Identification of Defect Sites on MgO(100) Thin Films by Decoration with Pd Atoms and Studying CO Adsorption Properties

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Abstract: CO adsorption on Pd atoms deposited on MgO(100) thin films has been studied by means of thermal desorption (TDS) and Fourier transform infrared (FTIR) spectroscopies. CO desorbs from the adsorbed Pd atoms at a temperature of about 250 K, which corresponds to a binding energy, E_b, of about 0.7 ± 0.1 eV. FTIR spectra suggest that at saturation two different sites for CO adsorption exist on a single Pd atom. The vibrational frequency of the most stable, singly adsorbed CO molecule is 2055 cm^{-1}. Density functional cluster model calculations have been used to model possible defect sites at the MgO surface where the Pd atoms are likely to be adsorbed. CO/Pd complexes located at regular or low-coordinated O anions of the surface exhibit considerably stronger binding energies, $E_b = 2-2.5$ eV, and larger vibrational shifts than were observed in the experiment. CO/Pd complexes located at oxygen vacancies (F or F$^+$ centers) are characterized by much smaller binding energies, $E_b = 0.5 \pm 0.2$ or 0.7 ± 0.2 eV, which are in agreement with the experimental value. CO/Pd complexes located at the paramagnetic F$^+$ centers show vibrational frequencies in closest agreement with the experimental data. These comparisons therefore suggest that the Pd atoms are mainly adsorbed at oxygen vacancies.

1. Introduction

The chemical activity of oxide surfaces is largely dominated by the presence of extended or point defects. Depending on the ionic or covalent nature of the oxide, on its crystalline structure, and on the preparation of the material, a great variety of defect centers can form at the surface. For the case of a highly stoichiometric oxide, such as MgO, at least nine different point defects have been identified and described in the literature.[1] These defect centers can have quite different properties and characteristics. Low-coordinated O anions at steps and kinks are known to exhibit a pronounced basic character and react stronger than terrace sites with incoming molecules via electron transfer from the surface to the adsorbate.[2] F$^+$ and F centers contain one or two electrons trapped in the cavity left behind by the missing O ion.[3,4] Therefore these centers act as good electron sources for charge-transfer reactions[5,6] or can facilitate the heterolytic dissociation of H_2 or H_2O.[7] Cation vacancies result in localized holes on the surface, which then exhibit enhanced reactivity.[8] Hydroxyl groups, OH, can favor nucleation of metal clusters[9] and introduce inhomogeneous electric fields at the surface.[10] The complexity of the problem is increased as the point defects can be located at terrace, step, and kink[11] sites and as they can be isolated, occur in pairs or even “clusters”. Furthermore, the concentration of the defects is usually low, making their detection by integral surface sensitive spectroscopies very difficult. A microscopic view of the metal/oxide interface, however, and a detailed analysis of the sites where the deposited metal atoms or clusters are bound become essential in rationalizing the observed phenomena and designing new materials with known concentrations of a given type of defects.

Each of these defects has a direct and characteristic influence on the properties of adsorbed species. This becomes particularly important in the analysis of the chemical reactivity of supported metal atoms and clusters.[12,13] The defects not only act as nucleation centers in the growth of metal islands or clusters,[14,15] but they can also modify the catalytic activity of the deposited

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metal by affecting the bonding at the interface.[16-18] Recently, we have shown that isolated, mass-selected Pd clusters, deposited on a MgO(100) thin film grown on Mo(100), exhibit peculiar activities and selectivities in the polymerization of acetylene to form benzene and aliphatic hydrocarbons.[19] This strongly size-dependent behavior is related to the distinct electronic and geometric properties of the metal clusters, making this new class of materials extremely interesting for the understanding of the structure−property relationship. Free Pd atoms, which do not promote the acetylene-to-benzene cyclization, have also be shown to become active catalysts when deposited on the MgO surface.[17,20] In detail, Pd atoms deposited at the regular 5-fold coordinated sites of the MgO surface are inert and only Pd atoms bound to defect sites, either low-coordinated O anions or O vacancies (F centers), become catalytically active.[20] In addition, it has been shown experimentally and theoretically that the F centers are also important in promoting the CO oxidation occurring on Au clusters deposited on MgO.[16]

In this paper we report a combined theoretical and experimental study on the adsorption properties of CO molecules interacting with isolated Pd atoms deposited by soft-landing techniques on a MgO(100) thin film grown on a Mo(100) substrate.[21] We used CO as a probe molecule for the identification of the site where the Pd atoms are adsorbed. The adsorption energy, E_b, of CO has been measured by thermal desorption spectroscopy (TDS) and the results have been compared with those predicted by quantum-chemical calculations based on the gradient-corrected density functional theory (DFT) and on cluster models. The vibrational frequencies, ω, of the adsorbed CO molecules have been measured by Fourier transform infrared (FTIR) spectroscopy and computed by means of a vibrational analysis. The comparison of the E_b and ω from theory and experiment allows for a realistic hypothesis on the identification of the MgO defect sites where the Pd atoms are most likely to be adsorbed.

