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Kinetic Monte Carlo modeling of CO desorption and adsorption on Pd(110) surface

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Abstract

Desorption and adsorption of carbon monoxide on Pd(110) is modeled and simulated, aiming at gaining atomic level understanding of experimentally observed rates. The model parameters are fitted to reproduce the temperature programmed desorption spectra and molecular beam surface scattering data. Desorption turns out to be best described as thermally activated, the activation energy depending on the detailed nearest neighbor site occupation configuration. For a good fit, the adsorption induced surface reconstruction needs to be included in the model. Also, desorption needs to be modeled with a precursor state included. However, surface diffusion was not found to be essential. With these ingredients the coverage dependent sticking coefficient can be successfully simulated in the temperature range from 300 to 500 K. Furthermore, the experimentally observed saturation coverage—temperature dependence is correctly predicted from the balance between simultaneous adsorption and desorption.

Keywords: Kinetic modeling; Monte Carlo; Pd(110); Carbon monoxide; Adsorption

1. Introduction

Adsorption and desorption are essential elementary steps in most surface processes like catalytic reactions. These are the key steps in catalytic CO oxidation and in many cases the rate limiting steps for the whole reaction. Therefore, the combined process deserves a closer look aiming at a thorough understanding of all related factors. Carbon monoxide is one of the most inspected single adsorbate molecules, one reason being that it is a component of the automobile exhaust gases. Another reason is that it is a good model adsorbate and its behavior is known experimentally and understood theoretically in many model cases, now [1–3]. However, it is still an object of intensive research due to variable behavior at different surfaces [2,4–8]. The conventional active materials in catalytic exhaust converters are Rh, Pt, and Pd [7]. Here we concentrate on CO on Pd(110) surface.

Using molecular beam surface scattering (MBSS) technique Hirsimäki et al. [9,10] observed the CO adsorption at Pd surfaces to be strongly dependent on the translational energy of the adsorbing molecule and weakly on surface temperature, but being structure insensitive, i.e., similar at different Pd surfaces. The saturation coverage per unit area, for example, is the same for Pd(320) and Pd(110) [4]. However, they assume the resulting adsorbate configuration to be strongly adsorption energy dependent, too. Most important feature is that adsorption is not dissociative, which is also the basis of our model: the molecule can be treated as a basic unit in both adsorption and desorption.

Jones et al. [11] observed the adsorption of CO on Pd(110) to decrease with increasing temperature. However, the adsorption was considerably weaker and the saturation coverages were lower than the ones observed by Hirsimäki et al. at all temperatures. This is due to different types of CO exposure, see below.

Adsorption–desorption processes have been simulated with various methods, too. Weinketz [12] simulated thermal desorption with a dynamic Monte Carlo method including surface diffusion. It was found that for the correct desorption rate the diffusion jump rate needs to be only an

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order of magnitude larger than desorption rate. Larger diffusion rates do not effect essentially on desorption even in case of considerable neighbor interaction. Desorption simulations to model the temperature programmed desorption (TPD) spectra of Lehner et al. [13] using kinetic Monte Carlo method support the conclusions of Weinketz.

Nordmeyer and Zaera [14] studied the parameters affecting the kinetics of adsorption. In their model, a precursor state was included and effects on sticking coefficients were evaluated. The experimental sticking coefficients were somewhat lower than the theoretical. Main reasons for that were found to be island formation of adsorbates and site revisiting in the precursor state. These effects were removed by allowing the molecule at the precursor state to adsorb anywhere on the surface, not only onto neighboring sites.

In this study we model and simulate CO desorption and adsorption on Pd(110) surface. We fit our model to the above discussed experimental results [4,9,10] to gain atomic level understanding of experimentally observed rates and to analyze the reaction mechanism in details. In particular, we aim at finding the relevance of activation, precursor states, surface diffusion, surface reconstruction and collective effects. The simulations are carried out by a kinetic Monte Carlo method (kMC), where parametrization of reaction rates of probabilities can conveniently be done.

In the next section we introduce our model and in the third section we discuss about fitting, and based on that, interpretation of experiments. The last section is conclusions.

2. Model

We model the surface by a 1000×1000 square lattice of surface sites with periodic boundary conditions. Thus, each site has eight neighboring sites in direct interaction. Hexagonal neighborhood with six neighbors is obtained, where needed, through shifting every second row by a half lattice constant. In each time step all surface sites are updated in random order according to the master equation of kinetic Monte Carlo scheme.

