Surface Chemistry

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Origin of Thermal and Hyperthermal CO₂ from CO Oxidation on Pt Surfaces: The Role of Post-Transition-State Dynamics, Active Sites, and Chemisorbed CO₂

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Abstract: The post-transition-state dynamics in CO oxidation on Pt surfaces are investigated using DFT-based ab initio molecular dynamics simulations. While the initial CO₂ formed on a terrace site on Pt(111) desorbs directly, it is temporarily trapped in a chemisorption well on a Pt(332) step site. These two reaction channels thus produce CO_2 with hyperthermal and thermal velocities with drastically different angular distributions, in agreement with recent experiments (Nature, **2018**, 558, 280–283). The chemisorbed CO_2 is formed by electron transfer from the metal to the adsorbate, resulting in a bent geometry. While chemisorbed CO_2 on Pt(111) is unstable, it is stable by 0.2 eV on a Pt(332) step site. This helps explain why newly formed CO₂ produced at step sites desorbs with far lower translational energies than those formed at terraces. This work shows that steps and other defects could be potentially important in finding optimal conditions for the chemical activation and dissociation of CO₂.

ransition-metal-catalyzed CO oxidation is not only of practical importance, for example in pollution control and fuel cells,^[1] but also serves as a prototype for fundamental studies aimed at understanding surface dynamics and heterogeneous catalysis.^[2] It is well established that CO oxidation on Pt surfaces takes place via a Langmuir-Hinshelwood mechanism, where oxygen atoms formed by dissociative chemisorption of O₂ react with adsorbed CO.^[3] Yet, despite a large body of accumulated knowledge,^[3,4] the elementary chemical mechanism has only recently been revealed.^[5] Using the newly developed method of velocity-resolved kinetics,^[5] two reaction mechanisms were found, which are reflected in the bimodal CO₂ product velocity distribution with different

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angular distributions. The major reaction channel produces CO_2 with a broad angular distribution and thermal velocity distribution, while a minor channel yields CO_2 with a hyperthermal velocity distribution and a narrow angular distribution. Since oxygen adatoms bind more strongly at steps than at terraces, one can vary the concentration of step-bound vs. terrace-bound O by controlling the step density, O coverage, and temperature. This allowed the experiment to demonstrate that the thermal products stem from CO oxidation occurring at the more active step sites, while the hyperthermal products come from reactions occurring on terraces.^[5] This conclusion is important because it argues against the prevailing view that the bimodal CO_2 distribution is the result of a single reaction controlled by a single transition state.^[4c]

An important question left unanswered by the prior work^[5] is why the two reaction channels have different distributions of CO₂ velocities. The thermochemical energy release of CO oxidation is similar for reactions at steps and terraces—in both cases the transition state is substantially higher in energy than the asymptotic product. Why, then, should it be that the energy of the barrier is channeled into CO₂ translation when the reaction occurs on terraces, but not when the reaction occurs at steps? Since the bimodal CO₂ distribution has been observed on several metal surfaces,^[4c-j] a clear understanding of its origin has important implications beyond this system.

Here, we report theoretical investigations of the posttransition-state dynamics in CO oxidation on Pt surfaces using ab initio molecular dynamics (AIMD) based on density functional theory (DFT) with the Perdew-Wang (PW91) functional.^[6] We find that CO₂ formed at terrace sites of Pt(111) desorbs directly with hyperthermal velocities whereas CO_2 formed at a step site on Pt(332) is temporarily trapped in a chemisorption well before desorbing with much lower velocities. The chemisorbed CO₂ is bent and formed by partial electron transfer from the metal to the adsorbate. On Pt(111), chemisorbed CO₂ also exists, but it is energetically unstable with respect to CO_2 gas, whereas at the Pt(332) step-site it is stable by 0.20 eV. The explanation of the experimentally observed reaction dynamics and the discovery of a chemisorbed and activated form of adsorbed CO2 are the key findings of this work. This work also provides an important insight into catalytic CO₂ conversion: steps (and other defects) can play a crucial role in stabilizing this chemically activated form of chemisorbed CO_2 , which is a likely intermediate in CO_2 dissociation reactions.

To perform these studies, we first determined the structures and energetics of adsorbed CO, O, and CO_2 on the Pt(111) and Pt(332) facets using DFT. Since the PW91



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Figure 1. Top: Adsorption sites investigated on Pt(332) and Pt(111) for both O and CO. A: atop, B: bridge, F: fcc, H: hcp sites. Center and bottom: Optimized geometries of CO (center) and O (bottom) adsorbed on different Pt(111) and Pt(332) sites. The corresponding adsorption energies (relative to CO and O) at these sites are also given.

functional yields adsorption energies for CO and O in reasonable agreement with experimental values, no correction of dispersion forces was undertaken because it would overestimate the well-established CO adsorption energy.^[7] Details of the DFT calculations can be found in the Supporting Information with additional results (Tables S1– S3 and Figure S1). The adsorption geometries and energies of both reactant species are shown in Figure 1 and listed in Table S1. In general, the adsorption is stronger at step sites than at terrace sites, apparently due to the undercoordinated nature of the Pt atoms near a step edge. These results are in general agreement with previous theoretical studies of this system, as discussed in the Supporting Information.

