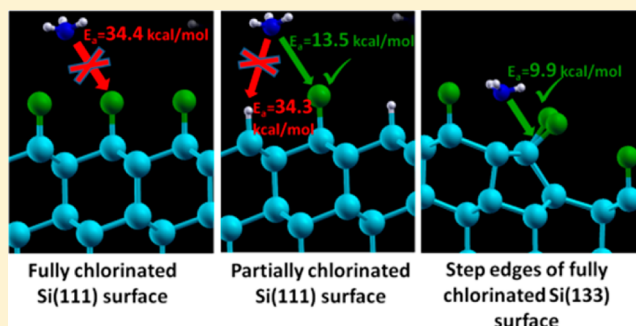


Tailoring the Surface Reactivity of Silicon Surfaces by Partial Halogenation

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Supporting Information

ABSTRACT: Density functional theory was used to investigate the reactivity of partially chlorinated and stepped silicon surfaces with molecules having N, O, and S head groups in relation to the development of selectively functionalized surfaces. The activation energy barriers for the formation of Si–N, Si–O, and Si–S bonds by breakage of the Si–Cl bond are very sensitive to steric factors and this fact can be used to tune the surface reactivity. Whereas the fully chlorinated Si(111) surface has high energy barriers in the range 34–64 kcal/mol for the reactions with NH₃, H₂O, H₂S, CH₃NH₂, CH₃OH, and CH₃SH molecules, the partially chlorinated surface has much lower barriers in the range 13–34 kcal/mol, indicating that some molecules may react at almost room temperature with the SiCl groups. The reactions of these molecules on SiH groups have high energy barriers for all surfaces (in the range 33–42 kcal/mol) indicating that they form a matrix of unreactive groups around the reactive SiCl sites. Unlike the fully chlorinated Si(111) surface, the SiCl groups on the reconstructed step edges are very reactive, showing the lowest activation energy barriers. The different reactivities of SiCl groups on the terraces and step edges of fully chlorinated stepped silicon surfaces may allow the formation of molecular lines along the reactive step edges.



INTRODUCTION

Nanotechnology,^{1,2} biotechnology,³ microelectronics,⁴ and biosensing⁵ applications require selective organic functionalization of substrates with good electrical properties such as silicon.^{6–8} A requisite to selectively functionalize a surface is to have surface groups with different reactivities and with the appropriate 2D distribution. One approach to achieve this goal is to take advantage of the enhanced reactivities of surface features such as the step edges of vicinal surfaces or the dimer rows of the Si(100)–(2 × 1) reconstruction.

However, the challenge is to functionalize unreconstructed flat surfaces in order to have the most reactive groups embedded in a matrix of less reactive groups. The rich surface chemistry of the H–Si(111) surface can be used for this purpose. Chabal and co-workers have developed a procedure to obtain a well-defined nanopatterned OH coverage on H–Si(111).⁹ The procedure starts by immersing the hydrogenated surface in anhydrous methanol to yield a surface in which each methoxy group is surrounded by six SiH groups. By further immersion in HF(aq), every Si–OCH₃ bond is replaced by a Si–F bond which after exposure to pure water for 90 s results in a 1/3 ML OH and 2/3 ML H-terminated Si(111) surface.

The formation of surface SiOH groups without subsurface oxidation is of utmost importance. SiOH groups reduce incubation times in atomic layer deposition (ALD) experiments

of oxides such as Al₂O₃, ZrO₂, and HfO₂.⁴ These oxides have a high dielectric constant and therefore are an alternative to SiO₂. Recently, Chabal and co-workers¹⁰ reported that phosphonic acid reacts more readily with Si–OH surfaces without subsurface oxide than Si–OH surfaces with subsurface oxide. On this model surface, the authors showed that a perfectly ordered layer of monodentate phosphonic acid molecules can be chemically grafted at room temperature.¹⁰

In this work we show that the different reactivities of SiH and SiCl surface groups in partially chlorinated silicon surfaces open pathways for the selective functionalization of flat Si(111) surfaces, therefore allowing the formation of nanopatterns on such surfaces. We also show that the high reactivity of the step edges of fully chlorinated surfaces could also be used for the selective functionalization of vicinal surfaces.

The H–Si(111) surface can be chlorinated by several methods^{11–18} described in the literature: gas phase reactions with Cl₂ induced by UV irradiation,^{11,12} thermal activation,^{13,14} and wet chemistry using a solution of PCl₃ in chlorobenzene solvent.^{15,16} Chabal's group reported a method¹⁷ in which

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hydrogen-terminated silicon surfaces are chlorinated using a Cl_2/N_2 mixture.

During the chlorination process, there is a mixed coverage surface, partially covered with hydrogen and partially covered with chlorine. The coverage of Cl atoms is controlled by varying the exposure time of the hydrogenated surface to the Cl_2/N_2 mixture.¹⁸ After an exposure time of 3 min at a temperature of 95 °C, a 50% chlorine coverage is obtained.¹⁸ The chlorination can be monitored by the IR frequency shifts of the Si–H and Si–Cl stretching modes, as they are sensitive to the local environment.^{19,20}

In previous work,²¹ we showed that the reactivity of the Cl–Si(100) (2×1) surface toward ammonia is governed by a balance of electrostatic and steric effects. Steric factors arise from surface features such as the size of the halogen atom and its surface concentration. The effect of steric factors is to increase activation energy barriers. On the other hand, the ionic nature of the transition state (resembling an ammonium chloride moiety) has a stabilizing effect which lowers the energy barriers. In turn, the ionicity of the transition state depends on the nature of the reacting headgroup. Therefore, there are many variables which can be controlled to tune the surface reactivity in order to selectively functionalize a partially chlorinated surface.

Although there are several experimental studies of the reactivity of molecules containing O, N, and S atoms with chlorinated and hydrogenated Si(111) surfaces,^{9,15,16,22–30} there are but a few theoretical studies of their reactivity as yet.^{21,23,27,31} Neither theoretical nor experimental studies have been carried out over the reactivity of the *partially* chlorinated surfaces.

The calculations reported in this work represent the reactions as they occur in the gas phase and do not account for acid–base properties of the small molecules in liquid phase reactions. The high energy barriers obtained on the fully hydrogenated and chlorinated silicon surfaces correlate with the high temperatures reported experimentally in the gas phase. When the reactions occur in the liquid phase, the reacting temperature is much lower, as has been recently reported for the reaction of H–Si(111) with neat anhydrous liquid methanol.^{9,30} The acid–base properties methanol are probably responsible for the enhanced reactivity in the liquid phase.