2. Experimental and Computational Details

2.1. Experiment. Palladium atoms are produced by a recently developed high-frequency laser evaporation source.[22] The positively charged atomic ions are guided by home-built ion optics through differentially pumped vacuum chambers and are size-selected by a quadrupole mass spectrometer (Extranuclear C50/mass limit: 4000 amu). Palladium atoms are then deposited under soft-landing conditions ($E_{kin} \sim 0.2$ eV/atom) onto a magnesium oxide thin film of 10−15 monolayers (ML) thickness. Upon impact the atomic ions are neutralized either on defect sites (F centers) or by charge tunneling through the thin MgO films. We deposited only 2.0% ML of Pd atoms (1 ML $= 2.25 \times 10^{15}$ clusters/cm^2) at 90 K to land them isolated on the surface and to prevent island formation on the defect-free terraces of the MgO(100) films. In fact, recent Monte Carlo simulations showed that at these low coverages (1% ML) 92% of the atoms are landing isolated on the surface.[23] As will be shown below, vibrational frequencies of adsorbed CO indeed point toward the existence of isolated Pd atoms at 90 K, which become mobile between 250 and 300 K. The MgO(100) films are prepared in situ for each experiment; they are epitaxially grown on a Mo(100) surface by evaporating magnesium in a $^{16}O_2$ background and subsequently annealing the sample to 1000 K. These films show bulklike structural and electronic properties as observed by low electron energy diffraction (LEED), X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), and electron energy loss spectroscopy (EELS).[24] However, extended defects such as steps and kinks as well as point defects are detected by scanning tunneling microscopy.[22]

After Pd deposition the samples are dosed at 90 K, using a calibrated molecular beam doser, to about 5 Langmuir of ^{12}CO or ^{13}CO, respectively. In thermal desorption experiments the sample is heated with a rate of 2 K/s and the desorbing molecules are detected by a mass spectrometer (BALZERS QMG 421). The Fourier transform infrared (FTIR) measurements are performed in single reflection mode. All the spectra are taken at 95 K and 512 interferograms are averaged.

2.2. Theory. The interaction of CO with Pd atoms adsorbed on low-coordinated O sites or F centers of the MgO surface has been studied with embedded cluster models.[25] The use of a large set of +2 and −2 point charges, PC, placed at the lattice positions around the cluster guarantees that the Madelung potential inside the cluster is properly reproduced. To prevent the artificial polarization of the oxide anions at the cluster border, an effective core potential (ECP), which provides a simple representation of the finite size of the Mg^{2+} core, is associated with the positive charges around the ion cluster.[26] This kind of approach has been widely tested, in particular for MgO, versus more elaborated embedding schemes, periodic calculations, and very accurate experimental measures on single crystals. A test case has been that of CO on MgO for which all possible theoretical methods have been applied, showing the adequacy of the cluster approach.[27]

The binding energy and the vibrations of CO molecules adsorbed on Pd atoms have been obtained with gradient corrected density functional theory (DFT). We used the hybrid Becke3 functional for exchange[28] and the Lee−Yang−Parr functional for correlation,[29] B3LYP. The MgO sites have been modeled by the following clusters: $O_{13}Mg_{13}$ represents a five-coordinated O_{5c} ion at a terrace or, by removing one O atom, the corresponding F_{5c} or F_{5c}^+ centers; $O_{10}Mg_{10}$ models a four-coordinated O_{4c} ion at an edge site or the corresponding F_{4c} or F_{4c}^+ centers; and O_7Mg_3 models a three-coordinated O_{3c} ion at the corner and the F_{3c} or F_{3c}^+ centers. The convergence of the results versus the size of the cluster has been checked for the case of Pd adsorbed on O_{5c} or F_{5c} sites. The larger $O_{13}Mg_{13}$ cluster has been compared with the O_9Mg_5 cluster; some differences are found in the properties of adsorbed Pd (e.g. the Pd binding energy is about 4% larger and the distances are slightly shorter with the $O_{13}Mg_{13}$ cluster), but the CO properties are similar, with oscillations of ±0.1 eV for the adsorption energy, ±0.02 Å for the geometries, and ±7 cm^{-1} for the frequencies. For the study of geminal $Pd(CO)_2$ dicarbonyls we used an O_9Mg_5 model of the MgO substrate.

