Modeling of phase transitions and reaction between coadsorbed oxygen and hydrogen on Pd(111)

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Abstract. We propose kinetic Monte Carlo simulation of O and H co-adsorption experiment on Pd(111). At 200 K we obtain structural phase transition \((2 \times 2)_O \rightarrow (\sqrt{3} \times \sqrt{3})_O\) with increase of H-coverage by considering O-O, H-H and O-H interactions and several kinetical processes. We also demonstrate how reverse phase transition \((\sqrt{3} \times \sqrt{3})_O \rightarrow (2 \times 2)_O\) occurs at \(T = 205\) K due to hydrogen dissolution into the bulk when hydrogen income is terminated. At higher temperature we observe the vanishing of \((2 \times 2)_O\) oxygen islands due to water-formation reaction for different reaction rates and paths.

1. Introduction
Oxygen and hydrogen co-adsorption on transition metal surfaces is intensively studied for almost three last decades due to its important role in heterogeneous catalysis and corrosion. The interest is also stimulated by the structural phase transitions occurring on the surface. Detailed understanding of these phenomena requires accounting for several simultaneously proceeding kinetic processes as well as for interactions between adsorbate and substrate-adsorbate atoms. For example, adsorbed H-atoms can drastically change the structure and properties of oxidized surfaces even in the absence of water-formation reaction. Hydrogen adsorbed on oxidized Pd(111) enhances the diffusion of O-atoms and induces structural phase transition \((2 \times 2)_O \rightarrow (\sqrt{3} \times \sqrt{3})_O\). This phase transition occurs [1, 2] in such a temperature range \((150 - 200\, \text{K})\) in which O-atoms have very low mobility (activation energy for diffusion is \(0.4 - 0.5\, \text{eV}\) [3]) when there are no hydrogen atoms. Above 205 K H and O system transforms back to \((2 \times 2)_O\), if adsorption of additional H-atoms is terminated. Only with further increase of temperature (at \(T \approx 220\, \text{K}\)) ordered oxygen islands shrink in size evidencing water formation due to reaction between co-adsorbed O and H [1]. Here we propose the results obtained by modeling of this experiment. The O–O, H–H and O–H interaction parameters and rates of the processes were chosen to fit the changes of experimentally observed ordered oxygen structures in extremely narrow temperature range \((200 - 220\, \text{K})\).

2. Model and phase transitions
In our kinetic Monte Carlo simulations we use pair algorithm approach [4, 5], since the model contains bimolecular steps, e.g., diffusion and reaction. The main idea of the algorithm is to consider two nearest neighbor (NN) sites simultaneously and account for all possible processes therein. The processes considered in our simulation on a (111) lattice (side length \(L = 48a\), where \(a\) denotes Pd lattice constant) are O and H diffusion via NN fcc adsorption sites, H
Figure 1. Snapshots of our calculations at $T = 200$ K and $c_H = 0.5$ (a) and $c_H = 0.6$ (b). O-atoms are represented by filled and H-atoms - by open circles. Oxygen correlation functions (c) and (d) at the corresponding coverages: black dots represent the CF of the $(\sqrt{3} \times \sqrt{3})_0$ phase, open squares - CF of the $(2 \times 2)_0$ phase.

dissolution to subsurface and segregation back to the surface, and the reaction between O and H (see table 1).

Performing simulation with the initial O-coverage $c_O = 0.2$ and varying H-coverage $c_H$ from 0.4 to 0.7 we obtain $(2 \times 2)_0 \rightarrow (\sqrt{3} \times \sqrt{3})_0$ phase transition (see snapshots and pair correlation functions (CFs) at $T = 200$ K in Fig. 1). CF is defined as $c_{OO}(r)/c_O^2$, where $c_{OO}(r)$ is concentration of O–O pairs at a distance $r$. In the mean-field approximation $c_{OO}(r) = c_O^2$,

| Process | Definition | Formulae | Parameters |
|---------|------------|----------|------------|
| O and H | O + □ → □ + O | $k^X = \frac{2k_B^X \exp(-E^X_k/k_B T)}{1+\exp((E^X_k - E^X_\beta)/k_B T)}$ | $E^X_a = 0.4$ eV, $k^X_0 = 10^{12}$ s$^{-1}$ |
| diffusion | H + □ → □ + H | $X = O, H$ | $E^H_a = 0.1$ eV, $k^H_0 = 10^7$ s$^{-1}$ |
| H to bulk | H$^{surface}$ → H$^{bulk}$ | $k^1 = k^H_0 \exp(-E^H_1/k_B T)$ | $E^H_a = 0.46$ eV, $k^H_0 = 10^{13}$ s$^{-1}$ |
| H to surface | H$^{bulk}$ → H$^{surface}$ | $k^1 = k^H_0 \exp(-E^H_1/k_B T)$ | $E^H_a = 0.22$ eV, $k^H_0 = 10^7$ s$^{-1}$ |
| Reaction | O + H → OH + □ | $k^r = k^r_0 \exp(-E^r_a/k_B T)$ | $E^r_a = 0.35$ eV, $k^r_0 = 10^5$ s$^{-1}$ |