We therefore decided to investigate the reactivity of the partially chlorinated Si(111) surface toward reactants with N, O, and S head groups (NH_3 , H_2O , H_2S , CH_3NH_2 , CH_3OH , and CH_3SH) in relation to the development of selectively functionalized surfaces. The reactivities of the fully hydrogenated and halogenated Si(111) surfaces are also considered as a reference. The results show that the perfect H–Si(111) and Cl–Si(111) surfaces are unreactive at room temperature. However, the decrease of steric factors on partially chlorinated surfaces increase the reactivity of the SiCl group toward NH_3 , CH_3NH_2 , and H_2O to such extent that they could react at room temperature. Unlike the fully chlorinated Si(111) surface, the SiCl groups on the reconstructed step edges are very reactive showing the lowest activation energy barriers.

SURFACE MODELING AND THEORETICAL METHODS

A silicon slab with six layers was used to model the (111) face of silicon. The dangling bonds of the bottom surface were saturated with hydrogen atoms. We used $a_0 = 5.48 \text{ \AA}$ for the lattice constant as determined in a previous work.³² The

positions of all the adsorbate atoms as well as those of the four topmost Si layers were fully optimized. The silicon atoms of the lower bilayer were kept fixed in a bulk configuration. Calculations were performed using (2×2) and (3×3) unit cells.

Periodic density functional theory (DFT) calculations based on plane waves were performed as implemented in the Quantum Espresso code.³³ Norm-conserving ultrasoft pseudopotentials³⁴ were used for the atomic species. The PBE formulation was employed for the exchange and correlation functionals.³⁵ The electron wave functions were expanded in a plane-wave basis set up to a kinetic energy cutoff of 30 Ry (180 Ry for the density). Brillouin zone integration was performed using a ($4 \times 4 \times 1$) Monkhorst-Pack mesh.³⁶ A vacuum thickness of 10 Å was introduced between the slabs.

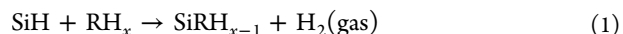
We also investigated the reactivity of the step edges of the chlorinated Si(111) surface. The step edge structure of this surface has been investigated experimentally and it is characterized by the presence of a stacking fault along the $[11\bar{2}]$ direction.³⁷ We used the Si(133) surface to model a step edge along the $[11\bar{2}]$ symmetry direction of the Cl–Si(111) surface. From a structural point of view, the Si(133) surface has short terraces with the 111 structure which facilitates the theoretical studies, mainly the time-consuming reaction path calculations.

Reaction pathways and energy barriers were calculated using the so-called “climbing image nudged elastic band” (CI-NEB) method³⁸ as implemented in the Quantum Espresso code.³² The method works by optimizing a number of intermediate images along the reaction path. For the identification of transition states, we followed the same procedure as in a previous study on the reactivity of halogenated Si(100) surfaces toward ammonia.²¹ In all plots, energy profiles will be presented as a function of the reaction coordinate, which is a reduced parameter ranging from 0 for reactants to 1 for products.

RESULTS AND DISCUSSION

We first consider the reactivities of the fully hydrogenated and chlorinated Si(111) surfaces which are taken as references in the study of the partially chlorinated surface and the reconstructed step edges of the fully chlorinated surface.

Reactivity of the H–Si(111) Surface. Figure 1 shows the energy profiles for the reactions of NH_3 , H_2O , and H_2S (Figure 1a), and CH_3NH_2 , CH_3OH , and CH_3SH molecules (Figure 1b), with the H–Si(111) surface. The reactions can be written as:



where the SiH group reacts with the RH_x adsorbed molecule (NH_3 , H_2O , H_2S , CH_3NH_2 , CH_3OH , or CH_3SH) to yield a Si NH_2 , SiOH, SiSH, SiN(H)CH₃, SiOCH₃, or SiSCH₃ surface group, respectively, with the release of a H_2 molecule. ΔE values reported below correspond to eq 1.

The energy profiles of Figure 1 show that, in all cases, the reactions involve only one step. Table 1 contains the activation energy barriers and the ΔE values for the reactions. For ammonia, both E_{act} and ΔE are very close to those found on the H–Si(100)– 2×1 surface in a previous work.²¹ Table 1 shows that the E_{act} and ΔE values for the formation of the Si– NH_2 and Si–NH(CH₃) surface groups are very similar, and the same holds for the formation of Si–OH and Si–OCH₃ groups and for Si–SH and Si–SCH₃ groups. Therefore, ΔE values are not

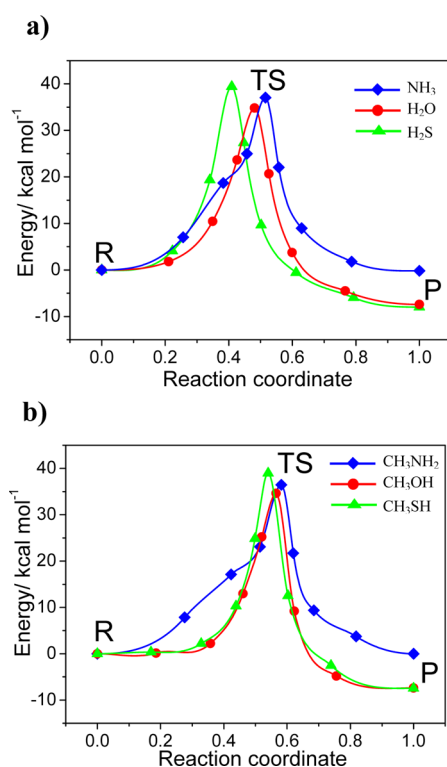


Figure 1. Energy profiles along the reaction coordinate for the reaction of (a) NH₃, H₂O, and H₂S and (b) CH₃NH₂, CH₃OH, and CH₃SH on H-Si(111). The points labeled R, TS, and P correspond to reactants, transition states, and products. The CI-NEEB calculations were performed on the SiH group of a 2 × 2 unit cell.

Table 1. Activation Energy Barriers and ΔE Values (in kcal/mol) for the Reactions with the H-Si(111) Surface

molecule	E_{act}	ΔE
NH ₃	36.7	-0.2
CH ₃ NH ₂	36.5	-0.02
H ₂ O	34.8	-7.4
CH ₃ OH	34.6	-7.4
H ₂ S	39.4	-8.0
CH ₃ SH	39.0	-7.5

affected by the presence of a CH₃ terminal group on the hydrogenated surface.

