

Unusual Two-Stage Kinetics of Ethylene Adsorption on Si(100) Unraveled by Surface Optical Spectroscopy and Monte Carlo Simulation

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The adsorption of ethylene on a Si(100)- 2×1 surface in an ultrahigh vacuum has been monitored at room temperature by use of real-time surface differential reflectance spectroscopy, which clearly demonstrated that the adsorption follows a two-stage process. About half a monolayer is obtained for 1 L, while the second stage is much slower, yielding the complete monolayer for an exposure of ~ 400 L. The kinetics over the full range has been successfully reproduced by a Monte Carlo calculation. The key point of this two-stage adsorption kinetic lies in the reduced adsorption probability (by a factor of several hundreds) on the Si dimers, neighbors of dimers which have already reacted, with respect to the adsorption probability on isolated dimers. This new kind of adsorption kinetics, due to a repulsion between already adsorbed molecules and additional molecules impinging on the surface, makes it a textbook case for a “cooperative” adsorption process.

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Catalysis, sensors, gas separation or sequestration, crystal or thin film growth, make the adsorption phenomenon of great scientific interest with a wide range of industrial applications: effluent decontamination, biological process, medical-device, or electronic-device manufacturing. Kinetic studies are of practical interest to determine the residence time required for completion of the adsorption reaction but they are also helpful to explore fundamental adsorption mechanisms. We report here an unexpected two step adsorption process observed during adsorption of ethylene on Si(100)-(2×1) under vacuum. Whatever the adsorbate on adsorbent systems (metallic-ion-surfactant-organic compound adsorbed on metal-semiconductor-insulator surfaces), multistep adsorption processes commonly occur in four situations: (i) adsorption on a heterogeneous surface [1–4] (several kinds of adsorption sites), (ii) reorganization of the submonolayer [5], (iii) multilayer formation [6], or (iv) diffusion of adsorbate across liquid to surface [3] (in the case of the liquid-solid interface). However, none of these situations applies to ethylene/Si(100)-(2×1). Indeed, in the framework of the Si(100)-(2×1) surface modification by organic compounds [7–10], numerous investigations stated that there is only one type of adsorption site, which is the silicon dimer where ethylene bonds in a “di- σ ” on-top configuration [11–25] [a very small minority (6%) is also linked to two Si atoms of adjacent dimers along a dimer row [19]]. Such configuration is preserved all along the adsorption process as we showed recently by optical studies [16], and eventually leads to full saturation obtained for 1 monolayer (1 ML), corresponding to one ethylene molecule for one Si dimer. The presently observed two-step kinetics appears therefore in contradiction with this single mode of adsorption. Actually, some authors have previously shown

that the sticking coefficient for ethylene on Si(100) decreases for coverages larger than about 0.5 ML [20,21,25]: Rochet *et al.* [20] showed that, at room temperature (RT), 0.5 ML is obtained with 0.3 L (1 L equals 10^{-6} Torr · sec), while 1000 L is needed for reaching the 1 ML saturation. Recently, the adsorption dynamics was investigated at different temperatures and the kinetics could be reproduced for temperatures above 25 K by using a model including a precursor state [26–28], but only until a half ML [14]. Nevertheless, the complete kinetics of adsorption was not obtained in these studies.

In this Letter, we present for the first time the full range of detailed kinetics of RT ethylene adsorption on Si(100), studied by optical surface differential reflectance spectroscopy (SDRS), which shows a fast adsorption stage until an intermediate saturation coverage of 0.45 ML, immediately followed by a much slower stage until the complete ML. We further show that the usual kinetics models, like the simple Langmuir model frequently observed for nondissociative adsorption on a surface [28], or the more advanced Kisliuk model, which takes into account the presence of a precursor state on the surface [26–28], fail to reproduce this two-stage kinetics. In contrast, we could reproduce it very well by a Monte Carlo (MC) approach including desorption and diffusion of a precursor state, and we demonstrated that the key point is the dramatic change of the adsorption probability on Si dimers, as a function of their immediate environment. Such analysis is supported by previous STM results [21] suggesting repulsive interactions between adsorbed molecules: at 0.5 monolayer (ML) ethylene is preferentially adsorbed alternately on one Si dimer out of two along every dimer row, as sketched in Fig. 1(c). This clear two-stage process in the

