Surface Chemistry

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Role of Rotational Alignment in Dissociative Chemisorption and Oxidation: O_2 on Bare and CO-Precovered Pd(100)**

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The adsorption of gas-phase molecules that approach solid surfaces in well-defined quantum states represents a fundamental step for the understanding of heterogeneous chemical reactions[1] and for better control over the growth of self-assembled layers.[2] This objective has been achieved only in a few cases to date (NO,[3,4] H_2,[5] CH_4[6,7]). Vibrational excitations and conversion of translational to vibrational energy were thereby found to account for strong enhancements in the dissociation probability. Less attention has been devoted to rotations because they involve less energy,[8] and are therefore important only for physisorption.[9,10] We show here that rotations as well as the alignment of the rotational axis play a role in the dissociative chemisorption of O_2 onto a CO–Pd(100) surface. The effect, which arises from the requirements needed to pass through the CO adlayer, leads to different sticking probabilities and average O–CO distances, and has possible general applications for controlling reactions and film growth.

The alignment of rotational angular momentum can be exploited to investigate stereodynamical effects in molecular adsorption processes.[9,11–13] Such an alignment, which consists of a propensity of molecules to populate specific helicity states (defined by the quantum number M, the projection of the rotational angular momentum along the propagation direction) can be naturally induced by collisions in seeded supersonic molecular beams (MBs). Diatomic, linear, and linear-like molecules flying in the MB with $M=0$ behave as cartwheels when impinging on the surface at normal incidence, while when M is maximum they move in a helicopter-like manner. In particular, it has been shown that for the interaction of C_2H_4 with an O_2-precovered Ag(100) surface,[9,11] and for C_3H_6/Ag(100),[12] molecules with helicopter-like motion adsorb more efficiently than cartwheeling ones only at intermediate hydrocarbon coverage. The stereo-insensitivity of the initial sticking probability S_0 and its coverage dependence indicated that the effect is due to the collision between trapped molecules, which still remember about their original alignment, and preadsorbed ones, which lie flat on the surface. Rotational alignment was found to be ineffective for more strongly bound systems such as σ-bonded C_2H_4/Pd(100)[13] and O_2/Ag(100) (interactions mediated via a chemisorbed molecular precursor). This result was attributed to steering forces turning the incoming molecule into the most favorable configuration and causing it to lose memory of its initial state.

For O_2 on CO-precovered Pd(100), however, we find that molecules moving as cartwheels stick better than those with helicopter-like motion and that molecular alignment also affects the initial sticking probability. The system under investigation is important because of the effective rate of CO oxidation on Pd(100) when exposed to molecular oxygen. Herein we focus on stereodynamical effects of O_2 on the S_0 value and on the production of CO_2.

According to Ref. [14], rotational alignment of O_2 is generated by collisions during a supersonic seeded expansion of O_2 diluted in lighter and faster carrier atoms, typically He and Ne. Under these conditions most of the oxygen molecules in the MB are relaxed in the ground rotational level ($K=1$)[15] and cartwheeling motion prevails on average over helicopter-like motion. In addition, as demonstrated[14] by the use of a high-resolution mechanical velocity selector (consisting of eight rotating slotted disks) the angular momentum of the O_2 molecules belonging to the slow tail (ST) of the velocity distribution are nearly randomly oriented (ca. 33 % in $M=0$),

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while those in the fast tail (FT) fly mostly with cartwheeling motion (> 80 %). In the present experiment (see the Experimental Section and the Supporting Information) the fraction moving as cartwheels are approximately 0.4 and 0.7 for the ST and FT regions, respectively.