Figures 2 a–c show the corresponding structures of reactant, transition state, and product for the reaction of NH₃, H₂O, and H₂S with H-Si(111), respectively. Figure 2d shows a top view of the structure of the transition states for NH₃, H₂O, and H₂S respectively. The structure for the reactants corresponds to the molecule adsorbed on a T4 surface site (it is on top of a silicon atom on the second layer). For each transition state, the formation of the X-Si bond (X = N, O, or S) and breakage of the Si-H bond is observed. As the reaction proceeds, the H-X bond is broken and the H₂ molecule is formed. The high energy barriers on the H-Si(111) surface are due to the important geometrical distortion of the molecules and the surface in the transition state²¹ where the X-Si, H-X, and H-H bonds are enlarged.

The high E_{act} values in Table 1 indicate that the H-Si(111) surface is unreactive toward the studied molecules in the gas phase at room temperature. Assuming a pre exponential factor of $\sim 10^{13}$ in an Arrhenius equation,^{39,40} the half-life for the

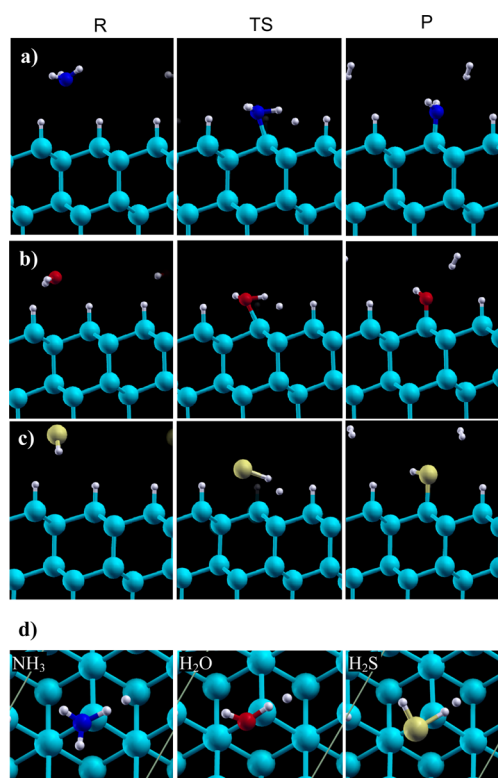


Figure 2. Structure of reactants (R), transition states (TS), and products (P) for the reactions of (a) NH₃, (b) H₂O, and (c) H₂S with the H-Si(111) surface. Calculations performed on the SiH group of a 2 × 2 unit cell.

reaction of NH₃ with the hydrogenated surface is about 500 years. This is in agreement with experimental results reported in the literature which indicate that the reaction of NH₃ and H₂O molecules in the gas phase with H-Si(111) to produce SiNH₂ and SiOH surface groups, respectively, occurs at temperatures higher than 350 °C.^{27,28}

However, the reactivity of the hydrogenated surface with pure methanol in the liquid phase is quite different. Chazalviel and co-workers²⁹ reported that the electrochemical reaction of anhydrous liquid methanol with hydrogenated porous silicon surfaces occurs at room temperature. The hydrogenated surface also reacts with long chain alcohols. The reaction of neat decanol with H-Si(111) was reported to occur at 85 °C.⁴¹ Michalak et al.^{9,31} reported the reaction of neat anhydrous liquid methanol with the H-Si(111) surface as a function of solution temperature and immersion time using Fourier transform infrared spectroscopy (FTIR). At 65 °C, the reaction of H-Si(111) with CH₃OH_(liq) results in partially methoxylated silicon surface with a coverage of approximately 30% of a monolayer. This result indicates that the reaction mechanism in the liquid phase is different. We think that the acid-base properties of methanol may be responsible for the enhanced reactivity. Probably, the reacting species in the liquid phase is the CH₃O⁻ anion, the conjugate base of methanol. However, this is beyond the scope of this paper.

Reactivity of the Cl-Si(111) Surface. Figures 3 and 4 show the energy profiles for the reactions of NH₃, H₂O, H₂S, CH₃NH₂, CH₃OH, and CH₃SH molecules with the Cl-Si(111) surface. All reactions start with the adsorption of each molecule on the chlorinated Si(111) surface and end with the formation of SiNH₂, SiOH, SiSH, SiNHCH₃, SiOCH₃, and

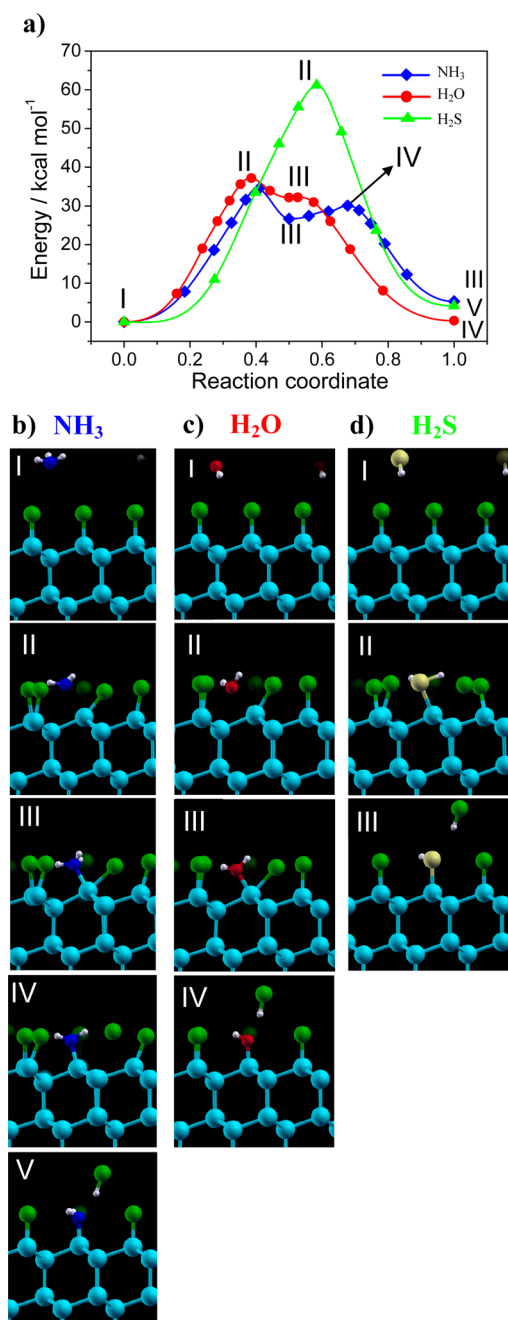


Figure 3. (a) Energy profiles along the reaction coordinate for reactions of NH₃, H₂O, and H₂S with the Cl–Si(111) surface. The panels show the structure of critical points for the reactions of (b) NH₃, (c) H₂O, and (d) H₂S.