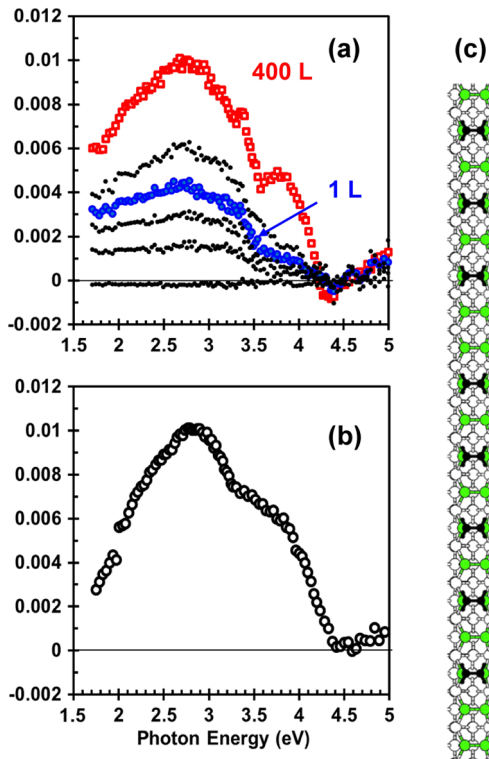


FIG. 1 (color online). (a): SDR spectra for 1 ML of ethylene (empty red squares obtained with 400 L), 0.45 ML corresponding to the scheme (c) (full blue circles, 1 L) and intermediate coverages. (b) SDR spectrum after saturation with atomic hydrogen, leading to a monohydride Si(100)- 2×1 : H surface (from Ref. [37]). (c) Scheme of a dimer row at 0.45 ML coverage.

ethylene/Si(100)-(2×1) adsorption kinetics makes it a model case for what could be called a cooperative adsorption process.

SDRS is a real-time surface-sensitive optical method, which is efficient for determining kinetics of adsorption or formation of layers [29–32], as the signal is in first approximation proportional to the amount of adsorbates [33–35]. Experimental details are given in the Supplemental Material [36]. Figure 1(a) shows SDR spectra obtained for different amounts of ethylene adsorbed at RT up to saturation of 1 ML obtained for 400 L. Their shapes are very similar to the one obtained for the 2×1 monohydride Si(100) surface, completely saturated by atomic hydrogen [Fig. 1(b)]. The monohydride surface maintains its 2×1 reconstruction with unbroken Si dimers, each surface Si atom being bound to one H atom [37]. The corresponding spectrum displays a dominant single feature, which is the optical fingerprint of adsorption on intact Si dimers. A very different two-peak spectrum (not shown) is obtained when the dimers are broken and all surface Si atoms saturated with two H (dihydride). The spectra for hydrogen have been reproduced recently by *ab initio* calculations [38]: their features originate from the modification of the optical transitions of the Si(100) surface, induced by the adsorption.

The similarity of the monohydride spectrum and of the ethylene-covered surface ones confirms that the Si dimers remain intact upon adsorption of ethylene. Moreover, the intensity of the SDR signal is proportional to the number of dangling bonds involved in the adsorption and, therefore, to the number of adsorbed molecules [37]. In other words, SDRS gives the amount of adsorbed molecules and provides a determination of the kinetics of adsorption. Figure 1 shows that the intensities of the monohydride and ethylene-saturated spectra are identical: the coverage is the same in both cases; i.e., the surface is saturated with ethylene (1 ML) for 400 L exposure. Similarly, the 1 L spectrum corresponds to 0.45 ± 0.02 ML coverage.