Figure 1 shows the partial pressure of O_2 in the chamber, measured by a quadrupole mass spectrometer (QMS), during exposure of the Pd(100) sample at 394 K to the ST or FT of the O_2 supersonic MB seeded in He at normal incidence. The sample is initially shielded by an inert cover (flag), so that no direct adsorption occurs. The background pressure typically increases by 2×10^{-10} mbar, mostly because of He, so that adsorption from the background over the time scale of an experiment (< 100 s) is also negligible. When the flag is removed (t_1) the beam strikes the reactive surface of the sample. The relative decrease in the QMS signal corresponds to the O_2 sticking probability S.[16] The lower traces refer to the interaction with bare Pd(100). No difference is observed between the FT and ST experiments, thus indicating either that steering is efficient in turning the molecule into the most favorable configuration for dissociation or that the interaction between Pd and O_2 is stereo-insensitive within the sensitivity of our experimental system (the error on S amounts to ca. 0.07). The upper O_2 traces correspond to adsorption on a surface precovered with 0.17 monolayer (ML) of CO. Differences in the ST and FT regions are evident both for S_0 and when O atoms accumulate on the surface. The CO_2 traces show that the reactivity is also markedly different for the two tails. The evolution with O_2 exposure is complicated by the formation and desorption of CO_2 which makes new free sites available. Such processes do not, however, affect S_0.

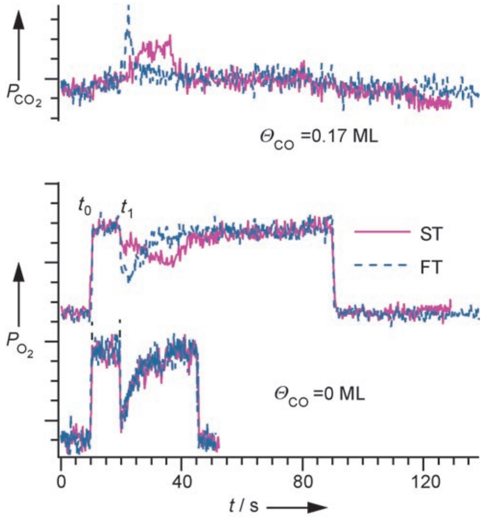

Figure 1. O_2 partial pressure, measured by a QMS not directly in line with the MB, as a function of time for the slow and fast tails of the MB interacting with the bare surface (lower traces) and with Pd(100) precovered with 0.17 ML of CO (middle traces). At time $t_0\approx10$ s the supersonic MB enters the UHV chamber but a flag prevents it from striking the sample; at time $t_1\approx20$ s the flag in front of the sample is removed and the beam hits the Pd surface. The top set of traces show the partial pressure of CO_2.

Similar data were recorded for various crystal temperatures T between 250 and 400 K as well as for a lower translational energy (0.26 eV, obtained by seeding O_2 in a He/Ne mixture). No dependence on T and a weak dependence on the translational energy[17] for the ST was found, which is in agreement with the direct and non-activated nature of the chemisorption process. Indeed, chemisorption is dissociative, as confirmed by inspection of vibrational spectra.[18,19] Therefore, we are confident that most of the difference between the results observed with the ST and the FT arises from different adsorption probabilities for molecules moving as helicopters and cartwheels. These findings have been confirmed by a more extensive investigation of the dependence of S_0 on CO precoverage, as measured using the O_2 MB seeded in He at two different temperatures. Experimental data are summarized in Figure 2; the results of a model calculation (discussed below) are also shown. We note that for a CO precoverage of 0.20 ML, the value of S_0 reduces by about 30 % for the FT with respect to that of the bare surface (mostly cartwheeling molecules) while it drops by more than 80 % for the ST (mostly molecules moving in a helicopter-like manner).

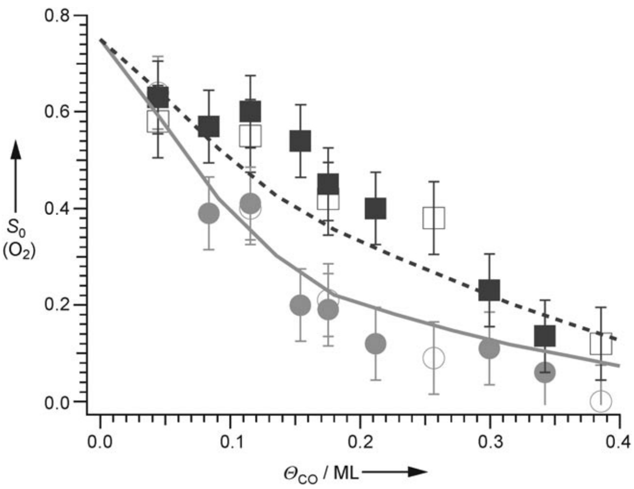

Figure 2. The initial sticking probability S_0 of O_2 as a function of CO precoverage Θ_{CO} (expressed in ML of the Pd(100) surface) for ST (circles) and FT (squares) at $T=313$ K (open symbols) and 394 K (filled symbols). The continuous and dashed lines are the results of a Monte Carlo model calculation of S_0 for ST and FT, respectively, as described in the text.

