CO Oxidation on a Single Pd Atom Supported on Magnesia

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The oxidation of CO on single Pd atoms anchored to MgO(100) surface oxygen vacancies is studied with temperature-programmed-reaction mass spectrometry and infrared spectroscopy. In one-heating-cycle experiments, CO_2, formed from O_2 and CO preadsorbed at 90 K, is detected at 260 and 500 K. Ab-initio simulations suggest two reaction routes, with $Pd(CO)_2O_2$ and $PdCO_3CO$ found as precursors for the low and high temperature channels, respectively. Both reactions result in annealing of the vacancy and induce migration and coalescence of the remaining Pd-CO to form larger clusters.

Molecular-scale understanding of the energetics and mechanisms of catalytic reactions could open new avenues to the design of catalysts with specific functions [1,2]. To this aim model catalysts are used [2] to extract information on reactivities at conditions relevant to catalysis [3–5]. A most fruitful approach to gain insights into the reaction mechanisms of catalytic processes is the combination of experiments and high-level atomic scale simulations. Indeed, such recent joint studies revealed the reaction mechanism of the oxidation of CO on Au_8 clusters [6] and the polymerization of acetylene on Pd_n ($n \leq 30$) clusters deposited on MgO(100) films [7].

Here we report on studies of the oxidation of CO by a model catalyst consisting of single Pd atoms anchored on oxygen surface vacancies (F-centers, FCs) of a MgO(100) film. After low-temperature (90 K) coadsorption of O_2 and CO the formation of CO_2 was detected by temperature-programmed-reaction (TPR) mass spectrometry in single-heating-cycle experiments. *Ab initio* density-functional simulations were performed to identify relevant molecular precursors as well as to study the CO_2 formation mechanisms. The determination of two initial molecular complexes adsorbed on MgO(100), $Pd(CO)_2O_2$, and $PdCO_3CO$, is supported by good agreement between the measured and calculated CO vibrational frequencies. The former complex is involved in the formation of CO_2 at 260 K, and the decomposition of the carbonate complex leads to CO_2 desorption at 500 K. Both reaction routes induce annealing of the surface FC and migration of the remaining Pd-CO unit to form larger Pd clusters.

Model catalyst preparation and experimental results.— Size-selected atomic Pd cations were deposited on an *in situ* prepared MgO(100) thin film [8]. The low-kinetic-energy (0.2 eV) deposition of only a 0.45×10^{-2} of a monolayer (ML) of Pd at a substrate temperature of 90 K reduces greatly the migration of the Pd atoms bound to the FCs (whose concentration is 10^{-2} ML). Indeed, a recent comparison of *ab initio* calculations and FTIR studies of CO adsorbed on the supported Pd atoms provided clear evidence for single Pd atoms bound to the FCs of the

MgO(100) support. The observation of two different vibrational bands at 90 K suggests the presence of at least two CO molecules adsorbed on monodispersed Pd atoms (see Ref. [9] and below). A recent study on the cyclotrimerization of acetylene also revealed that the FC-trapped Pd atoms are stable up to 300 K [7].

First, we verified that the clean MgO(100) thin films are inert for the oxidation reaction; i.e., no CO_2 was formed in a one-heating-cycle experiment after adsorbing O_2 and CO or vice versa [10]. When Pd atoms are trapped on the FCs, preadsorption of oxygen and subsequent saturation by CO leads to the formation of carbon dioxide, with desorption peaks at 260 K and at around 500 K (Fig. 1). The existence of two desorption peaks suggests the presence of two different reaction mechanisms. Note that when CO is preadsorbed prior to O_2 the oxidation reaction is suppressed, indicating CO poisoning.

Information pertaining to the mechanism of the CO oxidation on FC-trapped Pd atoms was obtained by measuring the CO vibrational bands during reaction (see insets to Fig. 1). At 95 K three features in the FTIR spectrum of ^{13}CO are observed. The infrared absorption at 2125 cm^{-1} originates from CO adsorbed on extended defect sites on the MgO(100) thin films [11]. The broad band with a peak at around 2045 cm^{-1} and a shoulder at 2005 cm^{-1} indicates adsorption of at least two CO molecules. Heating to 165 K results in a band at 2005 cm^{-1} with a shoulder at 2035 cm^{-1}. The decreased intensity of the high-frequency band suggests partial desorption of the high-frequency CO molecule prior to the oxidation reaction. At 250 K, close to the temperature of maximum CO_2 desorption, the shoulder at 2035 cm^{-1} almost disappears, indicating oxidation of the ^{13}CO molecule with a vibrational frequency of 2035 cm^{-1}. Further heating to 410 K results in the disappearance of the band at 2005 cm^{-1}. This correlates with the formation of CO_2 and the observed desorption of molecular CO (not shown). In addition, a new vibrational band with a frequency of 1830 cm^{-1} appears between 250 and 300 K. The disappearance of this band above 600 K correlates with complete CO oxidation and molecular CO desorption.