SiSCH₃ surface groups together with a hydrogen chloride molecule interacting with the next nearest surface group through a hydrogen bond. The energy profiles in Figures 3 and 4 indicate that there are different reaction mechanisms for each molecule.

The energy profiles of the reactions of NH₃ (Figure 3a) and CH₃NH₂ (Figure 4a) with Cl–Si(111) show that there are two elementary reaction steps with their corresponding transition states. They are connected by an intermediate in which the silicon atom is pentacoordinated. The same is true for reaction of H₂O with Cl–Si(111) (Figure 3a). For all the other molecules, the mechanism consists of a single step.

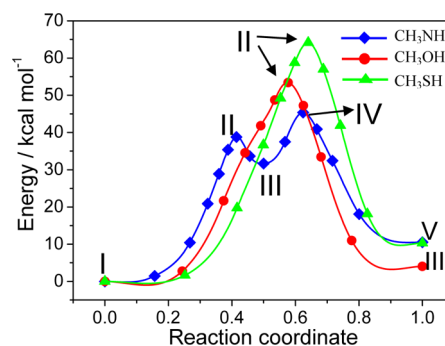


Figure 4. Energy profiles along the reaction coordinate for the reactions of CH₂NH₂, CH₃OH, and CH₃SH with the Cl–Si(111) surface. The structure of the critical points labeled I–V is shown in Figure S2 of the Supporting Information.

Table 2 summarizes the activation energies and energy changes for the reactions of NH₃, H₂O, H₂S, CH₃NH₂,

Table 2. Activation Energy Barriers and ΔE Values (in kcal/mol) of the Reacting Molecules with the Cl–Si(111) Surface^a

molecule	E_{act}	ΔE
NH ₃	34.4	3.4
CH ₃ NH ₂	38.8	13.7
H ₂ O	37.2	0.1
CH ₃ OH	47.2	4.0
H ₂ S	61.2	4.1
CH ₃ SH	64.1	10.3

^aTwo energy barriers and ΔE values are tabulated for NH₃, CH₃NH₂, and H₂O because they have a two-step mechanism.

CH₃OH, and CH₃SH molecules with the Cl–Si(111) surface. For those molecules which have a two-step mechanism, both values are given. It is noted that, for the same headgroup, the methylated compounds have slightly higher energy barriers. This is due to the higher steric repulsion between the methyl group and the chlorine atoms of the surfaces. This trend is also observed in the ΔE values. The high activation energy barriers indicate that these molecules are not reactive with the fully chlorinated surface at room temperature.

Figures 3b,c,d show the corresponding structures of the critical points in the energy profiles for the reactions of NH₃, H₂O, and H₂S molecules, respectively. Figure S1 in the Supporting Information shows the top view of each transition state. The reaction of NH₃ produces a pentacoordinated silicon complex intermediate in the first step in which the silicon atom is bonded to the three silicon atoms of the second layer, to the chlorine atom, and to the ammonia molecule (Figure 3b, panel III). In the second step, the chlorine atom abstracts a hydrogen atom of ammonia producing the HCl molecule which is hydrogen bonded to the surface SiNH₂ group (Figure 3b, panel V).

Figure 3a shows that the reaction mechanism has also two steps for H₂O. In the first step, the formation of the pentacoordinated silicon intermediate is observed (Figure 3c, panel III). In the next step, a hydrogen atom is abstracted by the chlorine atom producing an HCl molecule hydrogen-bonded to the SiOH group (Figure 3c, panel IV).

The energy barriers on the fully chlorinated Si(111) surface are surprisingly higher in comparison to the fully chlorinated

Si(100) surface.²¹ The pentacoordinated silicon structure (Figure 3b, panel III and Figure 3c, panel III) is a dative bonded complex, formed by the interaction of the positively charged silicon atom and the lone pair of ammonia or water. We found this intermediate in the reaction of ammonia with the Cl–Si(100)– 2×1 surface.²¹ However, the dative bonded complex is more stable on Cl–Si(100)– 2×1 . Its formation has a small energy barrier of 6.4 kcal/mol for ammonia on Cl–Si(100)– 2×1 whereas the barrier on Cl–Si(111) is 34.4 kcal/mol as shown in Figure 3a. This shows the high sensitivity of the reaction to steric factors. On the more compact chlorinated 111 surface, the penetration of the reacting molecule to reach the silicon atom is more difficult and it produces an important surface relaxation, as can be observed in the structure of transition states in Figures 3b–d. In turn, the voluminous S headgroup of H₂S has the highest energy barrier.

These results therefore indicate that the fully chlorinated Si(111) surface is essentially unreactive when exposed to an atmosphere of NH₃, H₂O, or H₂S. This is in agreement with experimental observations of Rivillon et al. who studied the hydroxylation of Cl–Si(111) by water vapor exposure as a function of substrate temperature using in situ infrared absorption spectroscopy. They observed that the surface is unreactive when exposed to water atmospheres at temperatures between 100 and 300 °C.²⁴ This is also consistent with a study using high resolution electron energy loss spectroscopy showing that, at room temperature, the fully chlorinated Si(111) surface is stable to water vapor exposure.¹⁵

The energy profiles along the reaction coordinate in Figure 4 show that for CH₃OH and CH₃SH the reaction mechanism has only one step, whereas the reaction of CH₃NH₂ has two elementary steps mediated by the formation of a pentacoordinated silicon intermediate. Side and top views of the structures of the molecules for the critical points of the energy profiles are shown in Figures S2 and S3 of the Supporting Information, respectively.

The increasing energy barriers with molecular size observed in Table 2 are due to the surface relaxation required to reach the transition state. From an energetic point of view, steric effects can be quantified from the energy difference ΔE_{surf} required to distort the fully chlorinated surface to the surface structure of the transition state. ΔE_{surf} is thus calculated as follows: we take the structure of the transition state, we remove the atoms of the adsorbate, we perform a single point energy calculation, and we subtract from this value the equilibrium energy of the fully chlorinated surface which is the reference.