The observed steric effect is very different from that reported previously for ethylene and propylene on Ag(100)[11,12] because:

a) O_2 alignment not only affects the coverage dependence of S, it also affects S_0. The magnitude of the reduction of the S_0 value for molecules moving with helicopter-like motion indicates that the effect cannot be explained by the mere blocking of sites by preadsorbed CO;
b) cartwheeling O_2 molecules stick better than ones moving in a helicopter-like fashion, while the opposite holds true for ethylene and propylene;
c) the sticking event takes place directly for O_2, while it is mediated by a precursor for the hydrocarbons.

To the best of our knowledge, this is the first experimental evidence of an influence of molecular alignment on the initial sticking probability and on the rate of oxidation.

We propose that the steric effect in the initial sticking probability of O_2 on the CO-precovered surface is due to the larger number of free sites required to allow for a molecule with helicopter-like motiom to land between CO molecules (sitting in bridge sites, see Ref. [20]). To support this hypothesis we carried out a Monte Carlo simulation on a lattice model for the investigated system. In particular, we used the same code and parameters for the interaction energy between adsorbed CO already employed by one of us[21] to reproduce the coverage dependence of the heat of adsorption of CO on Pd(100). More details are reported in Figure 3 A.

We set up the model to compute the probability P_{MC} of finding four free (bridge) sites in a square (I), six free sites (II), and a more complicated set of twenty free sites (III). These arrangements are illustrated in Figure 3 B. The results are displayed versus CO coverage in Figure 3 C. Configurations I and II may be adequate for the landing of a molecule in (or close to) an upright position, with the O–O bond (nearly) perpendicular to the surface, provided that CO can be displaced during dissociation of O_2 to allow the oxygen adatoms to occupy next-neighbor sites. This is reasonable since the adsorption energy of oxygen atoms is much larger than that of carbon monoxide.[21] Moreover, in our experimental conditions, oxygen atoms cannot occupy first neighbour sites in the final state, otherwise it would already be possible to reach a local coverage greater than 0.5 ML at low exposure. On the contrary, experiments show that high coverage phases are produced only for a total coverage exceeding 0.45 ML.[20] The much more stringent configuration III corresponds to the eight (fourfold hollow) sites requirement for dissociation of O_2 on oxygen-precovered Pd(100)[22] if it is supposed that all bridge sites belonging to the seven first neighbors of the two oxygen adatoms (green in the figure) are empty. This array is certainly sufficient for the landing and dissociation of oxygen molecules moving with a helicopter-like motion and does not require CO to move. The final results of the model (see Supporting Information) have been obtained assuming a fraction of 0.42 and 0.72 for the cartwheeling molecules in the ST and FT, respectively. The value of S_0 for the bare surface (0.75) is thus multiplied by the probability of having four bridge sites, as in I, for the cartwheeling molecules and a set as in III for molecules with helicopter-like motion. Figure 2 shows that, despite its simplicity, the model provides an acceptable description of the experimental data.