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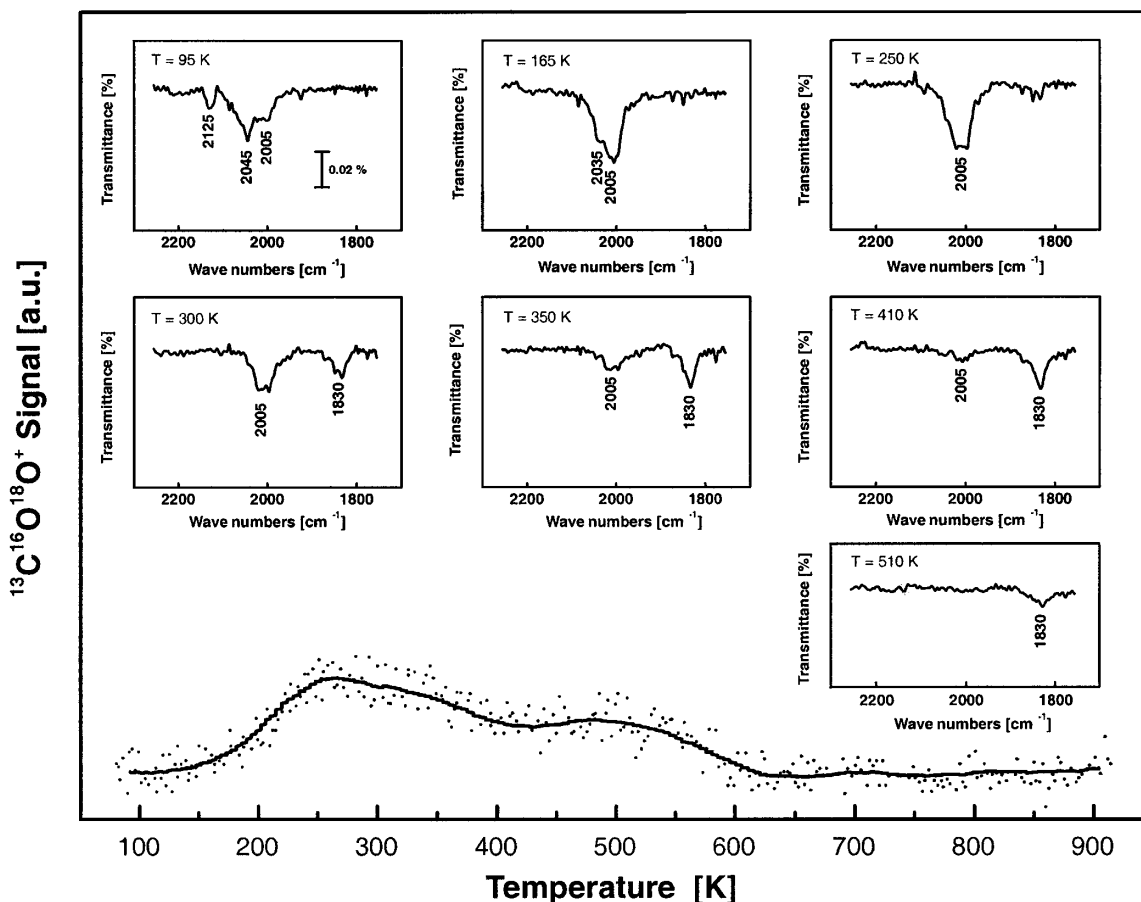
FIG. 1. A TPR spectrum showing formation of CO_2 on a MgO(FC)-Pd sample after preadsorption of O_2 and saturation with CO at 90 K. The insets show the infrared spectra of adsorbed ^{13}CO after heating the sample to the indicated temperatures. All the spectra were recorded at 90 K.

Theoretical methodology and results.— The calculations were performed using the Born-Oppenheimer (BO) local-spin-density (LSD) molecular dynamics method (BO-LSD-MD) [12] with the generalized gradient approximation (GGA) [13] and employing norm-conserving nonlocal scalar-relativistic [14] (for the Pd atom) pseudopotentials [15]. Such calculations yield accurate results pertaining to geometries, electronic structure, and charging effects of various neutral and charged coinage metal clusters [16] and nanostructures [17]. The magnesia surface was modeled by a finite region ("cluster") of atoms, whose valence electrons are treated fully quantum mechanically (using the BO-LSD-MD), embedded in a large (2000 charges) point-charge lattice, as described in our study of the Au_8/MgO model catalyst [6].