The coverage vs dose, real-time measured during exposure to ethylene, is drawn in Fig. 2. High (a) and low (b) doses are shown, together with a semilogarithmic representation (c). A two-step kinetics is clearly seen, with a fast initial stage leading to about 0.45 ML coverage obtained after 1 L [Figs. 2(b) and 2(c)], and a second much slower stage which eventually leads to saturation at 1 ML [Figs. 2(a) and 2(c)]. This unusual behavior explains why the issue of ethylene saturation on Si(100) has been a long-time debate. This two-stage kinetics cannot be explained

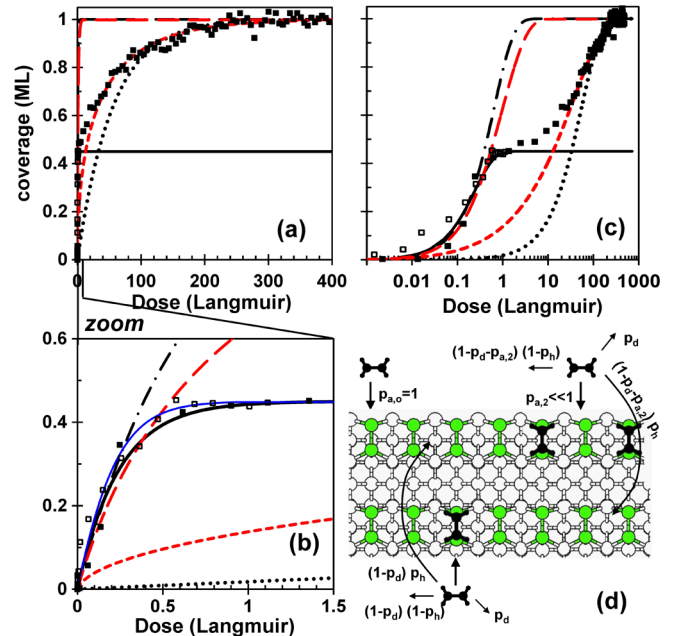


FIG. 2 (color online). Ethylene coverage as a function of exposure for large (a) and small (b) exposures; (c) is a semi-logarithmic representation. Empty and filled black squares, experimental points from two sets of experiments. Thick black continuous line, Langmuir kinetics for $\theta_{\text{sat}} = 0.45$ ML; black dotted and black dot-dashed lines are Langmuir kinetics for $\theta_{\text{sat}} = 1$ ML; thin blue continuous line is the Kisliuk model for $\theta_{\text{sat}} = 0.45$ ML and $K = 0.7$; red short-dashed curve is the Kisliuk model for $\theta_{\text{sat}} = 1$ ML and $K = 95$, red long-dashed curve is the Kisliuk model for $\theta_{\text{sat}} = 1$ ML and $K = 2.2$. (d) Scheme of precursors, with probabilities of adsorption, diffusion, hopping, and desorption.

by a simple process of adsorption. The sticking probability $s(\theta)$ of an impinging molecule to be finally chemisorbed [39] is proportional to the slope of the curve giving the coverage θ as a function of the dose D [28,40]. From Fig. 2(b), one can understand that this slope decreases progressively from a maximal value at the beginning of the adsorption to a value very close to zero when θ reaches about 0.45 ML. The first stage appears at first sight similar to the Langmuir kinetics [28], for which $s(\theta)$ follows a linear decrease given by $s(\theta) = s_0(1 - \theta/\theta_{\text{sat}})$, where θ_{sat} is the coverage at intermediate saturation, i.e., $\theta_{\text{sat}} = 0.45$ ML (Fig. 3). It leads to an exponential law given by $\theta(D) = \theta_{\text{sat}}(1 - e^{-s_0 D/\delta})$, where δ is a constant. This kinetics is drawn in a thick continuous black line in Fig. 2. As expected, it reproduces correctly the first part of the kinetics until about 0.45 ML, but not the second part, where the experimental coverage progressively reaches 1 ML. This intermediate saturation $\theta_{\text{sat}} = 0.45$ ML, smaller than the ideal coverage of 0.5 ML for molecules adsorbed on one dimer out of two [21], is explained by the statistical distribution of the adsorbed molecules, with some couples of unoccupied dimers at intermediate coverages [Fig. 1(c)]. A Monte Carlo (MC) calculation for one infinite dimer row, where adsorption on a given dimer is ruled out if one of its two close neighbors has previously reacted, yields $\theta_{\text{sat}} = 0.432 \pm 0.001$ ML. For the vicinal samples used here, with limited dimer rows of 8 or 9 dimers, it gives $\theta_{\text{sat}} = 0.467 \pm 0.001$ ML. These values are in good agreement with the experimental result of 0.45 ML. Now, if we use the actual final saturation, i.e., $\theta_{\text{sat}} = 1$ ML, in Eqs. (1) and (2), the Langmuir model cannot reproduce the whole kinetics, but only the very initial kinetics (black dot-dashed curve in Fig. 2) or the very final one (black dotted curve). The previous results show that the Langmuir model fails to describe the full adsorption kinetics whatever the parameters.