After characterizing the adsorption energy minima, saddle points were determined using the nudged elastic band method.^[8] This was done for the $O + CO \rightarrow CO_2$ reaction (TS1) and for the conversion of chemisorbed CO_2 to physisorbed CO_2 (TS2) for a number of O/CO adsorption site combinations. As shown in Figure 2, five distinct transition state combinations were found that connect gas-phase CO_2 to dissociatively adsorbed CO and O. Note that the initial states (adsorbed CO and O) of these five reaction paths, denoted as TR1 for the terrace reaction and SRX (X = 1-4) for step reactions, are not necessarily the most stable adsorption sites for the reactants—they are merely the states directly connected to each transition state TS1 (More details on these pathways can be found in Table S3 and Figures S2–S6). The TS1 energies are consistent with (though systematically higher than) the activation energies obtained in recent experiments^[5] (see also the Supporting Information).

The most important result is that the lowest TS1, which is associated with the step reaction (SR1), leads to a stable chemisorbed CO₂ with an adsorption energy of -0.20 eV. This chemisorbed CO₂ is bent due to partial electron transfer from Pt to the LUMO of CO₂^{*b*-}, as observed on other metal surfaces.^[9] The chemisorbed bent *b*-CO₂ further converts to a physisorbed linear *l*-CO₂ before desorption, as also observed on other metal surfaces.^[10]

While we unambiguously predict a stable chemisorbed *b*-CO₂ at Pt(332) step edges, only a dynamical calculation can show if the descent from the transition state (TS1) leads to its formation in CO oxidation. Naively, one might think that this is unlikely, because the energy release from TS1 (1.13 eV) is much larger than the shallow minimum potential well (-0.20 eV). To clarify this, AIMD calculations initiated at the transition states of paths TR1 and SR1 were performed (details and additional results are given in the Supporting Information; Table S4 and Figure S7–S9). Briefly, the initial velocities of the system at TS1 were sampled with a Boltzmann distribution at the experimental surface temperature ($T_s = 593 \text{ K}$) and 100 trajectories were launched. Following

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Figure 2. Energetics of various reaction paths for CO oxidation on Pt surfaces (TR1 and SRX (X = 1-4) for terrace and step reactions, respectively). All energies are with respect to the CO₂ + Pt asymptotic limit. Insets on the right show the geometries of various TS1 saddle points.

Path TR1, all 100 trajectories resulted in direct and fast desorption of CO₂. The CO₂ translational energy distribution has a maximum at 0.75 eV while the angular distribution peaks sharply near the surface normal (see Figure 3). This clearly resembles experimental observations of the hyper-thermal channel, which had an average translational energy of 0.64 ± 0.08 eV and a cos⁸ θ angular distribution.^[5] In contrast to this behavior, Figure 3 also shows angles and energies of trajectories following Path SR1, which saw the molecule trapped in the chemisorption well before eventual desorption (Figure S7). The lifetime of the chemisorbed CO₂ is ≈ 1 ps here, but it could be longer because we neglected electronhole pairs of the metal substrate.^[11] It is clear that the low



Figure 3. Calculated angular and translational energy distributions of CO_2 formed at the terrace and step sites on Pt(111) and Pt(332), respectively. The scattering angle (θ_t) is defined as the polar angle to the surface normal.

energy and broad angular distributions of the desorbed CO_2 produced via path SR1 are consistent with the thermal channel seen in experiment,^[5] confirming and more importantly explaining the assignment of Ref. [5]. The dynamics along paths SR2–SR4 were not studied because they are expected to behave similarly to path TR1 due to their similar energy diagrams (Figure 2).

To further explain how the initial CO₂ is trapped at the step site, we note that the molecule is highly excited internally as it slides down from the reaction saddle point (TS1). As a result, it gains only little energy in the translational mode. This can be clearly seen from the perspective of the Sudden Vector Projection (SVP) model^[12] in which the energy disposal in a product mode is predicted by its overlap with the reaction coordinate at the transition state. As shown in Figure 4, for both the TS1s of paths TR1 and SR1, the largest projections are with the three vibrational modes of CO_2 and there is a small projection for the translation along the surface normal (Z). This is readily understandable, since TS1 features a bent CO₂ geometry with the initial CO bond significantly elongated. As a result, the energy release from TS1 is mostly deposited into the vibrational modes of CO2. In Path SR1, the energy gain along the surface normal is not enough to overcome TS2, leading to a temporary trapping in the chemisorption well. Movies of representative trajectories in these two channels that confirm this analysis can be found in the Supporting Information.



