkoxysilanes in the reaction with isolated silanol groups can be explained by the higher proton affinity of the oxygen atom of the Si—O—Si group, compared to the Cl atom in the Si—Cl group [17]. The rather difficult question of how many alkoxygroups of one trialkoxysilane molecule participate in the chemical bonding has been studied by high resolution of ^{29}Si and ^{13}C NMR nuclei and the conclusion was that in the case of dehydrated silicas, mainly monodentate and some bidentate species are formed. Reactions involving all three alkoxy groups do not occur on the surface of dry silica [17].

The conclusion of our results is the strong selectivity of the modifier PTES to the different points of fixation on the surface silica. The adsorption and reaction on isolated silanols are less stable energetically than on geminal OH. The reactivity is higher on the geminal silanols due to a more favorable adsorption, which leads toward a final state of increased stability. The adsorption on the isolated silanols is feasible, too, but the difference is the stability of the

molecules of silane once adsorbed. If we consider the arrival of a PTES molecule to the surface silica, the molecule of the modifier will prefer the site of the higher stability. Therefore, we can conclude that the difference between the two sites is due to the major stability on the geminal silanols for the adsorption and the formation of the final product of reaction. Considering the different importance of both surfaces in amorphous silica (85% of isolated hydroxyls), the species would be mainly monodentate, but there would be bidentate species, too.

Acknowledgements

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