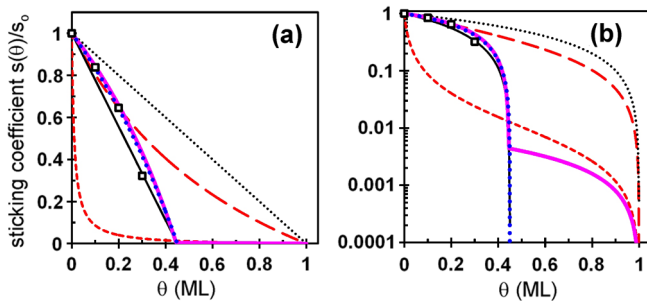


FIG. 3 (color online). Sticking coefficient as a function of coverage in linear (a) and logarithmic (b) representations. Black squares show experimental results from Ref. [14] at 317 K. Black dotted and thin continuous curves [linear in (a)] are Langmuir results for $\theta_{\text{sat}} = 1$ and 0.45 ML, respectively. Blue dotted curve is the Kisliuk model for $\theta_{\text{sat}} = 0.45$ ML, with $K = 0.7$. Red long-dashed and short-dashed curves show the Kisliuk model for $\theta_{\text{sat}} = 1$ ML, with $K = 2.2$ and 95, respectively. Purple thick continuous curve is the Monte Carlo result.

Following Ref. [14], the more realistic adsorption mechanism developed by Kisliuk [26,28] can be used, starting from a physisorbed precursor which can adsorb into the chemisorbed state, desorb from, or diffuse along the surface with different probabilities. Formulas are given in the Supplemental Material [36]. Fixing $\theta_{\text{sat}} = 0.45$ ML, the calculation permits us to reproduce the experimental data slightly better than the Langmuir one [thin continuous blue line in Fig. 2(b)]. This agrees with Ref. [14] where the first part of kinetics at RT was reproduced by Kisliuk model. The corresponding sticking coefficient is drawn in Fig. 3 in the blue dotted line, and agrees actually with data from Ref. [14]. However, in this article the second stage of adsorption was not obtained, as their experiment was not sensitive for $s(\theta) < 0.02$. In our case, we checked that the use of the Kisliuk approach with $\theta_{\text{sat}} = 1$ ML gives also better results than the Langmuir model, for the initial or for the final kinetics (long and short red-dashed curves in Fig. 2), but not simultaneously for both. The corresponding variations of $s(\theta)$ are also drawn in Fig. 3.