We investigated the correlation of ΔE_{surf} with different geometrical parameters and we found that the surface relaxation mainly depends on the tilt angle of the Si–Cl bond of SiCl groups surrounding the reacting SiCl group, as shown in the inset of Figure 5. As the reaction proceeds, the leaving chlorine atom of the reacting SiCl group interacts with the surrounding SiCl groups inducing a tilt of their Si–Cl bonds with respect to the surface normal.

Figure 5 shows the correlation of ΔE_{surf} with the average tilt angle of the Si–Cl bonds surrounding the reacting SiCl group. The trend in ΔE_{surf} values can be divided into two different behaviors: for NH₃, CH₃NH₂, and H₂O, ΔE_{surf} values range between 27 and 35 kcal/mol. On the other hand, for CH₃OH, H₂S, and CH₃SH, ΔE_{surf} values increase nearly twice as much, between 65 and 75 kcal/mol. Steric effects are predominant for the S containing molecules. For the same headgroup (H₂O vs CH₃OH and NH₃ vs CH₃NH₂) the trend in activation energy

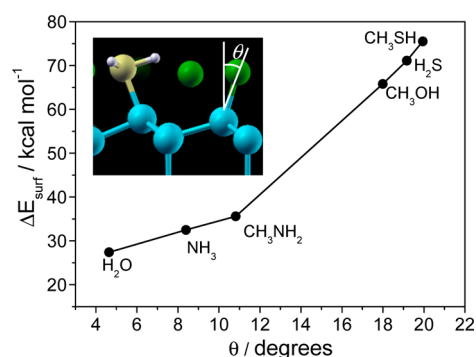


Figure 5. Surface relaxation for the structure of transition states as a function of the average tilt angle of the Si–Cl bond of SiCl groups surrounded the reacting SiCl group. The tilt angle is defined with respect to the surface normal. The inset shows an example of the structure of the transition state in the reaction of H₂S.

barriers (Table 2) also correlates with the molecular size. However, in the comparison of H₂O vs NH₃ and CH₃OH and CH₃NH₂ (which have similar sizes) the relevant parameter is the nucleophilicity of the molecule. The most basic molecules are better nucleophiles. Thus, NH₃ and CH₃NH₂ are better nucleophiles than H₂O and CH₃OH, respectively. Therefore, NH₃ has a lower barrier than H₂O, and CH₃NH₂ has a lower barrier than CH₃OH.

The most voluminous molecules have the highest activation energy barriers due to the higher repulsion of the leaving chlorine atom with the surrounding SiCl groups (see inset of Figure 5). As a consequence, one way to reduce the steric contribution to activation energy barriers is to reduce the surface coverage of chlorine atoms. In the next section we consider the reactivity of partially chlorinated Si(111) surfaces in the context of selective surface functionalization.

Reactivity of the Cl/H–Si(111) Surface. The partially chlorinated surface is experimentally obtained upon exposition of the H–Si(111) surface to a mixture of N₂/Cl₂ for only three minutes.¹⁸ We will consider the reactivity of adjacent SiH and SiCl groups.

As the CI-NEB calculations are very time-consuming, the reactivity on the partially chlorinated surface was studied on a model surface with a 50% coverage SiH surface groups and 50% of SiCl surface groups using the (2 × 2) unit cell. However, in the case of the NH₃ adsorbate, we also performed calculations with a (3 × 3) unit cell in order to evaluate the influence of the surface coverage. We considered the reaction of NH₃ with a SiCl group to yield the pentacoordinated silicon intermediate (Si₃)Si(Cl)(NH₃), which is the rate limiting step as we saw in the previous section. Figure 6a shows the energy profiles along the reaction paths and Figures 6b–d show the ammonia molecule adsorbed on the different surface patterns yielding coverages of 33%, 66%, and 88%, respectively. The corresponding energy barriers are 15.6, 15.1, and 16.8 kcal/mol, respectively. For a chlorine coverage of 50% we obtained a barrier of 13.5 kcal/mol on the (2 × 2) unit cell. On the fully chlorinated surface, the energy barrier is 34 kcal/mol irrespective of the unit cell. Therefore, except for the 100% surface coverage, the energy barriers are not very sensitive to the surface coverage.

In the case of the 50% surface coverage of chlorine atoms (for which the energy barrier is 13.5 kcal/mol), the half-life of the reaction of NH₃ with the SiCl group is 1 × 10⁻³ seconds at 25 °C. This value is to be compared with the half-life of 500 years obtained above for the reaction of NH₃ with the fully

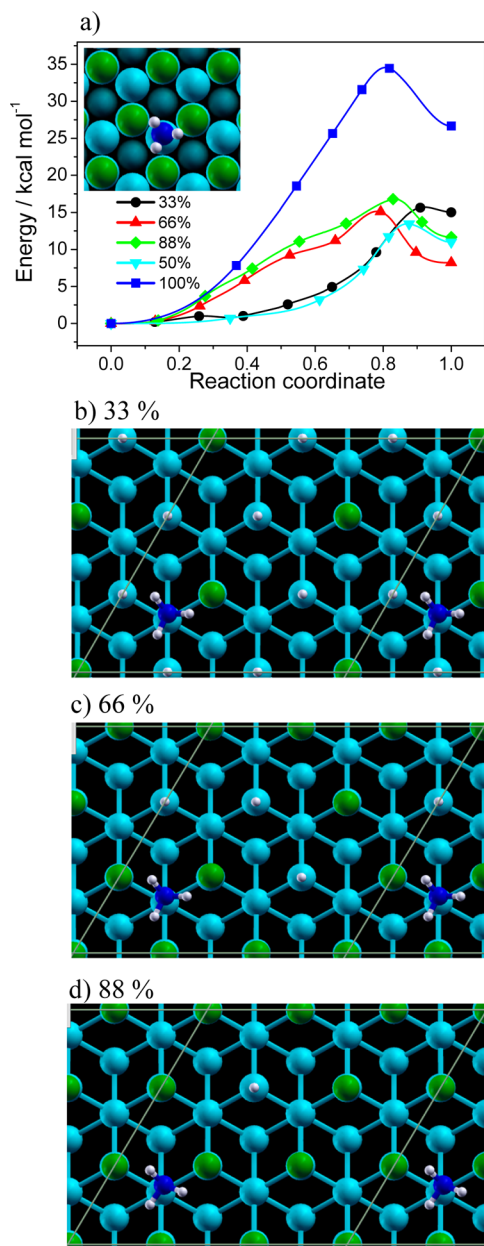


Figure 6. (a) Energy profiles along the reaction coordinate for the reaction of NH_3 to yield the pentacoordinated silicon intermediate calculated on a (2×2) unit cell (50% and 100% coverages) and a (3×3) unit cell (33%, 66%, and 88% coverages). The inset shows a top view of NH_3 adsorbed on the fully chlorinated surface. Structure of the initial adsorbed molecule on the (3×3) unit cell for chlorine coverages of (b) 33%, (c) 66%, and (d) 88%.

hydrogenated surface. These results show that the SiCl groups of the partially chlorinated surface readily react at room temperature.