Figure 4. Projections of the CO_2 translational and vibrational modes onto the reaction coordinate (RC) at TS1 for SR1 (left) and TR1 (right) on Pt(332) and Pt(111), respectively.

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For CO₂ produced in CO oxidation at metal surfaces, substantial internal excitation is observed in experiment.^[13] To further test the validity of our theoretical approach, we calculated the nascent vibrational state distributions of the desorbed CO_2 (see Figure S8) using a normal-mode analysis (NMA) method.^[14] The calculations show excitation in all three vibrational modes, consistent with previous experimental observations.^[13] Unfortunately, experiments are ambiguous as to whether internally hot products are formed at terrace or steps or both, since they were carried out on polycrystalline Pt or even Pt oxide, both likely containing many step defects.^[13] While our AIMD simulations found that internally hot products come from both channels, this needs to be confirmed by future experiments. Approximations in the theoretical model overlook several important issues, as discussed in the Supporting Information.

In addition to the characterization of several energy minima, saddle points, and the post-transition-state dynamics, another significant outcome of this work is the prediction of a chemically activated form of CO₂ on stepped Pt surfaces. In fact, there is substantial albeit indirect experimental evidence supporting this finding. For example, infrared reflection absorption spectroscopy has identified a transient signal with a frequency of 1630 cm⁻¹ during CO oxidation on Pt(100)^[15] and by isotopic labeling, this species was assigned to a vibration from a bent chemisorbed form of CO2.^[16] Our calculated harmonic frequencies for the chemisorbed b-CO₂ at the step site are 1709, 1097, and 686 cm⁻¹. The asymmetric stretching frequency (1709 cm⁻¹) represents a likely candidate for the experimentally observed transient feature. Furthermore, a chemisorbed CO2 species was identified using Cs⁺ reactive ion scattering from a Pt surface-the desorption energy of this species was estimated to be 0.48 eV,[17] substantially higher than our PW91 value (0.2 eV), but close to the DFT result with a dispersion correction (D3) (0.45 eV, see the Supporting Information).

The insight that Pt steps can stabilize a chemically activated form of CO_2 may be useful to develop an improved CO₂ catalysis.^[18] The chemisorbed CO₂ found here represents a potential key intermediate in Pt-catalyzed CO₂ chemistry. The charge transfer into the antibonding CO₂ orbital results in a bent CO₂ geometry, which has been suggested as the necessary precursor for CO₂ dissociation.^[9] Such a precursor has been observed on several metal surfaces and predicted by DFT calculations, notably on Fe and Ni,^[10] although no such species has been computationally identified on Pt. Recent theoretical studies of the dissociative chemisorption of CO₂ identified the key dynamical role played by the chemisorbed CO₂ species on transition-metal surfaces.^[10b,19] This work shows that investigations of steps and other defects could be potentially important in finding optimal conditions for the chemical activation of CO2. Also, the apparent excitation of the asymmetric stretching vibration in the CO₂ production as seen in our dynamics simulations suggests that this mode may be helpful in dissociative CO₂ adsorption, as already proposed.[10b, 19a]

To summarize, static DFT and AIMD studies of CO oxidation on Pt surfaces have revealed mechanistic insights into the experimentally observed bimodal velocity distribu-

tion of the desorbed CO_2 . It is shown that there are multiple reaction pathways associated with various active sites. DFT calculations suggest lower-barrier reactions at step sites compared to the reaction on (111) terraces, underscoring the importance of defect sites in catalysis, as also observed in many other heterogeneous processes.^[20] More importantly, AIMD calculations found that the initial CO₂ formed at a step site is trapped in a chemisorption well and desorbs with low translational energies and a broad angular distribution, while the corresponding CO₂ at a terrace site desorbs directly with high translational energies near the surface normal, in agreement with experimental observations. The existence of chemisorbed CO₂ with a bent geometry due to charge transfer is supported by experimental evidence of an active mode at 1630 cm⁻¹ in CO oxidation on Pt surfaces. The trapping is made possible by the characteristic feature of the transition state, which channels most of the energy release into the CO₂ internal modes. Detailed balance suggests that this chemisorbed CO₂ should also serve as an important precursor in the catalytic activation of CO₂.

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Conflict of interest

The authors declare no conflict of interest.

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Origin of Thermal and Hyperthermal CO₂ from CO Oxidation on Pt Surfaces: The Role of Post-Transition-State Dynamics, Active Sites, and Chemisorbed CO₂



Mind the step! DFT-based ab initio molecular dynamics studies reveal the origin of the experimentally observed bimodal CO_2 velocity distribution on Pt surfaces. While CO_2 formed at terrace sites desorbs directly with high velocities, it is trapped in a chemisorption well when formed at step sites. This is due to an electron transfer to an antibonding CO_2 orbital and leads to a desorption with low velocities and a broader angular distribution.

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