Rather than the previous analytical models, which cannot reproduce the two-step kinetics, a two-dimensional MC approach allows us to take into account different surroundings of the adsorption sites, which are expected to influence the adsorption probability. The observation that, at coverage of 0.45 ML, one out of two neighbor dimers is bound to ethylene permits us to set up the rules for the MC model over the whole coverage range. Following the Kisliuk approach, we consider the existence of a physisorbed precursor state above a dimer, which can convert into the chemisorbed state if the dimer is unoccupied, desorb back to the gas, diffuse along the dimer row or hop to a neighbor row. For a precursor above an “isolated” empty dimer (i.e., whose both neighbor dimers are empty), the conversion probability $p_{a,0}$ is taken equal to 1, and the desorption and diffusion probabilities are zero. Above an empty dimer with one or two occupied neighbors (named single or double hampered dimer in the following), the probabilities of conversion are $p_{a,1} < 1$ and $p_{a,2} < 1$, the probability of desorption is p_d , the probability of diffusion along the dimer row toward next site is $(1-p_{a,1}-p_d)(1-p_h)$, the probability of hopping to one of the next rows is $(1-p_{a,1}-p_d)p_h$. For a precursor above an occupied dimer, the probability of desorption and the one of diffusion or hopping are p_d' and $1-p_d'$, respectively. We assume in the following that p_d' is equal to p_d . These processes are schematized in Fig. 2(d). The influence of the various parameters is discussed in detail in the Supplemental Material [36]. Briefly, it is shown that considering hopping between rows (two-dimensional MC) or only diffusion along a dimer row (one-dimensional MC) almost does not change the results, and in the following p_h will be taken equal to 0.5. The study above suggests that the two-stage kinetics with an intermediate saturation at 0.45 ML requires that the $p_{a,1}$ and $p_{a,2}$ are $\ll 1$. Consequently, in

the first stage ($\theta < 0.45$ ML) with $p_{a,o} = 1$, the kinetics initial shape is essentially set by the rate of desorption, i.e., by p_d , with no influence of $p_{a,1}$ and $p_{a,2}$. The best result is obtained for $p_d = 0.3 \pm 0.1$, as drawn in the inset of Fig. 4(a) by the continuous purple line. Results for p_d equal to 0.1 and 0.8 are also shown, giving faster or slower adsorptions, respectively. Using $p_d = 0.3$, we can now determine the conversion probabilities $p_{a,1}$ and $p_{a,2}$. Very small values are required in order to get good agreement with experiment, and the best one is obtained for $p_{a,2} = 0.0022 \pm 0.0002$ and $p_{a,1} \approx 2 \cdot p_{a,2}$ (purple continuous line in Fig. 4). A smaller (larger) value of $p_{a,2}$ leads to a slower (faster) kinetics, as it is shown by green curves in Fig. 4. Some latitude is possible for $p_{a,1}$, which is expected to be equal or larger than $p_{a,2}$, and the kinetics is correctly reproduced for values of $p_{a,1}$ ranging between $p_{a,2}$ and $3p_{a,2}$. This shows that the conversion probability is about 200 to 500 times smaller on “hampered” Si dimers than on isolated dimers ($p_{a,o} = 1$). Interestingly, very recent *ab initio* calculations have shown that in a similar system, ethylene on Ge(100)-(2 × 1), the conversion probability is decreased by a factor of 10 (200) on single (double) hampered dimer [41]. This in line with our experimental data, although the difference between the two kinds of hampered dimers is not as large for Si as the one calculated for Ge. The sticking coefficient $s(\theta)$ corresponding to our results is drawn by the purple continuous line in Fig. 3, and compared with the ones of the Langmuir and Kisliuk models. It follows a law close to the Kisliuk one (calculated for $\theta_{\text{sat}} = 0.45$ ML) until intermediate coverage, and follows a second similar law, but strongly reduced, for the second stage.