Gaussian-type atomic orbital basis sets were used to construct the Kohn−Sham orbitals. The basis set used for the Mg and O ions of the substrate cluster is the 6-31G;[30] when a O atom is removed to form a F center one has to adopt a sufficiently flexible basis set to describe the electron localization in the vacancy. This can be achieved by adding floating functions at the cavity center[3,31] or by using a more diffuse basis set on the neighboring Mg ions.[31] Here we adopted this second

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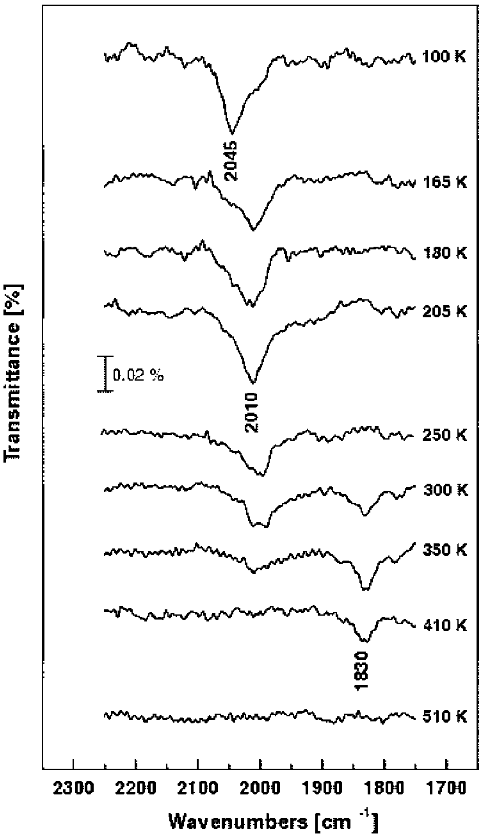

Figure 1. Infrared spectra of ^{13}CO adsorbed on deposited Pd atoms (2% ML) on a thin MgO(100) film grown on Mo(100). Shown are the spectra after annealing the sample to the indicated temperature. All spectra were taken at 95 K and 512 interferograms are averaged.

strategy and we used for the Mg ions around the vacancy a 6-31++G basis set. The Pd atom was treated by an 18-electrons ECP, which includes in the valence the $4s^2 4p^6 4d^{10}$ electrons; the basis set is of double-ζ plus polarization type.[32] For CO we used a 6-311G* basis. The use of the larger 6-311+G(2d,2p) basis gives adsorption properties for CO adsorbed on Pd/O_{5c} which differ at most by 0.04 eV for the binding energy, 0.001 Å for the geometry, and 10 cm^{-1} for the vibrational frequency. The binding energies, E_b, have been corrected for the basis set superposition error (BSSE).[33] The geometry of CO, Pd, and the first neighbors on the MgO surface has been fully optimized by means of analytical gradients. A full vibrational analysis, based on second derivatives of the total energy, has been performed to compute the harmonic frequency of CO in selected cases. For the cases where CO is normal to the surface, ω_0(CO) has been determined by fitting the potential energy curve by a fifth-degree polynomia. With the 6-311G* basis set the CO ω_0 computed at the B3LYP level is 2221 cm^{-1}, while the experimental harmonic frequency is 2170 cm^{-1}.[34] Therefore all the frequencies have been scaled by a factor of 2170/2221 = 0.977 to take into account the overestimate of the free CO ω_0. All the computed vibrational shifts are given with respect to the harmonic ω_0 for free CO, 2170 cm^{-1}; all the experimental shifts are given with respect to the anharmonic ω_e, 2143 cm^{-1}.[34] The calculations have been performed with the GAUSSIAN98[35] program package.