Probabilities of each possible elementary event i depend on the time step Δt as

$$p_i = K_i \Delta t, \tag{1}$$

where K_i is the corresponding reaction rate, which for activated events grows exponentially with increasing temperature. It is important to keep the sum of all event probabilities for a site well below one to keep the second order or multiple event probabilities negligible. For this reason we scale down the time step with increasing temperature in order to keep the sum of event probabilities of each site below 0.35.

This is the standard scheme of kMC and a variation of it is found to be good for simulation of surface catalytic reactions, too [15].

In the following, we first consider desorption, as adsorption always involves desorption process, too, except for the initial sticking at clean surfaces.

2.1. Desorption

For desorption of CO from CO covered Pd surface we found it best to model the rate with the simple Arrhenius relation

$$K_\mathrm{d} = \nu_\mathrm{d} \mathrm{e}^{-E_\mathrm{d}/kT}, \tag{2}$$

where ν_d is the pre-exponential factor and E_d is the neighborhood dependent activation energy of desorption. The pre-exponential factor was found to be very insensitive and not necessary to fit at all. Thus, we use the experimental value of Kato et al. [2], 10^{13} s^{-1}, which corresponds to the vibrational frequency of CO molecule at the bridge site of full coverage surface. The neighborhood dependent activation energy is the key parameter in fitting. It includes all the interactions between the adsorbate and surface, and between the adsorbates.

Pd(110) surface is known to reconstruct as a result of adsorption of CO, at high enough temperatures [1]. At coverages θ below 0.3 or above 0.9, the structure of the adsorbate layer does not depend on temperature. At 300 K, a missing row reconstruction occurs at $0.3 < \theta < 0.75$. Above the coverage 0.75, this Pd surface reconstruction is lifted but the CO molecules form a hexagonal structure on the surface. This is what we model with the hexagonal adsorbate layer.

Reconstructions changing the neighborhood structure offer a special challenge for kinetic Monte Carlo simulations. On the other hand, within the kinetic Monte Carlo technique the neighborhood dependent parametrization can be taken into account, which is not directly possible using rate equation simulations, for example.

2.2. Adsorption

The total adsorption rate is

$$R_\mathrm{a} = Zs, \tag{3}$$

where Z is the collision frequency of the gas molecules at the surface and s is the sticking probability. The collision frequency is

$$Z = \frac{\Phi}{N_\mathrm{s}}, \tag{4}$$

where Φ is the flux of the incoming molecules (taken from experiments here) and N_s denotes the density of the surface sites. The sticking coefficient is also coverage and neighborhood dependent as

$$s(\Theta, T) = f(\Theta)\sigma_0(T), \tag{5}$$

where $\sigma_0(T)$ is the temperature dependent initial sticking coefficient of clean surface and $f(\Theta) \leq 1$ can be used for more detailed modeling with $\Theta = (\theta, \text{neighborhood structure})$. Note that the experimentally observed sticking coefficient $S(\theta)$ results from simultaneous competing adsorption and desorption.

In first order adsorption process a molecule may adsorb only in case it hits an empty surface site and it always scatters back from an occupied one. We were not able to simulate the present case of adsorption successfully as a first order process with the sticking coefficient (5), but with one involving a precursor state [17]. This is accomplished by giving for the incoming molecule a chance to adsorb not only onto the site it hits but also onto the neighboring site with a probability to be fitted.

3. Simulations

The parameter fitting was done to the experimental data observed by Hirsimäki et al. [4,16] and that of Jones et al. [11]. Desorption was fitted to the temperature programmed desorption (TPD) [16] and adsorption to the data for coverage dependence of sticking coefficient within the temperature range 300–500 K. In the former experiments two kinds of CO exposures for sticking were used, a thermal background and a supersonic molecular beam [16], whereas the latter experiments included the thermally distributed molecules, only [11].

3.1. Desorption

For the best fit the activation energy of desorption is parametrized with increasing activation energy in decreasing number of neighbors. This can be interpreted as a repulsive adsorbate–adsorbate interaction. This approach with eight neighbors is not able fit the low temperature–high coverage TPD data. Following Raval et al. [1] and modeling the high and full coverage case ($\theta > 0.75$) with hexagonal model with six neighbors fits better to the TPD spectra.