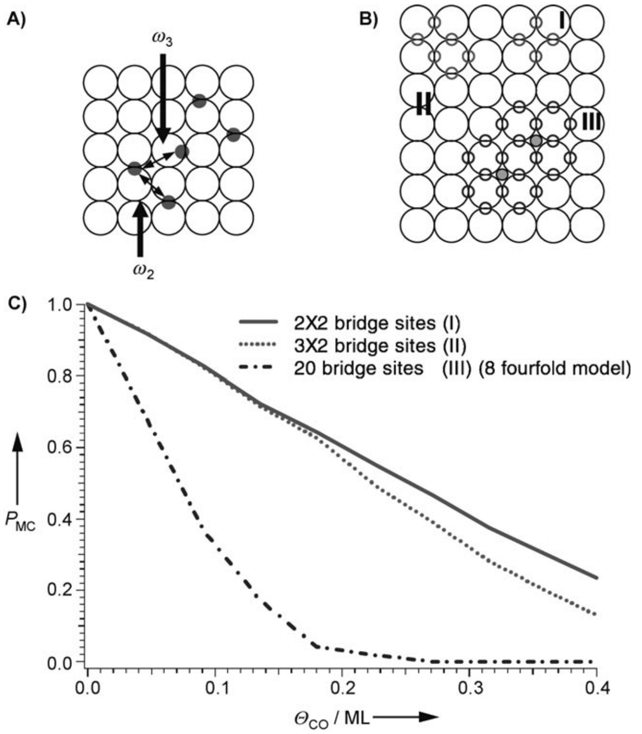

Figure 3. A) Illustration of the interaction between first (ω_2) and second (ω_3) neighbor sites occupied in the $c(2\sqrt{2}\times\sqrt{2})R45°$ structure which corresponds to a CO coverage of 0.5 ML. A strong repulsive interaction is imposed on closer molecules to prevent occupation of neighboring sites, which experimentally does not occur below 0.5 ML. The values of ω_2 (25 KJ mol^{-1}) and ω_3 (2.5 KJ mol^{-1}) are taken from Ref. [21], where they have been used to fit the coverage dependence of the heat of adsorption of CO. The value of the CO–Pd bond is set to the experimental value of 170 kJ mol^{-1}, which corresponds to the heat of adsorption of CO in the low coverage limit. B) Schematic diagram of the configurations I–III corresponding to the squared array of four bridge sites (I), the rectangular shaped set of six free bridge sites (II), and the array of twenty free sites (III; unfilled circles) obtained by eight fourfold hollow sites blocked by two oxygen atoms (filled circles). C) Probability P_{MC} of finding different sets (I–III) of free bridge sites versus CO precoverage as obtained by Monte Carlo simulation.

From Figure 1 we see that CO oxidation proceeds rapidly with the FT and more slowly for the ST regions. Although a detailed analysis of this phenomenon will be presented elsewhere, we point out here that the different behavior corresponds to the rate of reaction in an O–CO layer where the two reactants are in close contact (FT) and in a layer where they are further apart (ST). This effect is due to the lower heat of adsorption of O close to CO which reduces the activation barrier for oxidation,[23] thereby yielding a faster reaction for O resulting from the cartwheeling O_2 molecule. Our study thus discloses a rich reaction dynamics which was hidden to date because of the lack of experimental techniques able to control molecular alignment.

In conclusion we have demonstrated that both the initial sticking probability of O_2 on CO-precovered Pd(100) and the rate of CO_2 production are strongly affected by the alignment of the incoming molecules, being definitively larger for molecules moving in a cartwheeling than a helicopter-like fashion. This result is explained by the more stringent requirements for the landing of the latter species on the CO-precovered surface.

Since O_2 moving in a helicopter-like manner can only stick in larger holes in the CO adlayer, we propose that molecular alignment may be used to prepare mixed CO–O layers with different average distances between the O and CO. We have moreover shown that this largely affects the yield of CO_2 in the prototype Pd-O-CO system. This finding may open up the possibility of employing the deposition of molecules with controlled alignment for the growth[24] of more-ordered layers.

Experimental Section

Sample preparation: The Pd(100) sample was a 10-mm diameter disk, cut within 0.1° off the nominal surface plane. Its surface was prepared in an ultrahigh vacuum (UHV, base pressure 2×10^{-10} mbar) following the method given in Ref. [20] (see Supporting information). Surface cleanliness was checked by Auger electron spectroscopy and, in a separate set of experiments, also by high-resolution electron energy loss spectroscopy (HREELS). The temperature was measured by a Chromel-Alumel thermocouple, spot-welded to the sample.

Determination of the degree of alignment: A mixture of O_2 (4%) seeded in He was employed and the MB source conditions were kept as close as possible to those of Ref. [14]. The velocity selector consists of only two rotating disks,[25] a setup which allows for easy insertion into the apparatus and for the largest possible transmission. Since the degree of alignment achieved for O_2 molecules cannot be measured in situ, we rely on the experimental observations in Ref. [14] and to the guidelines discussed in Ref. [26]. The control of molecular alignment has therefore been inferred indirectly by explicitly taking into account, through a Monte Carlo simulation (see the Supporting Information), velocity and angular resolution conditions employed both in our sticking probability measurements and in previous experiments.[14]

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