3. Experimental Results

Figure 1 shows the infrared spectra of ^{13}CO adsorbed on supported Pd atoms. ^{13}CO is adsorbed at 95 K and the sample is then annealed to temperatures going from 100 K up to 510 K. At 100 K a broad band at 2045 cm^{-1} with a shoulder at 2010 cm^{-1} is observed. [36] The existence of the two bands indicates the presence of two different CO adsorption sites. Adsorption of an isotopic mixture of ^{12}CO/^{13}CO results in a strong exchange of carbon monoxide adsorbed on the two sites (see below). In view of the very low Pd coverage on the surface, the two different adsorption sites are therefore likely to exist on a single Pd atom. The intensity of the 2010 cm^{-1} band increases after annealing the sample to 165 K and concomitant desorption of part of the adsorbed CO. The two observed frequencies are typical for on-top bound CO molecules. The integrated absorption intensity of the band at 2010 cm^{-1} is increasing up to 205 K and disappears continuously when annealing up to 350 K. A new band at 1830 cm^{-1} appears at 300 K, typical for CO adsorbed at bridge sites as also observed on certain macroscopic Pd surfaces at low coverage.[37] First principles DFT calculations on CO adsorbed on a Pd_2 cluster formed at an oxygen vacancy give a ^{12}CO stretching frequency of 1877 cm^{-1}.[38] This suggests that at 300 K the Pd atoms become mobile on the surface and form clusters as already observed for Pd on Al_2O_3.[39] CO can leave the on-top sites and bind at the bridge or open sites of the cluster where it is more strongly bound. At 350 K most of the on-top bound CO has desorbed from the sample, whereas the bridge-bound CO desorption is completed only at 500 K. Desorption of CO at these two temperatures is independently observed by TDS. Figure 2a shows the CO-desorption spectrum up to 400 K of ~2% ML Pd-atoms deposited on the MgO(100) film. For comparison Figure 2b shows the CO-desorption spectrum from a clean MgO(100) thin film. The difference spectrum (Figure 2c) clearly indicates that CO is desorbing from the deposited Pd-atoms between 200 and 340 K. A Redhead analysis of the TDS spectrum using a temperature of maximal desorption rate of 260 K, a heating rate of 2 K/s, and a preexponential factor of 10^{13} s^{-1} results in an energy of desorption of 0.7 ± 0.1 eV. A decreased CO desorption temperature in comparison to single crystals (400−550 K) was also observed when going from large to small Pd particles grown on Al_2O_3 films.[40]

To study this system in more detail, experiments with differently labeled CO molecules were performed. If we adsorb ^{12}CO instead of ^{13}CO onto the same surface held at 95 K, we observe a distinct absorption peak at 2090 cm^{-1} and a broad shoulder at around 2055 cm^{-1} (Figure 3a). These are the same vibrational fingerprints as for ^{13}CO (Figure 1), but shifted by the well-known isotopic shift, resulting in a frequency of 2090 and 2055 cm^{-1}. In addition, a small absorption is observed at 2172 cm^{-1} typical for CO adsorbed on low coordinated Mg^{2+} sites of the MgO(100) thin film.[41] As observed for ^{13}CO, the distinct peak at 2090 cm^{-1} disappears and the feature around 2055 cm^{-1} gains intensity after annealing the sample to 180 K (Figure 3b). This phenomenon is reversible as redosing of ^{12}CO and subsequent annealing, see Figure 3c,d, leads to the same spectra as shown in Figure 3a,b. The reversibility indicates that the system is thermally stable, i.e., Pd monomers remain trapped at the defect sites, up to at least 180 K. The change

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(36) Although the shoulder is weak, its existence was reproduced several times. (See, e.g., Figure 3a, which shows the same result for ^{12}CO.)

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(41) The intensity of the IR-absorption peak of CO on low-coordinated Mg^{2+}-sites is decreasing with film thickness. The absorption cross section of CO on 10−15 ML thick films is close to zero.

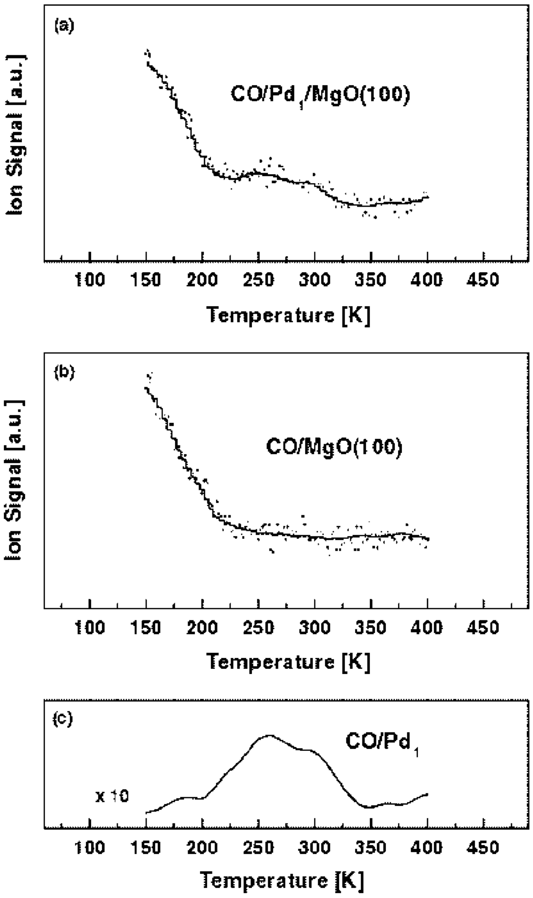

Figure 2. Thermal desorption spectra of ^{12}CO up to 400 K from (a) a sample consisting of a thin MgO(100) film with ∼2% ML Pd atoms and (b) a clean MgO(100) thin film. Dots, data; full line data smoothing with adjacent averaging (25 points). In panel c, the difference spectrum of the smoothed data is shown.

