

Computer modeling of dissociative gas adsorption on laser-roughened surfaces

Paweł Szabelski^{a,*}, Tomasz Pańczyk^b

^aDepartment of Theoretical Chemistry, Maria Curie-Skłodowska University, pl. M.C. Skłodowskiej 3, 20-031 Lublin, Poland

^bGroup for Theoretical Problems of Adsorption, Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Kraków, Poland

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Abstract

A simple computer model of dissociative adsorption of diatomic molecules on a solid surface with laser-induced defects was proposed. The defects (ablation craters) were assumed to have either cubicoid or pyramidal shape, depending on the approximation level. Special attention was paid to the influence of a degree of structural disorder on the adsorptive properties of the surface. In particular, both equilibrium adsorption isotherms and temperature programmed desorption (TPD) spectra of non-interacting diatomic molecules from the surfaces subjected to a different number of laser pulses were simulated. The observed changes in the adsorptive properties of the surface were explained using simple geometric arguments linking the adsorption probability for a single molecule with the topography of the surface. For example, it was demonstrated that, for a sufficiently large number of laser pulses (N), the adsorption probability scales with $1/\sqrt{N}$, regardless of the assumed crater shape. The obtained results also indicate that, in general, the surface roughness greatly affects the TPD spectra while it has minor influence on the shape of the adsorption isotherms.

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1. Introduction

Vast majority of gases used in chemical synthesis occurs in a diatomic (O_2 , H_2 , N_2) or a poly-atomic (H_2O , SO_2 , NH_3 , CH_3OH , hydrocarbons) form. Obviously, to react usually a single diatomic molecule must dissociate and next form new bonds with different atoms or functional groups. The effectiveness of this process can be substantially improved by the application of a solid catalyst on whose surface the reacting species adsorb (concentrate) and dissociate. When chemical composition and structure of the catalyst are properly chosen the rates of the two contributing processes mentioned above can be greatly increased or decreased if desired. In consequence, the net reaction rate can be controlled by chemical as well as by structural modification of the external surface of the catalyst grain. In the latter case,

of a particular importance are random defects as well as ordered nanostructures including terraces, steps or kinks on metallic crystals. These structural imperfections can occur naturally but they can be also introduced on purpose using different techniques such as, for example, laser ablation [1–4].

In practice, laser-induced rising of surface defects on solid surfaces involves a sequence of laser pulses focused on selected points on the surface. In this process a laser beam produces local surface damage whose range is dependent on the applied laser intensity as well as on the beam geometry [1,5,6]. Obviously, the disordered area created by a single laser pulse is not limited to the cross-section area of the laser beam and frequently it extends far beyond [1]. Therefore, the overlapping of laser spots can occur even when a laser beam is focused in turn on two points that are theoretically far enough to prevent the overlapping. This effect can make it difficult to interpret experimental results linking for example a number of laser pulses with disordered area and thus to predict structural and adsorptive properties of the surface.

* Corresponding author. Tel.: +48 81 537 5518; fax: +48 81 537 5685.

E-mail address: szabla@vega.umcs.lublin.pl (P. Szabelski).

Apart from direct experimental measurements, adsorptive properties of the resulting laser-damaged surfaces can be also estimated by computer simulations. In the previous works [7–9] we simulated the adsorption of monomolecular adsorbates on a surface with defects generated by laser pulses of a random spatial distribution. The obtained results suggest that the roughening of the surface which is induced by the laser ablation can substantially increase the adsorption energy of a single molecule and thus enhance the adsorption process. However, in the case of dissociative adsorption the influence of surface roughness can have much more complex nature. This is mainly because of the assumption of two adjacent adsorption sites placed at the same level which are required for a successful adsorption/dissociation event. In this context, even subtle changes in the surface structure which are induced by laser irradiation can lead to profound changes in the adsorption probability. The main objective of the present study is to describe formation of this structure as well as to examine the influence of the surface roughness on the adsorption of probe diatomic molecules.

2. Theory

The spatial/temporal development of laser-induced defects is modeled on a square $L \times L$ lattice of discrete sites. The position of each site is described by the coordinates x and y while its depth by $s(x, y)$. Periodic boundary conditions in both directions are applied to minimize edge effects. At the beginning of the simulation the surface is assumed to be perfectly flat. That is, $s = 0$ for all the sites. In the next step, the surface is subjected to N randomly distributed “laser pulses”. During each pulse the laser beam produces a square spot of side d which delimits external perimeter of the crater. At the same time the depth of each site within the spot is increased by $h_s(r)$ where r is the distance between the site and the symmetry axis of the crater (in maximum metrics). During the simulation the depth of each lattice site is appropriately updated such that the following condition is fulfilled:

$$s_{N+1}(x, y) = s_N(x, y) + h_s(r) \tag{1}$$

where the lower indices refer to the surface after $N + 1$ and N pulses, respectively.