A single Pd atom binds strongly to the oxygen vacancy (binding energy of 3.31 eV), with a slight amount of charge (0.15 e) transferred to the adsorbed atom. In comparison, the binding energy of Pd atoms to terrace oxygen sites is only 1.16 eV. The enhanced binding to the FCs is also reflected in the corresponding bonding lengths of 1.65 and 2.17 Å for MgO(FC)-Pd and MgO-Pd, respectively [18].

Binding of two CO molecules saturates the MgO(FC)-Pd system; occupying the MgO(FC)-Pd system with three CO molecules leads to spontaneous (barrierless) desorption of one of the molecules. In the most stable configuration the two CO molecules are inequivalent; one CO binds on top and the second adsorbs on the side of the Pd-atom [9(b)] (this top-side geometry is similar to that shown in Fig. 2a but without the O_2) , and the total binding energy of the two CO molecules is 1.62 eV. An alternative symmetric adsorption configuration, with the two CO molecules adsorbing on opposing sides of the Pd atom, is less stable by 0.61 eV than the top-side one [9(b)].

To study the oxidation mechanisms of CO on MgO(FC)-Pd the system was optimized first with coadsorbed O_2 and two CO molecules. Two stable geometric arrangements were found, with the most stable one shown in Fig. 2a where the CO molecules bind in a top-side configuration and the O_2 is adsorbed parallel to the surface on the other side of the Pd atom. This configuration (with spin $S = 0$) is 0.90 eV more stable than an alternative one ($S = 1$) where the O_2 is bound on top of the Pd atom and the two CO molecules occupy the side positions (not shown). The preadsorbed O_2 molecule enhances slightly the adsorption energy of the two CO molecules (1.78 eV) compared to the case without preadsorbed oxygen (1.62 eV). The adsorbed O_2 molecular bond is stretched and activated (1.46 Å
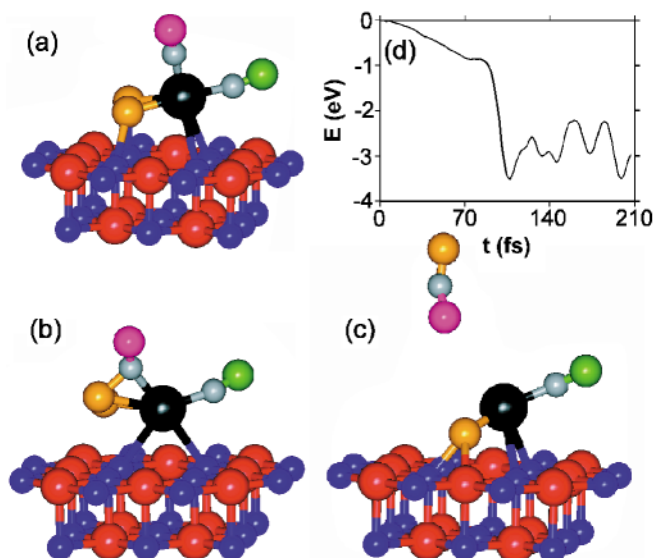
FIG. 2 (color). (a) Optimized structure of the MgO(FC)-Pd-$(CO)_2O_2$ complex. (b),(c) selected configurations, and (d) the potential energy vs time, recorded in an *ab initio* MD simulation where CO_2 is formed from the complex shown in (a). The simulation starts from the transition state shown in (b). The potential energy of the transition state is 0.84 eV above the optimized configuration shown in (a). (c) A snapshot at 210 fs, where the formed CO_2 is desorbing and the remaining O atom from O_2 molecule is moving towards the F center. The pertinent structural parameters in (a) are the following: top-CO: $d(C\text{-}O) = 1.149$ Å, $d(Pd\text{-}C) = 2.10$ Å, $\angle(Pd\text{-}C\text{-}O) = 178°$; side-CO: $d(C\text{-}O) = 1.164$ Å, $d(Pd\text{-}C) = 1.91$ Å, $\angle(Pd\text{-}C\text{-}O) = 166°$; O_2: $d(O\text{-}O) = 1.46$ Å, $d(O\text{-}Pd) = 2.09$ and 2.31 Å. The Pd atom is black, Mg and O ions of the substrate are blue and red, respectively, adsorbed O_2 is yellow, carbons are gray, and their respective oxygens are purple and green.

