QM/QM Study of the Coverage Effects on the Adsorption of Amino-Cyclopentene at the Si(100) Surface

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Received 12 December 2005; Revised 20 February 2006; Accepted 21 February 2006
DOI 10.1002/jcc.20513
Published online 18 September 2006 in Wiley InterScience (www.interscience.wiley.com).

Abstract: In this work, we have tested 30 different adsorption situations in several coverage scenarios for the 1-amino-3-cyclopentene (ACP) molecule on the Si(100) surface. We have used a five-spot testing zone inserted in the high-level part of a quantum-mechanical/quantum-mechanical study performed in a big cluster. By defining several different scenarios, each one with a typical adsorption energy, we were able to understand in detail the process of surface functionalization. We are able to justify why the functionalization of this silicon surface achieves only a coverage of ~0.5ML (half monolayer) and why the completely covered surface should be thermodynamically impossible to obtain.


Key words: Si(100); ACP; adsorption; coverage

Introduction

Theoretical adsorption studies are often performed and adsorption energies are calculated with no account for the coverage effects that may happen at the surface. Single molecule adsorption on a clean surface does not include the fact that real adsorption processes must be affected by the presence of other already adsorbed molecules. The interactions between the latter can lead to the formation of defects and disorganization and prevent complete coverage of the surface. Obviously, it would be better to be able to create perfect monolayers with no defects.1–3 Therefore, it is of utmost importance to study and define what is happening at the molecular level at the surface, when we are adsorbing many molecules with a view to form monolayers.

Trying to understand the processes involved in the monolayer formation with computational studies is difficult to accomplish mainly because of limitations in the size of cluster that we can build while still getting accurate energies for the adsorption processes. Large systems can be studied with molecular mechanics,4,5 but adsorption energies obtained from those calculations are not appropriate because of the oversimplification of the system and disregard of the explicit electronic parts. Medium-sized systems can be represented with semiempirical calculations6–9 but even in this case the associated energy errors are too large for the study of most of the molecular adsorption processes. Only relatively heavy DFT10–15 or higher level calculations16,17 can give results accurate enough for most purposes. However, in these cases the systems’ sizes are usually too small to correctly represent a surface area big enough to perform different adsorption situations on already occupied surfaces. Periodic system calculations18 could be of some help here but since they are basically ab initio calculations, the periodic cells cannot once again be very large because of CPU time restrictions. Additionally, if we are studying a single defect on a surface that same defect will be repeated at a cell’s length from it in all directions with possible consequences in the results. In this work, we try to circumvent these problems by using the hybrid quantum-mechanical/quantum-mechanical (QM/QM) ONIOM methodology.19–21 In this way, we can concentrate the computationally heavier calculations in the most important parts of the system, i.e. where the adsorption occurs, while still representing a sufficiently large surface area with a lower level and less computationally intensive method. We have previously used this methodology to simply represent the clean silicon(100) surface, as a first test and
Coverage Effects on the Adsorption of Amino-Cyclopentene at the Si(100) Surface

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Abstract: In this work, we study the coverage effects that influence the adsorption of amino-cyclopentene on the Si(100) surface. In a previous study, we have confirmed that the amino-cyclopentene can bind to the surface through the amino group of the adsorbed amino-cyclopentene (ACP) molecule and using sulfo-succinimidyl 4- (N-maleimidomethyl) cyclohexane-1-carboxylate to link the free amino group of the adsorbed ACP to the Si(100) surface. From an experimental point of view, the perfectly covered surface, with no defects, would allow for a better reproducibility of the results and a better protection against small molecules like oxygen and water that are known to oxidize the Si(100) surface.

Results and Discussion

Contrary to previous work where we only found one C-adsorbed ACP conformation, we have obtained two different conformations that are relatively similar in terms of energy. Figure 3 shows a clear example of this situation where we can observe that the central molecule can have the amino group closer (top) or farther (bottom) from the surface. These conformations differ by 2 kcal mol\(^{-1}\) and were spotted in several situations throughout our calculations, depending on the starting point geometry. The bottom structure with the amino group farther from the surface was consistently the most stable as well as the one that we had found previously. However, in another article using a different methodology,
though it is not very clear from the images, it seems that the top structure was found as the most stable. For consistency of the results, we decided to use only the bottom, most stable, conformation in all the calculations.

Table 1 shows the results obtained for the adsorption of one ACP molecule on the empty silicon surface followed by the data that concerns the adsorption of the ACP on a three-spot hole on the Si surface. What we can conclude from this information is that the three central positions of the testing zone are basically equivalent and that the adsorption energy in this situation is of around \(-39\) kcal mol\(^{-1}\). In our previous work, with a smaller cluster and without any other ACP molecules adsorbed in the lateral rows, we have achieved a \(-40\) kcal mol\(^{-1}\) for the adsorption energy of a single ACP molecule also using the SHC* basis set. The difference between these results is within the error inherent to the calculations, and this means that there is not a measurable interference between ACP molecules adsorbed right next to each other in parallel rows. More importantly, we can observe from the last three results that even if we have only one hole left on each side of the adsorbed molecule the adsorption energy is basically the same as for the completely clean surface.

This points to the fact that adsorption of ACP molecules on a Si(100) surface can reach a 0.5ML coverage with no observed interference between adsorbed molecules. Obviously, the dynamics of the process might be affected but we are not dealing with that in this specific work. What we know is that adsorbing a molecule in a completely clean surface or in a near half coverage one should have, ideally, the same adsorption energies. This is also in agreement with previous theoretical works where it was found that the 0.5ML coverage results were very similar to the adsorption of a single ACP molecule on a clean surface.