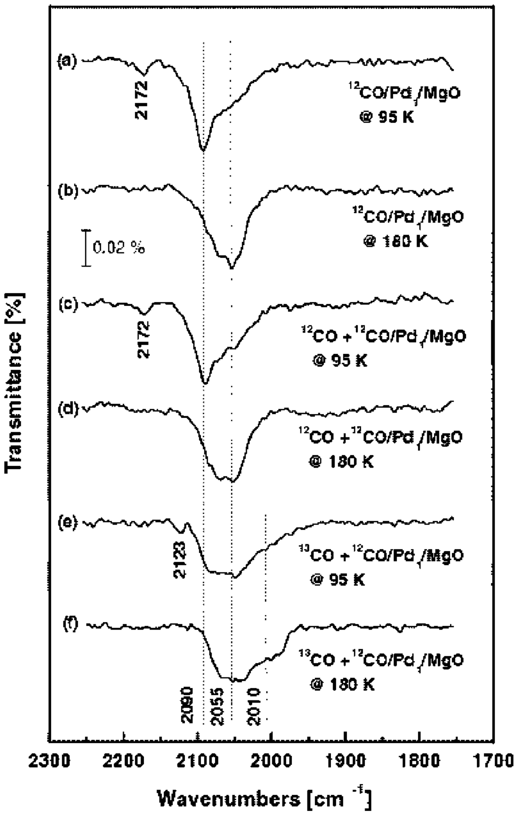

Figure 3. Infrared spectra of carbon monoxide adsorbed at 95 K (5 Langmuir) on 2% ML deposited Pd atoms on a MgO(100) thin film. (a) ^{12}CO adsorbed after sample preparation, (b) after annealing the sample to 180 K, (c) after redosing sample b to ^{12}CO, (d) after annealing sample c to 180 K, (e) after redosing sample e to ^{13}CO, and (f) after annealing sample e to 180 K

between the spectra taken before (Figure 3a,c) and after (Figure 3b,d) annealing to 180 K can be explained by the existence of a vibrational coupling. It is well-known that the band at high frequency gains intensity on the cost of the low-frequency peak if there exists vibrational coupling and if the angle between the adsorbed CO molecules is smaller than 90°.[42] For CO, vibrational coupling is observed when the frequencies of the two bands differ less than 100 cm^{-1}. In the example presented here, the two bands at around 2090 and 2055 cm^{-1} couple, resulting in high intensity of the 2090 cm^{-1} absorption band at 95 K. After desorption of CO from the high-frequency adsorption sites, the vibrational coupling disappears and the pure singleton absorption band at low frequency is observed. In principle, vibrational coupling can be suppressed by readsorbing ^{13}CO, as it possesses a different vibrational frequency. In our case, however, there is an important exchange between the two molecules at 95 K. This exchange results in a broad band observed in Figure 3e. The presence of this exchange is confirmed by heating the sample up to 180 K (Figure 3f) where CO on the low-energy binding site has desorbed. The resulting spectrum now shows two vibrational features at 2055 and 2010 cm^{-1}, where the peaks at 2055 and 2010 cm^{-1} are attributed to ^{12}CO and ^{13}CO adsorbed on the high-energy binding sites, respectively. In summary, these results revealed two different adsorption sites existing on or near the supported Pd atom with observed vibrational frequencies of 2090 (2045 cm^{-1} for ^{13}CO) and 2055 cm^{-1} (2010 cm^{-1} for ^{13}CO). The frequency at 2055 cm^{-1} (2010 cm^{-1} for ^{13}CO) is attributed to a single CO molecule adsorbed on a Pd atom deposited on MgO(100). This frequency is very close to the frequency (2052 cm^{-1}) attributed to single CO molecules on Pd atoms deposited on thin Al_2O_3 films.[43] In addition, the vibrational frequencies of CO of a PdCO complex in Ne, Ar, and Kr are 2056.4,[44] 2044.2[45]/2050,[46] and 2045[47] cm^{-1}.