FIG. 3 (color). (a) Optimized structure of the MgO(FC)-Pd-CO_3CO complex. (b),(c) selected configurations, and (d) the potential energy vs time recorded in an *ab initio* MD simulation where the carbonate complex is decomposing at around 500 K. Snapshots from this simulation are shown in (b) at 160 fs (just after the transition state) and (c) at 240 fs. The FC is filled by an O atom in (c). The pertinent structural parameters in (a) are the following: side CO: $d(C\text{-}O) = 1.160$ Å, $d(Pd\text{-}C) = 1.90$ Å, $\angle(Pd\text{-}C\text{-}O) = 166°$; CO_3: $d(Pd\text{-}O) = 2.07$ Å, $d(C\text{-}O) = 1.45$ Å, 1.23 Å, 1.29 Å with the long C-O bond forming to the Pd-bound oxygen. Colors as in Fig. 2, with the carbonate oxygens shown in yellow.

compared to the calculated gas-phase value of 1.25 Å). In addition, we found a stable carbonate complex $PdCO_3CO$ (Fig. 3a), whose binding energy is 4.08 eV larger than the aforementioned $Pd(CO)_2O_2$ complex.

Reaction mechanisms.—Two reaction mechanisms are proposed corresponding to the two CO_2 peaks observed experimentally (Fig. 1). At low temperatures the two relevant precursors are shown in Figs. 2a and 3a. The existence of the $Pd(CO)_2O_2$ complex (Fig. 2a) is supported by the agreement between the calculated and measured vibrational frequencies of the two inequivalently adsorbed CO molecules (see Table I). The absence of a clear FTIR signal corresponding to the carbonate species can originate from the adsorption geometry (see Fig. 3a) where the carbonate is bound at the side of the Pd atom and the CO_3 plane is only slightly tilted away from the surface, resulting in vanishingly small normal dynamic dipole components; however, the frequency of the side-bonded CO of this complex (2020 cm^{-1}) lies in the experimentally observed vibrational band.

Corresponding to the 260 K CO_2 desorption peak we propose the following reaction mechanism. First, in a competitive process, CO desorbs or is oxidized upon heating.
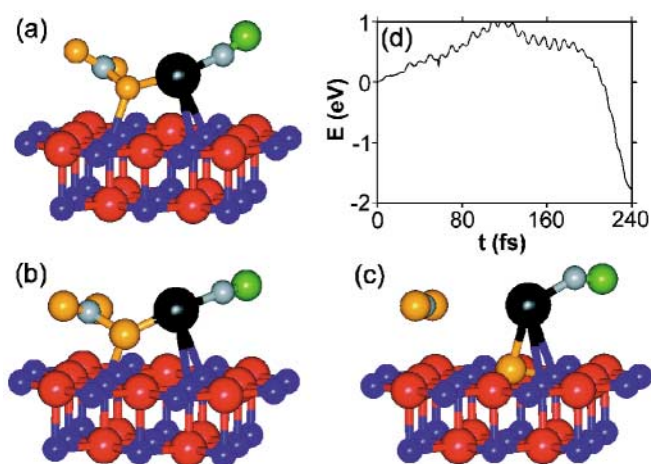
The theoretically estimated activation energies of the two processes are 0.89 eV for desorption (Table I) and 0.84 for oxidation, obtained from a series of constrained energy minimizations, where the top-CO molecule approaches the closest O atom of the O_2 molecule. The transition state leading to CO_2 formation is shown in Fig. 2b. After finding the transition state we performed a microcanonical MD simulation to study the reaction dynamics. The desorbing CO_2 molecule (Fig. 2c) carries away the major part ($\sim$2 eV) of the reaction heat of about 2.2 eV, partitioned as 0.1, 0.1, and 1.8 eV into the translational, rotational, and vibrational degrees of freedom, respectively, i.e., the desorbing molecule is vibrationally "hot". The remaining O atom of the complex fills the O vacancy under the adsorbed Pd atom (Fig. 2c), releasing 2.8 eV (not shown in Fig. 2d). Concomitantly with the annealing of the O vacancy the binding energy of the Pd atom is largely reduced from 3.31 to 1.16 eV, as discussed above. Note also that the binding energy of the remaining CO molecule to the Pd atom increases [the calculated binding energy of a CO molecule to a Pd atom adsorbed on the terrace of MgO(100) is 2.29 eV]. Consequently, migration of the Pd-CO unit, leading to formation of larger clusters, becomes energetically feasible [the calculated diffusion barrier for a Pd atom on the MgO(100) terrace is 0.43 eV]. Indeed, the observed vibrational band with a frequency of 1870 cm^{-1} appearing between 250 and 300 K (Fig. 1) is in close agreement with the calculated frequency of a CO molecule bridge bonded to an adsorbed Pd_2 dimer; for a Pd_2 adsorbed on a MgO(100) surface the calculated