The previous MC analysis gives a complete phenomenological explanation of the observed two-stage kinetics. It is remarkable that, in this approach, the intermediate

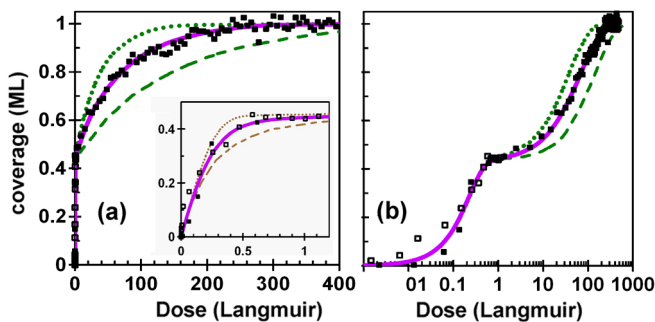


FIG. 4 (color online). Experimental coverage vs ethylene dose and Monte Carlo calculations in linear (a) and logarithmic (b) representations. Purple continuous line is best fitting with $p_d = 0.3$, $p_{a,2} = 0.0022$, and $p_{a,1} = 2 \cdot p_{a,2}$. Green dotted and dashed lines: $p_d = 0.3$, with $p_{a,2} = 0.005$ and $p_{a,2} = 0.001$, respectively (with $p_{a,1} = 2 \cdot p_{a,2}$). Inset of (a) shows initial adsorption, brown dotted and dashed lines are $p_d = 0.1$ and $p_d = 0.8$, respectively, and the values of $p_{a,1}$ and $p_{a,2} \ll 1$ are of little importance.

saturation at 0.45 ML is not an additional parameter, but is directly obtained from the calculation. This behavior cannot be explained by energetics at room temperature: the ethylene adsorption is highly exothermic whatever the coverage, and the difference between the adsorption energies at 0.5 and 1 ML is small, ranging between 0.03 and 0.08 eV as a function of the authors [16,42,43]. Consequently, the strong decrease of the sticking coefficient is likely due to kinetics effects. Different reaction pathways have been proposed for the adsorption of ethylene into the di- σ configuration on the Si dimers [15,42–46]. The asymmetric and the concerted [2 + 2] addition pathway have obtained most attention. Each involves a specific intermediate precursor which is weakly bonded to the surface and has to overcome an energy barrier to reach the same final chemisorbed state. Using the nudged elastic band method, the calculation of a minimum energy reaction path indicates that both the adsorption energy of the intermediate and the energy barrier evolve with coverage. For instance, in the concerted addition, the energy barrier to the final product is equal to 0.1 eV at low coverage but is equal to 0.46 eV at 0.5 ML. One can expect that this pathway, possible at low coverage, becomes forbidden at 0.5 ML, which should decrease the sticking coefficient. NEXAFS measurements suggest that additional reaction pathways could also be considered [17]. The coexistence of physisorbed and chemisorbed molecular species was indeed observed at 90 K, and the molecular plane of the physisorbed species was found to be perpendicular to the surface. As far as we know, such a physisorbed species has not been identified yet by theoretical calculations: the intermediates for the asymmetric and concerted [2 + 2] reactions present actually their molecular plane rather parallel to the surface plane. The issue of the role played by this species in the adsorption kinetics of ethylene on a hampered dimer is therefore open. More generally, the determination of the trapping probabilities for the incident molecules to physisorb into the possible intermediate precursors [39] appears to be crucial, and could depend on the different precursor states and on the coverage. To our knowledge, such an issue has not been quantitatively investigated so far. More theoretical analysis would therefore be needed to quantitatively understand at the molecular level the observed dramatic decrease of the sticking coefficient.

In conclusion, we could reproduce very well the experimental unusual two-stage kinetics for ethylene adsorption on Si(100) by means of a two-dimensional MC approach, showing that the adsorption probability onto a Si dimer drops dramatically, as a function of the very local environment of the dimer. Although out of the scope of this paper, it should be emphasized that numerical simulation could provide further insight into the elementary processes in play in this cooperative adsorption. Eventually, after the kinetics of the ethylene/Si(100)-2 × 1 adsorption process appears to be unraveled by this study, bare- and half-

covered surfaces provide two extreme model cases with strongly different sticking coefficients in order to test theoretical methods for evaluating kinetic constants of adsorption, which is still an elusive issue. Finally, the two-stage adsorption kinetics observed in the present case, unraveled by a Monte Carlo approach, appears as a textbook case which could possibly apply to other adsorption systems.

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