Table 3 shows the energy barriers and energy changes for the reaction of NH_3 , CH_3NH_2 , H_2O , CH_3OH , H_2S , and CH_3SH molecules with the adjacent SiH and SiCl surface groups. While the values of E_{act} for the reactions on the SiH group are similar to those on the fully hydrogenated surface (Table 1), the corresponding energy barriers on the SiCl group are much lower than on the fully chlorinated surface (Table 2). This indicates that, whereas the reactivity of the SiH surface group is not affected by the presence of neighboring SiCl groups, the

Table 3. Activation Energy Barriers and ΔE Values (in kcal/mol) of the Reacting Molecules with the Adjacent SiH and SiCl Groups of a Surface with a 50% Coverage of Cl Atoms

molecule	SiH		SiCl	
	E_{act}	ΔE	E_{act}	ΔE
NH_3	34.3	-0.4	13.5	5.0
CH_3NH_2	35.3	-0.3	15.1	4.7
H_2O	32.7	-6.7	20.2	1.2
CH_3OH	37.9	-7.4	24.9	5.0
H_2S	42.4	-5.5	32.7	3.8
CH_3SH	41.8	-4.5	33.6	5.7

reactivity of a SiCl surface group is highly altered when there are surrounding SiH groups due to the decrease of repulsive steric interactions.

Table 3 shows that the energy barriers for ammonia, methylamine, and water are such that the reaction can occur almost at room temperature on the SiCl group.

Figure 7a shows the energy profile when NH_3 , H_2O , and H_2S molecules react with the SiCl surface group. The corresponding structures for reactants, intermediates, transition states, and products are shown in Figures 7b,c,d, respectively. As in the case of the fully chlorinated surface, the reaction of ammonia has two steps. The pentacoordinated intermediate is first formed (Figure 7b panel III) with $E_{\text{act}} = 13.5$ kcal/mol and $\Delta E = 10.9$ kcal/mol. These values are 20 and 15 kcal/mol lower than on the fully chlorinated surface. The next step consists in a breakage of the Si-Cl and N-H bonds and the formation of HCl and SiNH_2 surface group (Figure 7b panel IV). This step proceeds with virtually no energy barrier (0.1 kcal/mol) and is exothermic with $\Delta E = -5.9$ kcal/mol. The overall ΔE for the reaction is 5.0 kcal/mol. The reactions of H_2O and H_2S with the SiCl group have only one step. The E_{act} values are 20.2 and 32.7 kcal/mol, respectively, and the ΔE values are 1.2 and 3.8 kcal/mol.

Figure 8 shows the energy profile for the reactions of CH_3NH_2 , CH_3OH , and CH_3SH with the SiCl surface group. The structure of the critical points labeled I-V is shown in Figure S4 of the Supporting Information. Like ammonia, the methylamine molecule reacts in two steps. First, the pentacoordinated intermediate is formed with $E_{\text{act}} = 15.1$ kcal/mol and $\Delta E = 11.6$ kcal/mol. In the second step, the formation of HCl in gas phase and SiN(H)CH_3 surface group is observed with an energy barrier and energy change of 0.9 kcal/mol and -6.9 kcal/mol. On the other hand, CH_3OH reacts in only one step. The reaction of methanol produces a SiOCH_3 surface group with activation energy of 24.9 kcal/mol and an energy change of 5.0 kcal/mol. In the reaction of CH_3SH we found a new equilibrium structure for the adsorbed molecule (local minimum at a reaction coordinate of 0.45 in Figure 8) and next the transition state is observed with $E_{\text{act}} = 33.6$ kcal/mol and an overall ΔE value of 5.7 kcal/mol. No pentacoordinate silicon intermediate was found for CH_3SH and CH_3OH . As with NH_3 , H_2O , and H_2S molecules, the methylated compounds have a lower energy barrier when compared to the fully hydrogenated and chlorinated silicon surfaces.

In order to evaluate the influence of steric effects in the activation energy barriers for the reactions on the SiCl group, we calculated ΔE_{surf} for the transition states. Figure 9 compares ΔE_{surf} values for the different reacting molecules for both the fully and the partially chlorinated surfaces. It can be observed

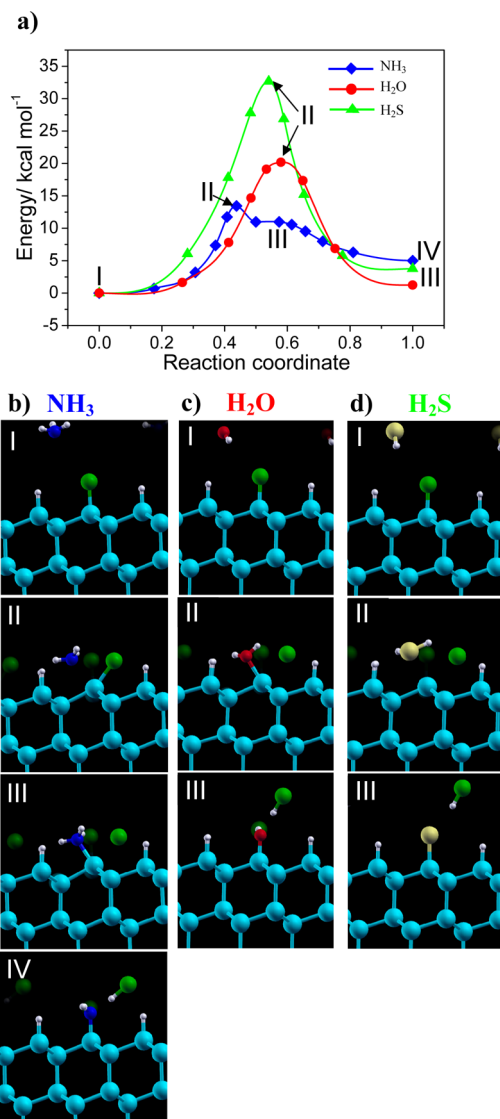


Figure 7. (a) Energy profiles along the reaction coordinate for the reactions of NH_3 , H_2O , and H_2S with a SiCl group on a surface with a 50% coverage of SiH and SiCl groups. The panels show the structure of critical points for the reactions of (b) NH_3 , (c) H_2O , and (d) H_2S with the SiCl group. The calculations were performed using a 2×2 unit cell having two SiCl groups and two SiH groups.

that, on the partially chlorinated surface, the surface relaxation is lower than on the fully chlorinated surface which correlates with trend in activation energy barriers.

