Ethylene on Si(100)2x1: unusual two-stage adsorption kinetics

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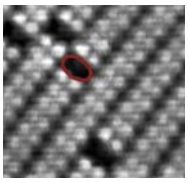
Presentation

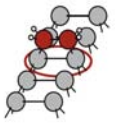
➔ **At room temperature, ethylene adsorbs in di-σ configuration**

➔ **Intermediate saturation for 0.45 ML**

➔ **Large sticking coefficient for initial coverage.**

➔ **Very small sticking coefficient for larger coverages, until full saturation (1 ML : 1 molecule per Si dimer).**

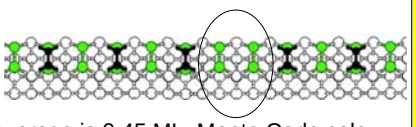




Mette et al, Chem. Phys Lett 483, 209 (2009)

We used real-time SDRS for monitoring the kinetics. The observed two-stage kinetics is very well reproduced by a Monte-Carlo approach.

Monte Carlo approach



At intermediate coverage, one dimer out of two is bound to ethylene. The ideal coverage should be 0.5 ML. The actual coverage is 0.45 ML. Monte Carlo calculation gives 0.432 ML for a nominal surface, 0.467 ML for a vicinal one.

An impinging molecule can:

1) on an isolated molecule, adsorb with probability $p_{a,0}=1$

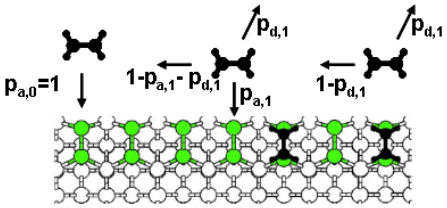
2) on an non-isolated molecule,

. adsorb with probability $p_{a,1}=1$

. desorb back to gas with prob. $p_{d,1}$

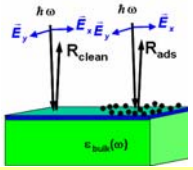
. diffuse along the dimer row $(1-p_{a,1} - p_{d,1})$

3) on an occupied dimer: desorb $(p_{d,1})$ or diffuse $(1-p_{d,1})$



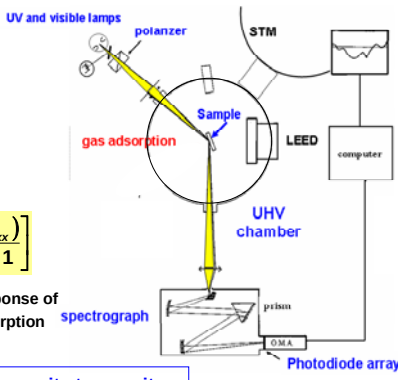
Surface Differential Reflectance Spectroscopy

Modification of the surface upon adsorption



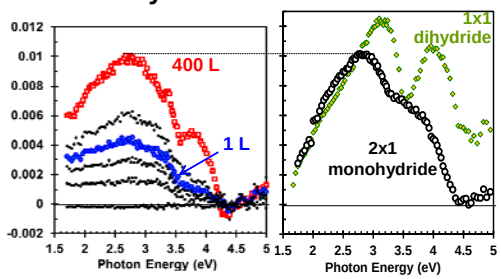
$$\frac{\Delta R}{R} = \frac{R_{clean} - R_{ads}}{R} = 4\frac{\omega}{c} Im\left[\frac{\delta(\Delta\varepsilon_{xx})}{\varepsilon_{bulk}-1}\right]$$

$\delta(\Delta\varepsilon_{xx})$ = change of the optical response of the surface due to the adsorption



~ 1 sec / spectrum : permits to monitor adsorption and to determine kinetics

Borensztein et al, PRL 95, 117402 (2005)



Same shape and entensity for C_2H_4 and 2x1monohydride:

- Dimers remain intact upon adsorption of C_2H_4 .

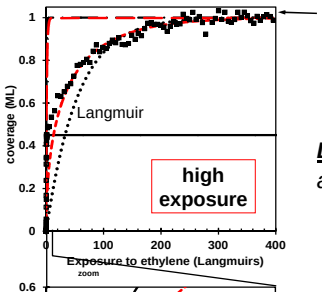
- Full saturation

SDR spectra for ethylene and for atomic hydrogene. The monohydride Si(100)2x1:H surface has intact Si dimers.

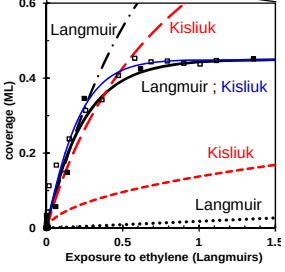
Analytical approaches: Langmuir or Kisliuk

Both approaches for non-dissociative adsorption, either direct (Langmuir) or with desorption+diffusion of a precursor (Kisliuk), lead to one stage kinetics and do not reproduce experiments

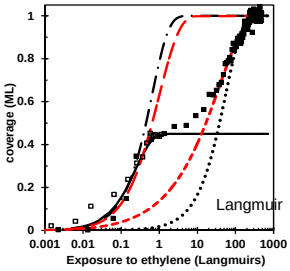
Kinetic results: experiment vs. calculation



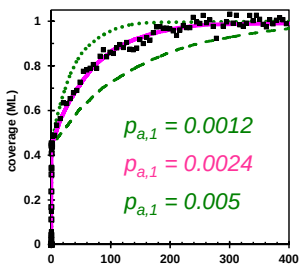
Langmuir *and* ***Kisliuk*** *approaches fail*



initial exposure



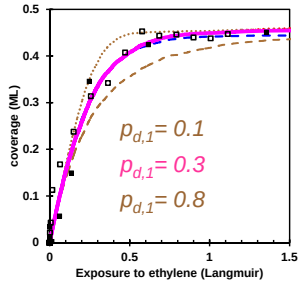
Log. representation

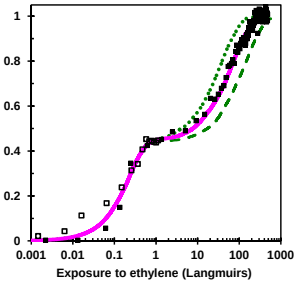


The ***Monte Carlo*** *approach gives a very good agreement for all exposures, with:*

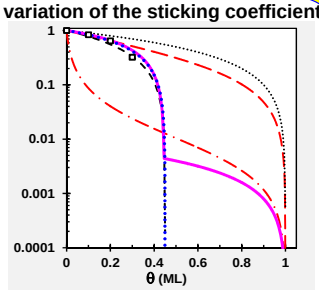
$p_{a,1}$ = 0.0024 ; $p_{d,1}$= 0.3

The sticking coefficient is reduced by a factor of 400 for non-isolated dimers.





variation of the sticking coefficient



Conclusion

The keypoint of the two-stage kinetics is a strong decrease of the adsorption probability on dimers beside an already reacted dimer. This could be due to steric hindrance and/or repulsion between already adsorbed ethylene and incoming molecules.

R. Coustel, Y. Borensztein, N. Witkowski, O. Pluchery Phys. Rev. Lett. 111, 096103 (2013)