4. Theoretical Results

On a free, unsupported Pd atom CO is bound by 1.71 eV with a frequency shift with respect to the gas-phase molecule of −97 cm^{-1}. This shift is explained by a substantial back-donation of charge from the metal 4d levels to the $2\pi^*$ antibonding orbital of CO. The computed shift is in excellent agreement with that measured from matrix isolation, from −87 cm^{-1} in Ne[44] to −98 cm^{-1} in Kr.[47] The optimal Pd−C distance is 1.871 Å, see Table 1. These values represent a reference to establish the kind of modification induced by the MgO substrate on the Pd−CO bonding. We first consider the case of Pd interacting with anion sites, O_{5c}, O_{4c}, or O_{3c}, Figure 4. The binding of a Pd atom with these sites increases monotonically from ≈1 eV (O_{5c}) to ≈1.5 eV (O_{3c}), and consequently the

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Table 1. Adsorption Properties of Pd and CO/Pd Complexes Adsorbed on O Anions and F and F^+ Centers Located at Terrace (5c), Edge (4c), and Corner (3c) Sites of the MgO Surface

	free	terrace			edge			corner		
	Pd−CO	O_{5c}	F_{5c}	$F_{5c}{}^+$	O_{4c}	F_{4c}	$F_{4c}{}^+$	O_{3c}	F_{3c}	$F_{3c}{}^+$
cluster		$O_{13}Mg_{13}$			$O_{10}Mg_{10}$			O_7Mg_3		
symmetry		C_{4v}			C_{2v}			C_{3v}		
z(Pd),[a] Å		2.210	1.524	1.497	1.981	1.092	1.124	1.760	0.694	0.693
E_b(Pd),[b] eV		0.96	3.42	2.10	1.35	3.64	2.41	1.51	3.66	2.35
z(PdCO),[a] Å		2.263	1.745	1.639	2.030	1.378	1.250	1.852	0.998	0.813
D(Pd−C), Å	1.871	1.847	1.969	1.973	1.849	2.007	2.014	1.833	1.991	1.998
D(CO), Å	1.143	1.149	1.146	1.136	1.148	1.144	1.131	1.156	1.147	1.134
E_b(CO),[c] eV	1.71	2.23	0.52	0.71	2.24	0.37	0.64	2.56	0.31	0.61
$\omega_0(^{12}CO)$,[d] cm^{-1}	2073	2030	2014	2092	2030	2026	2124	1995	2001	2105
$\Delta\omega(^{12}CO)$,[e] cm^{-1}	−97	−140	−156	−78	−140	−144	−46	−175	−169	−65
$\omega_0(^{13}CO)$,[d] cm^{-1}	2027	1985	1969	2045	1985	1981	2077	1950	1956	2059

[a] Vertical distance between the Pd atom and the surface plane. [b] Computed as $E(MgO) + E(Pd) - E(MgO/Pd)$ and corrected by the BSSE. [c] Computed as $E(MgO/Pd) + E(CO) - E(MgO/Pd/CO)$ and corrected by the BSSE. [d] All computed frequencies are multiplied by a scaling factor $f = \omega_0(^{12}CO\text{ exptl, }2170\text{ cm}^{-1})/\omega_0(^{12}CO\text{ theor, }2221\text{ cm}^{-1}) = 0.977$, which takes into account the small overestimate of the free CO ω_0. [e] Computed with respect to the CO harmonic gas-phase value, 2170 cm^{-1}.