TABLE I. Calculated CO binding energies (E_B) and ^{12}CO vibrational frequencies (ω^{th}), compared to the experimental frequencies (ω^{exp}, scaled for ^{12}CO from the values shown in Fig. 1 for ^{13}CO). The calculated dissociation energy, equilibrium bond length, and harmonic frequency of the gas-phase ^{12}CO molecule are 11.06 eV, 1.141 Å, and 2140 cm^{-1}, respectively, compared to the experimental values of 11.09 eV, 1.128 Å, and 2170 cm^{-1}. The CO vibrational frequencies are determined through molecular dynamics simulations stretching the equilibrium CO bond by 1% and observing the dynamics over a few harmonic vibration periods. All the calculated ω values include a correction factor of 2170/2140. The error estimate for the calculated frequencies is ± 10 cm^{-1}.

Complex	E_B (eV)	ω^{th}(cm^{-1})	ω^{exp}(cm^{-1})
MgO(FC)-Pd-(CO)$_2$-O$_2$	1.78[a]	2019/2088[b]	2050/2080
MgO(FC)-Pd-CO$_3$-CO		1687/2020[c]	
MgO(FC)-Pd$_2$-CO	1.95	1877[d]	1870
MgO-Pd$_2$-CO	2.87	1836[d]	1870

[a]Per 2 CO molecules.
[b]Side-CO/top-CO.
[c]Maximum of the CO$_3$ frequencies/side-CO.
[d]Bridge-bonded CO.

frequency is 1836 cm^{-1}, and for a Pd$_2$ adsorbed at an FC it is 1877 cm^{-1} (Table I). Desorption of the adsorbed CO molecule occurs at temperatures below 600 K. The calculated binding energy of the bridge-bonded CO to the dimer is 1.95 eV when it is adsorbed at an FC and 2.87 eV when adsorbed on a terrace, indicating that the Pd$_2$ dimer (with a bridge-bonded CO) is most likely to be located at an FC, as otherwise an even higher CO desorption temperature is expected. Such FCs are available since the density of the oxygen vacancies in our experiment is higher than that of the Pd atoms.

Formation of CO$_2$ at higher temperatures (corresponding to desorption around 500 K, Fig. 1) involves decomposition of the PdCO$_3$CO carbonate complex (Fig. 3a). This mechanism is observed in molecular dynamics simulations where the temperature is controlled to 500 K by Langevin dynamics. After the transition state (see Fig. 3b), overcoming an energy barrier of about 1 eV (see Fig. 3d), CO$_2$ leaves the complex parallel to the MgO surface with a total kinetic energy of about 0.25 eV, distributed approximately as 0.1 and 0.15 eV between the translational and vibrational modes, respectively, and with a vanishing rotational component. The remaining O atom fills the O vacancy (Fig. 3c) as found also for the lower-temperature CO$_2$ formation mechanism. The total exothermicity of this process is 1.8 eV (see the sharp drop in Fig. 3d for $t \geq 210$ fs). As in the low-temperature mechanism, the remaining Pd-CO can migrate and coalesce to larger clusters.

Finally, we remark that the relative abundance of the two surface precursors, Pd(CO)$_2$O$_2$ and PdCO$_3$CO, underlying the above reaction mechanisms may be dominated by kinetic factors; e.g., formation of the carbonate complex, although energetically favorable, could be hindered

by the requirement that the CO molecule will approach the preadsorbed side-O$_2$ rather than the Pd atom, as well as by a significant reaction barrier. Further studies of the low temperature formation of the carbonate complex, as well as efforts to identify such species (e.g., via HREELS), are warranted.

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[17] H. Häkkinen et al., J. Phys. Chem. B 104, 9063 (2000).
[18] A single CO molecule can bind in two adsorption configurations on the MgO(FC)-Pd system. In the on-top-configuration CO binds with an $E_B = 1.04$ eV and has a vibrational frequency of 2015 cm^{-1}, while in a side configuration $E_B = 0.57$ eV. An oxygen molecule also has two binding configurations to the MgO(FC)-Pd system. In the more stable on-top configuration (spin-triplet, $S = 1$) O$_2$ binds with an energy of 0.55 eV, whereas in the weaker spin-singlet ($S = 0$) side configuration (with the O$_2$ positioned similar to that shown in Fig. 2a but without the CO molecules) $E_B = 0.16$ eV. For a detailed discussion of the bonding of CO and O$_2$ to the MgO(FC)-Pd system, see Ref. [9(b)].