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Desorption of benzene from Pd (111): a simulation study

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Abstract. We describe a simulation study of benzene desorption from Pd (111).

Considerable effort has been dedicated in the last decade to understanding the elementary steps involved in the production of C_6H_6 from C_2H_2 on Pd (111) [1–3]. This process exhibits a number of interesting features, among them the presence of two benzene adsorbed species: a tilted species and flat species. One of the elementary steps of the process, i.e. C_6H_6 desorption from the Pd (111) surface, is in itself a puzzling problem since it has been difficult to reproduce thermal desorption spectra for such a surface covered by pure benzene.

Recently [4], what seems to be a promising model for benzene desorption from Pd (111), based on the effect of appreciable repulsive lateral interactions, has been simulated and tested against experimental desorption spectra with encouraging results.

In this work a more detailed simulation is performed, which shows why LEED patterns corresponding to benzene ordered structures, produced by those repulsive lateral interactions, are not observed.

The adsorption–desorption process of benzene on Pd (111) is simulated on a hexagonal lattice. It has been supposed that the adsorption site for C_6H_6 is a symmetric site [5], with the C_6 ring adsorbed on a hexagon of the lattice. The initial configuration has been simulated, trying to locate the rings on the surface in such a way that the benzene cannot be adsorbed on another benzene. This means that the C_6H_6 can perform small migrations on the surface until it finds a free place to adsorb in a flat position; these migrations are allowed through the thermal energy of the molecule. It is also allowed for a molecule that is trying to adsorb to produce small movements of its nearest neighbours in order to obtain enough room to adsorb in a flat position. In these conditions the maximum coverage of flat-lying molecules is 0.12 molecules per Pd atom. Figure 1 represents a snapshot of this situation. The adsorbed layer has small ordered patches that are not large enough to produce LEED patterns, confirming experimental findings [5].

The desorption process has been simulated using a Hamiltonian $H(i, j) = H_0 S(i, j) + \sum_{\mathrm{nn}} E_{\mathrm{int}} S(i, j) S_{\mathrm{nn}}$ where H_0 is the adsorption site energy, E_{int} is the NN interaction energy, $S(i, j)$ is 0 if the site is empty and 1 if it is occupied, S_{nn} is the occupation matrix for the nearest neighbours, and the sum is over all the nearest neighbours.

The reaction $C_6H_6 \rightarrow 6C+3H_2$ has been simulated with a reaction probability calculated from an activation energy E_r. This means that the benzene molecule can desorb or react with the following probabilities: $P_{\mathrm{des}} = \nu_d \exp(H/RT)\mathrm{d}t$ and $P_{\mathrm{reac}} = \nu_r \exp(E_r/RT)\mathrm{d}t$.

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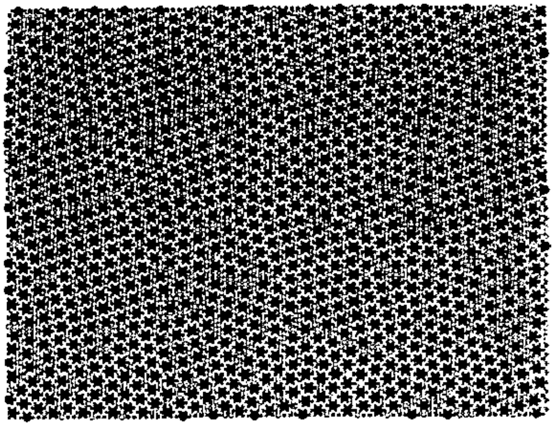

Figure 1. Snapshot of the Pd(111) surface at the maximum coverage 0.12 benzene molecules per Pd atom.

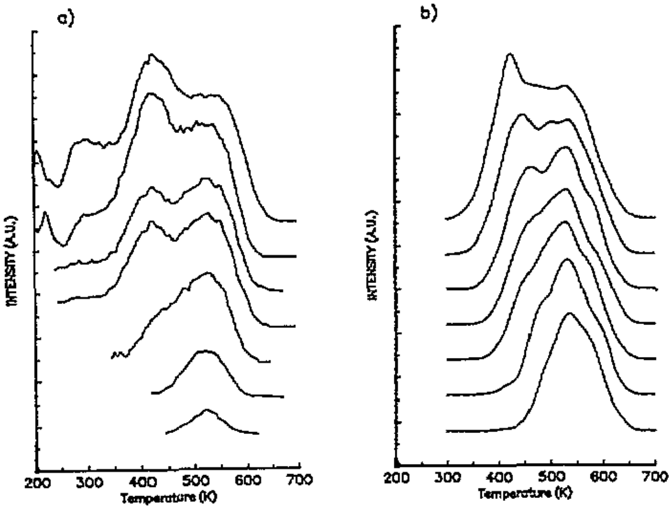

Figure 2. TDS for benzene on Pd(111) at different initial coverages. (*a*) Experiment: the first peak at low temperatures and higher coverages corresponds to tilted-molecules desorption. (*b*) Simulated spectra for the following values of the parameters: $H_0 = 28.7\,\mathrm{kcal\,mol^{-1}}$, $\nu_d = 10^9\,\mathrm{s^{-1}}$, $E_r = 23.3\,\mathrm{kcal\,mol^{-1}}$, $\nu_r = 10^8\,\mathrm{s^{-1}}$, $H_{int} = -1.9\,\mathrm{kcal\,mol^{-1}}$.

Both probabilities are tested against a random number uniformly distributed between 0 and 1.

During the simulation the molecules are able to move from the original site to a neighbouring site; this is done to keep the system close enough to thermodynamic equilibrium. These movements are selected with a probability $P_{\mathrm{jump}} = \exp(\Delta H/RT)$ where ΔH is the difference in energy between the initial and final states.

With this method thermal desorption spectra have been simulated and good agreement with experimental data [4] obtained (figure 2).

References

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