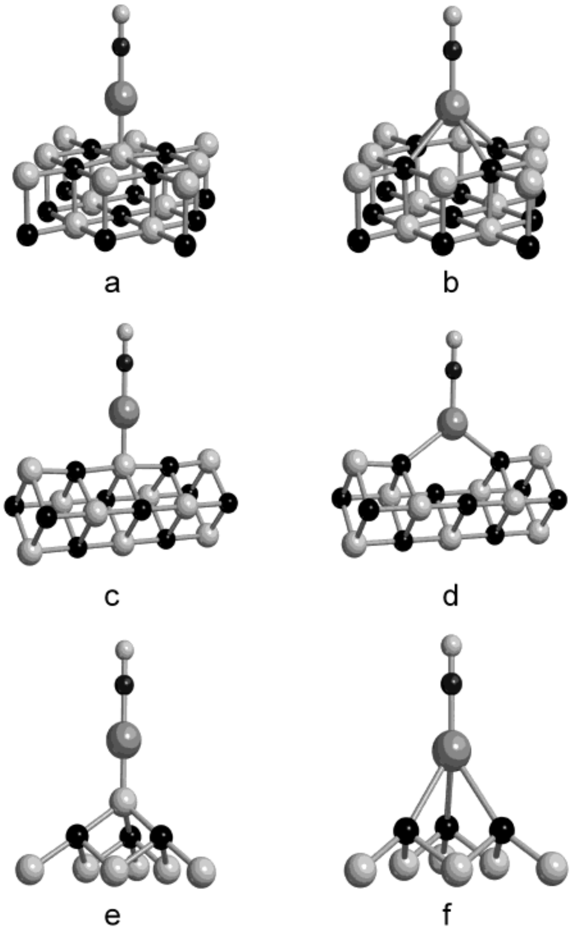

Figure 4. Cluster models used to study the CO/Pd/MgO bond: (a) CO/Pd/O_{5c}; (b) CO/Pd/F_{5c} and CO/Pd/$F_{5c}{}^+$; (c) CO/Pd/O_{4c}; (d) CO/Pd/F_{4c} and CO/Pd/$F_{4c}{}^+$; (e) CO/Pd/O_{3c}; and (f) CO/Pd/F_{3c} and CO/Pd/$F_{3c}{}^+$.

distance of the Pd atoms from the surface decreases, Table 1. On these sites the Pd−CO bond is quite strong and goes from 2.2 eV on Pd/O_{5c} to 2.6 eV on Pd/O_{3c}. The CO frequency is even more red shifted than in the case of free Pd; $\Delta\omega$ is −140 cm^{-1} for Pd on O_{5c} and O_{4c} sites, and −175 cm^{-1} for Pd/O_{3c}. While the differences in CO E_b and ω_0 are too small to be used for distinguishing between CO/Pd formed on O_{5c}, O_{4c}, or O_{3c} sites, the absolute values are sufficiently off from the experimental data for the Pd atoms to sit on these sites. In fact, the computed CO adsorption energies, 2.2−2.6 eV, are 3−4 times larger than the measured ones and the vibrational frequency shifts are twice as large. It is apparent that when Pd is bound on the O anions its electron density is higher than in the gas phase. This results in a reinforced bonding and in an increased back-donation. A similar effect has been observed for the interaction of acetylene on Pd/MgO.[20] Even considering the approximations present in our models, the differences are large enough to rule out the low-coordinated O sites to be the pinning centers of adsorbed Pd atoms.

As a second class of defects we consider the neutral O vacancies or F centers, Figure 4. We first noticed that on these sites the bonding of Pd is about three times stronger than on the O anions in agreement with other studies.[48,49] There is no large difference in Pd atom adsorption energy when the F center is located at a terrace, at a step, or at a corner site ($E_b \approx 3.5 \pm 0.1$ eV). Thus the Pd atoms are likely to diffuse on the surface until they become trapped at defect sites such as the F centers where the bonding is so strong that only annealing to high temperatures will induce further mobility. The formation of a strong bond at the MgO/Pd interface has a dramatic consequence on the Pd−CO binding energy, which is between 0.3 and 0.5 eV, depending whether the F center is at a corner or at a terrace site. This binding energy is 6−8 times smaller than that for Pd adsorbed on O_{nc}. The weak Pd−CO bonding is a direct manifestation of the so-called bond-order conservation theory;[50] in an A−B−C system the increase of the strength of the A−B bonding occurs at the expense of the B−C interaction and vice versa. The strong Pd/F_{nc} bond results in a weak Pd−CO interaction. The two electrons in the vacancy are largely delocalized over the empty 5s orbital of Pd, thus increasing its density.[51] This leads to a stronger Pauli repulsion with the CO molecule; the Pd−C bond distance is in fact 0.10−0.15 Å longer than that for low-coordinated O sites. The augmented electron density on the metal, however, reinforces also the back-donation mechanism so that the CO ω_0 for CO/Pd/F_{nc} is similar as for the low-coordinated O sites despite the longer Pd−C distance, Table 1. Thus, while the computed CO adsorption energies, 0.3−0.5 eV, are consistent, although somewhat underestimated, with the experimental TDS value, 0.7 ± 0.1 eV, the vibrational frequencies are somewhat too low compared to the experimental

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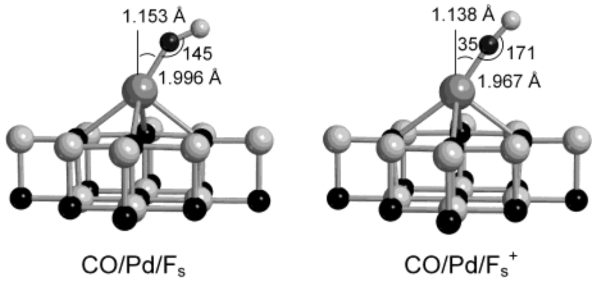