After trying several approaches including surface diffusion we ended up modeling the full coverage case (seven or eight neighbors in the rectangular lattice) with a coverage θ dependent activation energy

$$E_d = V_0 + (1 - \theta)V_p \quad (6)$$

and starting to count the individual neighbors from six downwards. Diffusion was also simulated but it was found not to be essential for the kinetics [17].

As the unit cell of underlying rectangular metal surface lattice is not square but parallel piped the case of six neighbors was modeled neighborhood structure dependent as follows. For the closest occupation of neighbor sites the highest activation energy E_{6a} is fitted, for the most open neighborhood E_{6c} and for the remaining intermediate case E_{6b}. This gives the best fit to the experimental data [16]

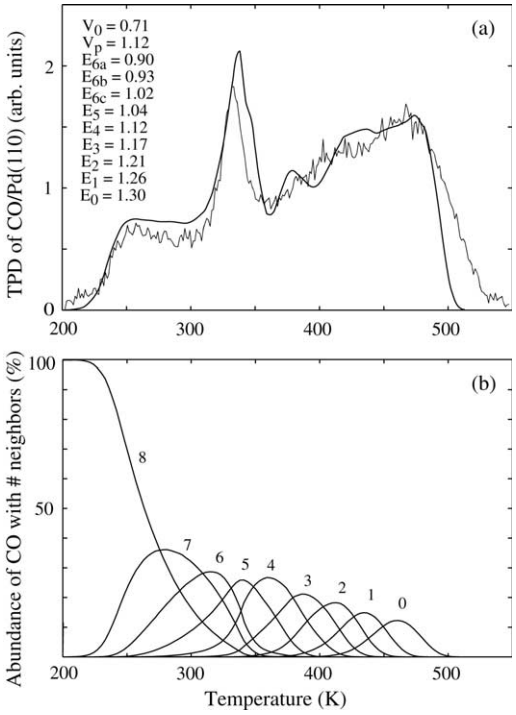

Fig. 1. Temperature programmed desorption (TPD) of CO from Pd(110) with the heating rate 3 K/s. (a) Fit of our model (smooth solid curve) to the experimental spectrum (thinner solid line) [4]. (b) Relative abundance of CO adsorbates with a given number of occupied neighbor sites, from simulation.

shown in Fig. 1a with parameters given in Table 1. The fit is sensitive to changes of the order of 0.05 eV in activation energies. In TPD studies the surface with initial coverage of one was heated with a rate 3 K/s beginning from 200 K, both in experiments and simulations.

Fig. 1b presents the relative abundance of CO adsorbates with a specific number of occupied neighbor sites. This clearly shows that the case of six neighbors is special. It is responsible for the strong peak at 320–350 K. Our conclusion to this is that the activation energy depends not only on the number of occupied neighboring sites, but also on the detailed structure of the neighborhood occupation in the orthorhombic surface lattice. Assignment of fitted activation energies to detailed adsorbate–adsorbate interactions calls for high quality DFT calculations for possible neighborhood geometries.

3.2. Adsorption

In simulation of adsorption process the simultaneous desorption has to be included. This was done using the desorption model of the previous section. Only the initial sticking coefficient σ_0 for the clean surface is free from desorption effects and it is taken directly from the experiments. At temperatures within 300–500 K it takes values in the range 0.95–0.8 and 0.55–0.25 in the supersonic molecular beam and thermal background experiments,

Table 1
Activation energies for desorption and their best fit values

Parameter	eV
V_0	0.71
V_p	1.12
E_{6a}	0.90
E_{6b}	0.93
E_{6c}	1.02
E_5	1.04
E_4	1.12
E_3	1.17
E_2	1.21
E_1	1.26
E_0	1.30

E_i ($i = 0 \cdots 5$) denotes the desorption energy in the case of i neighboring sites occupied. E_{6a}, E_{6b} and E_{6c} stand for the case of six neighbors, see text. Parameters V_0 and V_p are for the case of full or nearly full coverage, see text.