In the case of water, the opposite trend is observed. The reaction of water has different mechanisms on the fully and partially chlorinated surfaces. For the 100% chlorine coverage, the reaction has two steps (Figure 3a) and the rate limiting step corresponds to the formation of a pentacoordinated silicon intermediate (Figure 3c, panel III). In the transition state for this elementary step the Si–Cl bond length is 2.15 Å. On the other hand, at 50% chlorine coverage the reaction has only one elementary step and the Si–Cl distance in the transition state structure is 2.46 Å. Therefore, in the latter case, the surface is more relaxed and consequently has a larger relaxation energy in comparison. In its equilibrium state, the Si–Cl bond length of the fully chlorinated surface is 2.10 Å.

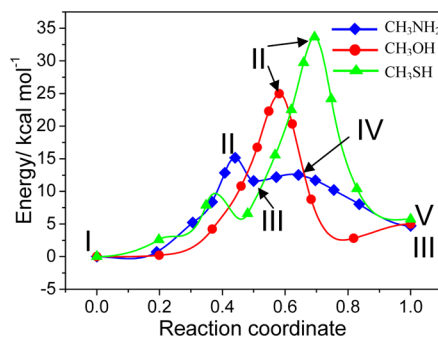


Figure 8. Energy profiles along the reaction coordinate for the reactions of CH_3NH_2 , CH_3OH , and CH_3SH with a SiCl group on a surface with a 50% coverage of SiH and SiCl groups. The structure of the critical points labeled I–V is shown in Figure S4 the Supporting Information. The calculations were performed using a 2×2 unit cell having two SiCl groups and two SiH groups.

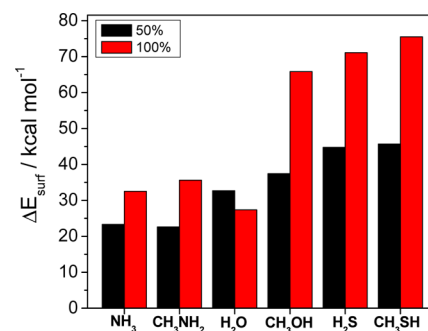


Figure 9. Surface relaxation of transition state structures in the reaction of the different molecules with a SiCl group of chlorinated surfaces with a chlorine coverage of 100% (red bars) and 50% (black bars).

We note that the contribution of steric effects to activation energy barriers can only be taken into account by using an extended model of the surface. Cluster models fail to describe the repulsion between chlorine atoms under high coverage conditions during the course of the reactions. For example, in the reaction of ammonia with a $\text{Si}_{17}\text{H}_{24}$ cluster model of the Si(111) surface having two SiCl surface groups, an activation energy barrier of 14.4 kcal/mol was reported for the formation of a SiNH_2 surface group.²³ This value is very close to the barrier of 13.5 kcal/mol that we obtained for the partially chlorinated surface (Table 3) but it is far from the barrier of 34.4 kcal/mol of the fully chlorinated surface (Table 2).

For partially chlorinated surfaces, the values of E_{act} show minor variations with the surface coverage. For example, in the case of a 25% chlorine coverage (where every SiCl group is surrounded by six SiH groups), the energy barriers for the reactions of CH_3OH , H_2S , and CH_3SH with the SiCl group are 25.0, 32.7, and 33.6 kcal/mol, respectively, which are very close to the values determined for a 50% surface coverage as shown in Table 3. Therefore, the role of unreactive SiH groups is to reduce steric effects, thus facilitating the reacting molecules to reach the silicon atom of the SiCl group. This implies that if full chlorination of the starting hydrogenated surface is not achieved, chemical reactions will begin on SiCl groups surrounding SiH groups and the surface functionalization will proceed with the formation of surface patches. This has been indeed observed by Eves et al.¹⁵ upon exposure of a chlorinated surface to lab air, where the oxidation was observed to proceed

rather slowly and in a patch-like fashion with substantial chlorine still present after >10 h exposure.

Reactivity of Step Edges of the Cl–Si(111) Surface.

With the aim of identifying structures which may lead to a selective functionalization process, we investigated the reactivity of SiCl groups in the step edge of a fully chlorinated surface. As reactions have less steric constraints along step edges, a higher reactivity is expected. For this purpose we used the NH₃ molecule as a probe. The step edge structure of the Cl–Si(111) surface is characterized by the presence of a stacking fault along the $[11\bar{2}]$ direction.³⁶

Figure 10 shows the energy profile along the reaction coordinate. The inset in Figure 10 labeled R shows the

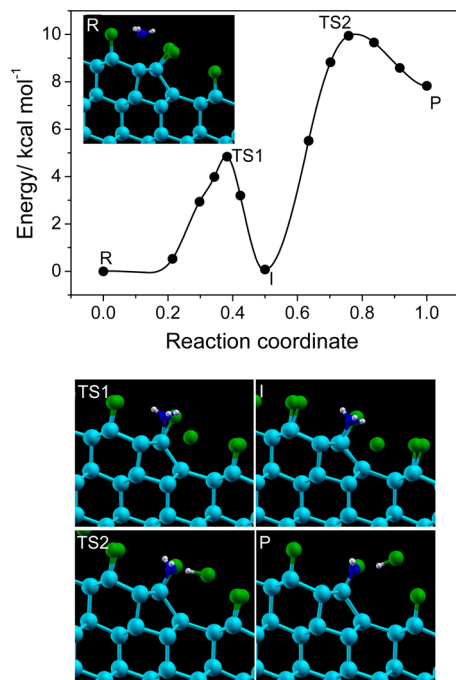


Figure 10. Energy profile along the reaction coordinate for the reaction of NH₃ with the SiCl group of a reconstructed step edge of the fully chlorinated surface. The panels show the structure of the critical points of reactants (R), transition states (TS), intermediate (I), and products (P). The calculations were performed using a 2×2 unit cell of the Cl–Si(133) surface.

equilibrium structure of the reactants: an adsorbed ammonia molecule on the reconstructed step edge. The panels labeled TS, I, and P show the structures of transition states, one intermediate, and products. The top views for these structures are shown in Figure S5 in the Supporting Information. The energy profile in Figure 10 indicates that the chlorinated step edge has a much higher reactivity than that of the fully chlorinated surface (see Table 2). In the first step, an ammonium chloride moiety is formed which is as stable as the adsorbed ammonia molecule. The energy barrier of this process is 4.8 kcal/mol and has $\Delta E = 0.072$ kcal/mol. As shown in the panel labeled I, the chloride anion is located within the step edge region. This structure resembles the reaction of ammonia through the dimers row of the Cl–Si(100)– 2×1 surface where an ammonium chloride intermediate is also formed with the chloride anion trapped within the interdimer row region.²¹ In the second elementary reaction step, the chloride anion leaves the step edge region abstracting a H atom

and forming the HCl molecule. This step has a barrier of 9.9 kcal/mol with $\Delta E = 7.76$ kcal/mol.