Table 2 shows the results obtained for the adsorption of one ACP molecule between previously adsorbed molecules and one or two empty spaces. The first thing that we can observe is that the first two results differ from all the other similar combinations by \(-9\) kcal mol\(^{-1}\). To understand this, we must recall that our cluster has seven dimers per row and so when we are adsorbing in the sixth position we only have another low-level ACP molecule at the seventh and last position. This low-level ACP molecule is not fixed and is free to move and this allows it to get farther from the central part and give some extra space for the adsorbing molecule. We can also see that if we are
adsorbing at the fifth position, this effect is almost completely lost and we start getting the typical $-26$ kcal mol$^{-1}$ adsorption energy.

Since the ACP molecules adsorb in a bent conformation (see Fig. 3), we might have expected that adsorption would be different depending on whether the empty space is located on one side or the other of the adsorbing ACP. However, the adsorption energy for these two situations is similar, which shows that there is basically no difference concerning the relative position of the adsorbing molecule and the surface hole. Moreover, the existence of a two spot hole is energetically equivalent to a one spot hole, which is coherent with the results shown in Table 1. Comparing the $-26$ kcal mol$^{-1}$ adsorption energy with the one obtained for the clean surface, we realize that the proximity effect of two ACP molecules at the surface costs roughly $13$ kcal mol$^{-1}$.

Table 3 shows the energies corresponding to the adsorption of one ACP molecule in a one spot hole two positions away from another one spot hole. That is, between the adsorbing molecule and another spot on the surface there is one adsorbed ACP molecule. In this situation, the adsorption energy is only $-13$ kcal mol$^{-1}$, $13$ kcal mol$^{-1}$ higher than the previous situation. This is what we would expect since we are now adsorbing the molecule in a one spot hole with one ACP molecule on each side. Once more, adsorption at the sixth position is roughly $-10$ kcal mol$^{-1}$ lower than all the others, which shows that this effect is basically constant and predictable.

Table 4 shows the last five combinations studied in this work where we tested the adsorption of a molecule in a single spot hole on an otherwise completely occupied surface. This situation provides the last step needed to get a perfect 1ML surface coverage and we can see that this adsorption is barely exothermic, with an energy of only $-5$ kcal mol$^{-1}$. Once more this should be expected since there is very little space to fit one extra ACP molecule in one hole. The repulsions are high, which can be observed from the difference between the $-39$ kcal mol$^{-1}$ for the clean surface adsorption and this one. Even though the full surface coverage might be a thermodynamic possibility, kinetics seem to dictate otherwise. In previous studies, it was found that the C-adsorption of ACP involved the formation of a three-atom transition state$^{23,35}$ that has been well characterized for cyclopentene,$^{10}$ ethylene,$^{36}$ and 1,3-dienes in general.$^{37}$ This structure forces the ACP molecule to lay down relatively close to the surface occupying much more space than it does when completely adsorbed. By taking this mandatory transition step into consideration, we clearly see that adsorption in a single spot hole should be indeed impossible and that even the previous combinations shown in Tables 2 and 3 may be affected by this.

It is interesting to notice that the energy for the first result in Table 4 is quite similar to the results in Table 3 and this is indeed understandable because the two situations are similar. A single ACP molecule is located between the adsorbing molecule and a hole on the surface. In this case, it is not exactly a hole but the end of the cluster, although the effect seems to be basically the same. This helps to predict what can happen with new combinations. For instance, the first two results in Table 2 point
to the fact that the adsorption energy for a combination such as _AA_ should be roughly $-35$ kcal mol$^{-1}$; the first result in Table 3 indicates that the _AAA_ situation should have an adsorption energy of roughly $-23$ kcal mol$^{-1}$.

With all the combinations studied here, we now have a proper description of most possible scenarios for the C-adsorbed trans-ACP molecule on the Si(100) surface. The most important conclusion is that it is impossible to obtain a 1ML ACP covered Si(100) surface. Indeed, STM images already showed that the typical cyclopentene functionalized Si(100) surface is mostly filled with molecules at a distance that is around double the distance seen between the silicon dimers.$^{32,33}$ We clearly see that forming the 0.5ML surface seems straightforward and that each molecule adsorbs as if the surface was completely clean. However, over 0.5ML, the situation gets more complicated due to the molecules proximity and the adsorption energies become less favorable. Moreover, steric hindrance avoiding the formation of interaction method can be used to successfully study surface coverage. Because of its size, the ACP molecule can be easily adsorbed without a significant perturbation until a 0.5ML surface coverage is achieved. However, there are significant repulsive interactions when the molecules come too close together on higher surface densities. In fact, when adsorbing one ACP molecule in a single-spot hole on an otherwise completely covered surface, we get adsorption energies approximate to zero. Moreover, due to the difficulty to achieve the typical transition state involved in the $[2 + 2]$ cycloaddition reaction, coverages over 0.5ML should be very difficult to get.

Finally, we have shown the suitability of hybrid QM/QM calculations used on large clusters. The energies seem reliable and most of the time concur with experimental works and much heavier calculation studies.

### Acknowledgment

H. R. R. S. gratefully acknowledges access to the Centres de Computació i Comunicacions de Catalunya (CEPBA-CESCA).

### References