In this study we consider two crater shapes which differ in the approximation level of real crater geometry. Namely, as the first approximation we assume that the crater has a cubicoïd shape (C), that is during the ablation the depth of each site within the spot is increased by the same $h_s(r) = h$. In the second, more realistic case [10], the pyramidal shape (P) is assumed with an additional condition that the crater radius decreases by one when the crater depth increases by one. This results in a pyramidal crater whose maximum depth, h is equal to $(d + 1)/2$. Fig. 1 shows the assumed shapes of the crater along with the parameters which characterize them.

To link adsorptive and structural properties of the surface we introduce the number of possible contact points, k that a single atom adsorbed on a given site can have with the surface. In practice, the number of contact points is a number of vertical

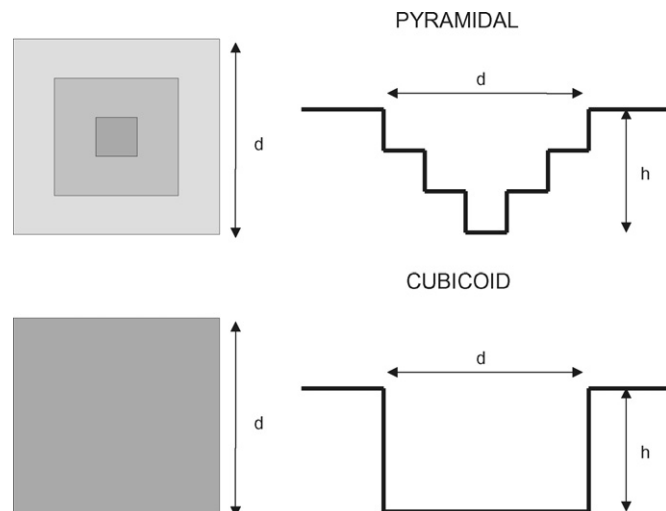


Fig. 1. Crater shapes assumed in the simulation: top view, left part; cross-section, right part. Craters with $d = 5$ and $h = 3$ are shown as an example. Shades of gray in the left part of the figure illustrate adsorption sites placed at different levels.

facets surrounding the site plus the horizontal facet below the adsorbed atom. Fig. 2 shows a fragment of the surface with a few adsorbed atoms having a different number of contact points. With this information provided, the adsorption energy for a single site can be calculated as $\epsilon_a = \epsilon_v + (k - 1)\epsilon_h$, where ϵ_h is the adsorption energy associated with the interaction of the atom with the horizontal facet under it and ϵ_v is the adsorption energy that originates from the interaction between the atom and a single vertical facet next to it. In this study we assumed $\epsilon_v = \epsilon_h = \epsilon$ such that for a single site $\epsilon_a = k\epsilon$.

Adsorption isotherms for laser-treated surfaces were simulated using the standard Grand Canonical Monte Carlo

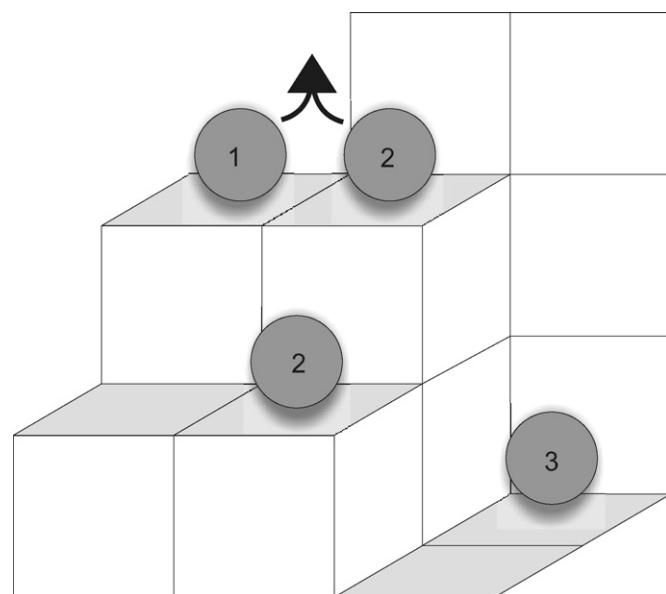


Fig. 2. A fragment of the roughened surface with a few adsorbed atoms having a different number of contact points with the surface (shown in the figure). The arrow indicates those atoms which are allowed to associate and desorb from the surface.

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