Table 1. Processes and main parameters used in our simulation. $E^X_\beta - E^X_\alpha$ describes energy difference between final $\beta$ and initial $\alpha$ states, where $E^X_\alpha,\beta = \sum_{i=1}^{3} v^X_i n^X_i + v^X_i n^X_i$, $E^H_a = v^H_o n^H_o + v^H_1 n^H_0$ and $n^O_i$ is the number of neighbours in coordination sphere $i$ and □ denotes an empty surface site.
which leads to CF equal to 1. The condition $\text{CF}(r) = 1$ allows us to estimate the oxygen domain radius $r_c$. O and H diffusion rates were taken in the activated form and the set of interaction parameters $v_i$ was chosen as follows: repulsion in the NN distance ($v_1^{O-O} = 160 \text{meV}$, $v_1^{H-H} = 16 \text{meV}$ and $v_1^{O-H} = 80 \text{meV}$), repulsion in the next-NN ($v_2^{O-O} = 16 \text{meV}$) and attraction in the $3^{\text{nd}}$-NN ($v_3^{O-O} = -6.4 \text{meV}$) distance [5]. We obtained H-coverage by directly distributing H-atoms on the surface fcc sites, thus avoiding extra parameters, needed when $c_H$ is obtained varying the ratio of adsorption and desorption rates. Note, that the rates (in activated form) of H dissolution to subsurface $k^\downarrow$ and segregation back to the surface $k^\uparrow$ are chosen to be more or less equal at $T = 200 \text{K}$, giving H-coverages of subsurface and surface 0.34 and 0.26 respectively at total $c_H = 0.6$. When located in subsurface, H-atoms are not assumed to diffuse, but they can segregate back to the surface with probability proportional to the segregation rate.

When the phase $(\sqrt{3} \times \sqrt{3})_O$ is achieved, the uptake of hydrogen is terminated in experiment [1]. Assuming the system with $c_H = 0.6$ (as in Fig. 1b) and increasing temperature, we have found a relative increase of $k^\downarrow$. At 204 K when $k^\downarrow/k^\uparrow = 1.25$, it causes the reverse transition $(\sqrt{3} \times \sqrt{3})_O \rightarrow (2 \times 2)_O$ due to a slight H dissolution to subsurface (see $T$-dependence of surface $c_H$ and behavior of corresponding CFs in Fig. 2).

![Figure 2](image-url)

**Figure 2.** Temperature dependences of (a) surface hydrogen concentration and rates $k^\downarrow$ and $k^\uparrow$ which promote $(\sqrt{3} \times \sqrt{3})_O \rightarrow (2 \times 2)_O$ phase transition at $T = 204 \text{K}$ and (b) CFs: black dots represent CF of the $(\sqrt{3} \times \sqrt{3})_O$ phase, open squares - CF of the $(2 \times 2)_O$ phase. (c) Snapshot and (d) CFs of both oxygen phases vs distance at $T = 204 \text{K}$. Linear size of oxygen domain $r_{(\sqrt{3} \times \sqrt{3})_O} \approx r_{(2 \times 2)_O} \approx L/2$.

3. Reaction

It is claimed in Ref.[1] that $(\sqrt{3} \times \sqrt{3})_O \rightarrow (2 \times 2)_O$ transition is not affected by the water formation reaction which starts to be really important only above 220 K. Therefore we had to choose such reaction rate, $k''$, that the reaction would be negligible at 200 K and it would not destroy the $(\sqrt{3} \times \sqrt{3})_O$ structure. Assuming in the beginning that the reaction proceeds only between surface O and H in the NN sites, we temporarily excluded dissolution and segregation processes and determined the reaction parameters which are presented in Table 1. The obtained $k''$ is for the first reaction step (O+H→OH) which is known [6] to be rate limiting (we assume the infinite rate for the second step of reaction). To compare, the parameter values $E_{a}^r = 0.3 \text{eV}$ and $k_0^r = 8.6 \times 10^6 \text{s}^{-1}$ were estimated from experiment [1]. Thus, in our simulation we had to maintain $k''$ much smaller. In Fig. 3 we show the time dependence of ratio of reacted O
Figure 3. Time dependence of reacted oxygen atoms number for different values of temperature when (a) oxygen reacts only with surface hydrogen and (b) oxygen reacts with both surface and subsurface hydrogen.

atoms number to initial O atoms number at different values of temperature when all processes (including dissolution and segregation) are considered. At $T = 200$ K the reaction does not play important role in oxygen phase formation, but it becomes more important at 210 K and higher temperature. It is also possible to evaluate how the reaction rate increases if surface O atom is allowed to additionally react with subsurface H atom located below it. It is seen from Fig. 3b that accounting for both reaction paths (horizontal and vertical, and using same $k^r$ for both) leads to drastic increase of reacted oxygen number up to $5 \times 10$ times. However such path of reaction would not leave enough hydrogen for direct $(2 \times 2)_O \rightarrow (\sqrt{3} \times \sqrt{3})_O$ phase transition at $T = 200$ K. Therefore we assume that either the reaction proceeds only between surface H and O atoms or the rate of “vertical” reaction path is very small.

4. Conclusions
Our simulation demonstrates that the phase transition $(2 \times 2)_O \rightarrow (\sqrt{3} \times \sqrt{3})_O$ is obtained with increase of H-coverage when repulsive interactions between O–O, O–H and H–H and main kinetic processes (H and O diffusion, O and H reaction, H dissolution to subsurface and segregation back to the surface) are considered. It is actually possible to find the interaction and kinetic parameters which would satisfy (in a very narrow temperature range, $205 - 220$ K): (1) the reverse phase transition due to hydrogen dissolution to the bulk and (2) water formation reaction between oxygen and remaining surface hydrogen. Allowing for the reaction between O and both surface and subsurface hydrogen, we find drastic increase of reacted water molecules number.

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