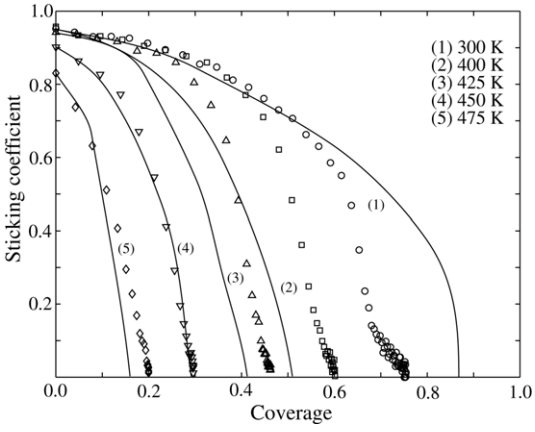

Fig. 2. Sticking coefficient as a function of coverage and temperature, from our simulation (solid curves) and from experiments (open dots) with monoenergetic molecular beam [4].

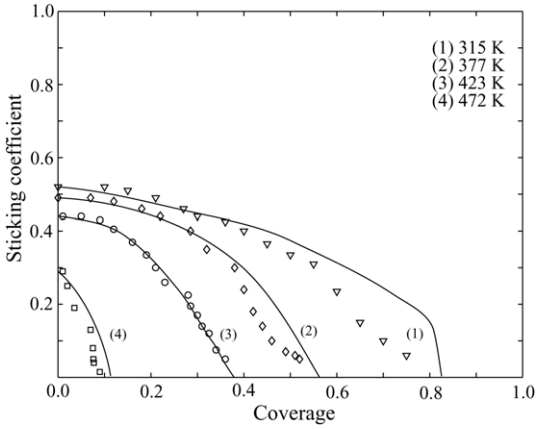

Fig. 3. Same as Fig. 2, but the experimental results are from thermally distributed molecules [11,16].

respectively. It should be noted that σ_0 was experimentally shown to be strongly dependent on the translational energy of the incoming CO molecule [10]. We are not trying to model this phenomenon here.

The only parameter or phenomenon to be fitted that remains is the adsorption via precursor process. Starting from the model above with $f(\Theta) = 1$ we found the best fit by allowing the incoming molecule to assume equal probabilities for adsorption onto the site it hits and onto the nearest neighbor sites. This is a simple model for the precursor state effect. Neglection of the precursor state effect leads to essentially linear $S(\theta)$, not fitting to experiments, but inclusion as described makes best curving downwards to the saturation coverage θ_s as seen in Figs. 2 and 3. Note that the only difference in simulations of these two different experiments is in $\sigma_0(T)$.

It is surprising how well the simulated saturation coverages agree with the experimental ones, the match being almost perfect in case of thermally distributed molecules. This proves that modeling of desorption is consistent with the adsorption, both of the processes simulated with a few parameters, only.

The simulated saturation coverage turns out to depend almost linearly on the temperature in the range 300–490 K and $\theta_s(T)$ from 0.9 to 0.1. This is in accordance with the experiments of Jones et al., but the not quite with MBSS of Hirsimäki et al.

The deviations between the simulations and experiments show that the high coverage limit is probably more sophisticated than the description of the present model. On the other hand, the deviations between the two experiments (Figs. 2 and 3) indicate that use of the controlled energy supersonic MBSS technique reveals the complexity and the energy dependence of adsorption. These details are averaged out with thermally distributed molecules and they are not included in our present model, either.

4. Conclusions

Modeling and kinetic Monte Carlo simulation of CO adsorption–desorption processes at the Pd(110) surface can be successfully carried out with the present scheme. Desorption is thermally activated following the Arrhenius behavior, the activation energy being not only coverage dependent as expected. Basically, the desorption activation energy of an adsorbate depends on the detailed nearest neighbor site occupation configuration, but at (almost) full coverage a collective coverage dependent factor improves the fit to the low temperature part of experimental TPD spectra considerably. The case of six nearest neighbors is special and responsible for the observed strong TPD peak.

Adsorption needs to be modeled with a precursor state included. Then, using the experimental initial sticking coefficients the coverage dependent sticking coefficient can be successfully simulated within the temperatures from 300 to 500 K. Furthermore, the experimentally observed close to linear saturation coverage–temperature dependence comes nicely out from simulations. Thus, the balance between

simultaneous adsorption and desorption is well described, too.

Adsorption from thermally distributed molecules is better described than that from a monoenergetic molecular beam. This suggests that there are subtle energy dependent factors in the kinetics related to steering-mediated adsorption dynamics, which are averaged out in the former case. These details are not included in the present model, but would be worth of a further study.

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