In summary, the overall energy barrier for the reaction of ammonia with a SiCl group of a step edge is 9.9 kcal/mol, whereas the same reaction with a SiCl group on the terrace of a fully chlorinated surface has a large energy barrier of 34.4 kcal/mol (Table 2). When the surface is partially chlorinated, the barrier decreases to 13.5 kcal/mol (Table 3). Therefore, SiCl groups at step edges are even more reactive than those on terraces at low coverages.

Selective Functionalization of the Si(111) Surface.

The concept of selective functionalization is related to the need to control the surface plane spatially in the functionalization process. While there are applications that require full coverage of the surface with organic monolayers, other applications need the control over the surface density of reactive sites.

As the reactivity of SiH and SiCl groups is very different, surfaces with a partial coverage of chlorine atoms may allow a selective functionalization of the surface by a chemistry route. Therefore, by controlling the initial chlorine surface coverage during the chlorination procedure, the surface density of molecules grafted to the silicon surface could be controlled as well.

From our results, we can predict some phenomena that have not been studied experimentally as yet. Table 3 shows a significant difference between the reactivities of adjacent SiH and SiCl surface groups. For example, for NH₃ and H₂O molecules, E_{act} values for the reaction with the SiCl group are 13.5 and 20.2 kcal/mol, respectively, whereas reactions with the SiH group have E_{act} values of 34.3 and 32.7 kcal/mol. As a consequence, part of the surface may be functionalized through Si–N or Si–O at almost room temperature.

Chabal and co-workers⁹ reported a novel method to produce a Si(111) surface with 30% of coverage of SiOH surface group without subsurface oxidation. The method has three steps: the H–Si(111) surface is initially uniformly patterned with methoxy groups with a coverage of 30%. This surface is immersed in an HF solution resulting in a partially covered F–Si(111) surface. Finally, the 30% SiOH termination can be achieved by immersion of the F–Si(111) surface in water. We calculated the reaction pathway for the reaction of H₂O with a SiF surface group on a surface with 25% of coverage of SiF and we obtained an energy barrier of 21.2 kcal/mol with $\Delta E = 2.0$ kcal/mol. This value is very close to the barrier of 20.2 kcal/mol obtained for the reaction of H₂O with a SiCl group in a partially chlorinated surface (Table 3), indicating that the SiCl group has similar reactivity to the SiF group toward water. This implies that the formation of SiOH groups could be accomplished in only two steps: first, the hydrogenated Si(111) surfaces can be partially chlorinated¹⁸ and, afterward, the resulting surface can be reacted with water to produce a partial coverage of silanol groups on the reactive SiCl sites. The same procedure could be used to obtain a surface with partial coverage of SiNH₂ and SiN(H)CH₃ surface groups. In the case of reactions involving the S headgroup, Table 3 shows that the higher energy barriers will require higher temperatures.

Fully chlorinated vicinal silicon surfaces seem to offer an opportunity to build molecular lines along the highly reactive step edges. We envisage a two step procedure in which the step edges are first functionalized via the formation of Si–N or Si–O bonds and then the Cl–Si(111) terraces are passivated via the formation of Si–C bonds by reaction with alkyl Grignards.¹⁶

In summary, the concept of selective functionalization relies upon the presence of reactive SiCl groups embedded in a matrix of unreactive SiH groups. It is the local surface structure around a SiCl group that is important. Once steric factors around a SiCl group are liberated by the appearance of adjacent SiH groups, the reactivity of SiCl greatly increases and the reactivity of SiH remains unaltered.

CONCLUSIONS

The reactivity of hydrogenated, chlorinated, and partially chlorinated Si(111) surfaces toward NH₃, H₂O, H₂S, CH₃NH₂, CH₃OH, and CH₃SH molecules was investigated using DFT and CI-NEB calculations, to identify elementary reaction steps and their corresponding energy barriers.

The reactions of NH₃, H₂O, H₂S, CH₃NH₂, CH₃OH, and CH₃SH molecules with H–Si(111) have large energy barriers in the range 33–42 kcal/mol (Table 1 and Table 3). For all molecules the reaction mechanism has only one step. The E_{act} values show that the hydrogenated Si(111) surface is unreactive with these molecules at room temperature. This result is in agreement with experimental observations that indicate that NH₃ and H₂O do not react with H–Si(111) surface above 350 °C.^{27,28}

The fully chlorinated surface is not reactive with the studied molecules showing larger energy barriers in the range 34–64 kcal/mol (Table 2). The reactions of NH₃, CH₃NH₂, and H₂O have two steps. The formation of the pentacoordinated silicon intermediate involves an important surface relaxation which is responsible for the high energy barriers. The energy barrier of 37.2 kcal/mol for H₂O explains the experimental observation that indicates that the chlorinated surface is unreactive in an atmosphere of water in the temperature range of 100–300 °C.²⁴ The reactions of CH₃OH, H₂S, and CH₃SH have only one step and show the highest energy barriers. Concerning the headgroup, the order of reactivity is N > O > S. This trend shows that while molecular size is important, nucleophilicity also plays a key role.

The high sensitivity of the reactivity of chlorinated surfaces to steric factors could be used for the design of selectively functionalized surfaces. One approach is to reduce the surface density of chlorine atoms by partial chlorination of the starting hydrogenated surface. Another approach is to take advantage of low steric factors at step edges which make them highly reactive. The energy barriers of the NH₃ probe molecule clearly illustrates the sensitivity of the reactions to the different surface features: 34.4 kcal/mol on the fully chlorinated surface, 13.5 kcal/mol on the partially chlorinated surface, and 9.9 on the step edges of a chlorinated vicinal surface.

ASSOCIATED CONTENT

Supporting Information

Additional figures as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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