Figure 5. Cluster models and optimal geometrical parameters of bond Pd−CO bound to a F_{5c} and an $F_{5c}{}^+$ center.

data: the computed shifts are of $-150/-170$ cm^{-1} while a shift of -88 cm^{-1} is deduced from FTIR. These results have been obtained by imposing that the CO molecule is bound on-top of Pd with its axis normal to the surface plane. We have, however, also considered a CO/Pd/F_{5c} case where no symmetry constraint is imposed. We found a new minimum where the molecule is tilted by 31° from the surface normal, Figure 5; the binding energy is 0.06 eV larger than that for the normal orientation, indicating a very flat potential energy surface for bending, but the CO frequency is even more red-shifted than for the normal orientation, $\Delta\omega = -217$ cm^{-1}. Thus, the release of the symmetry constraint does not change our conclusions.

The last group of defect sites considered in this work is that of the paramagnetic F^+ centers, Figure 4. These consist of a single electron trapped in the vacancy; their electronic structure has been studied in detail in polycrystalline MgO samples by EPR spectroscopy.[6,52] Formally these centers are positively charged as a single electron replaces an O^{2-} ion in the lattice. On these sites the binding of Pd is between that of the O_{nc} sites and of the F centers, Table 1. For instance, on $F_{5c}{}^+$, Pd is bound by 2.10 eV, while E_b for Pd on O_{5c} is 0.96 eV and that for F_{5c} is 3.42 eV. CO is bound on Pd/$F_{nc}{}^+$ by 0.6−0.7 eV, in close agreement with the experimental TDS spectrum. Also the vibrational frequencies are closer to those measured by FTIR than for the case of Pd on an F center. For CO normal to the surface plane the frequency shifts go from ca. -50 cm^{-1} for CO/Pd/$F_{4c}{}^+$ to ca. -80 cm^{-1} for CO/Pd/$F_{5c}{}^+$. Also in this case, however, the removal of the symmetry constraint results in a bent CO/Pd/$F_{5c}{}^+$ complex, Figure 5. The potential surface is very flat and CO is more stable in the bent than in the normal configuration by 0.01 eV only. The scaled harmonic frequency in this case is 2072 cm^{-1}; taking into account the anharmonic correction, ca. 15 cm^{-1}, one finds a value very close to the broad band centered around 2055 cm^{-1} in the experimental spectrum, Figure 3b/d.

Having established the possible Pd adsorption sites, we consider now possible models of surface complexes where more than a single CO molecule interacts with a Pd atom. To this end we have considered a model of a Pd atom on various MgO sites with two or three CO molecules adsorbed on it. Using a small O_9Mg_5 cluster we have considered a $Pd(CO)_2$ complex bound at O_{5c}, F_{5c}, and $F_{5c}{}^+$ centers. In all cases the geometry optimization leads to two equivalent CO molecules, which form an angle of about 125−130°; the molecules are at a distance of 1.95−1.98 Å from Pd and are tilted toward the Mg^{2+} cations of the surface, Table 2. On Pd/O_{5c} the second CO molecule is bound by 0.30 eV and E_b per CO molecule is 1.26 eV; the two C−O stretching modes lead to two frequencies at 2059 and 2018 cm^{-1}. On Pd/F_{5c}, the two CO molecules are bound by 0.66 eV/CO; the energy required to detach the first CO molecule is 0.58 eV, while the E_b of the second CO is 0.75 eV (the different cluster size and the fact that the results are not corrected by the BSSE explain the small differences with respect to the results reported in Table 1 for a single CO). The scaled frequencies are 1997 and 1966 cm^{-1}, much lower than in the experiment. Finally, on an $F_{5c}{}^+$ center the $Pd(CO)_2$ complex is stable by 0.73 eV/CO; the first CO dissociation requires 0.68 eV, while the second one has an E_b of 0.79 eV, Table 2. The vibrational frequencies, 2059 and 2029 cm^{-1}, are separated by 30 cm^{-1}, more or less the same difference as for the experimental bands, 2090 and 2055 cm^{-1}. Thus, the existence of two adsorption sites on supported Pd can be explained with the formation of geminal dicarbonyls. However, our theoretical results show the formation of two equivalent CO molecules with an angle of ca. 120°, while the higher intensity of the high-frequency band in the experiment is consistent with an angle between the CO dipoles smaller than 90°. This could be explained with an asymmetric $Pd(CO)_a(CO)_b$ complex where one of the CO molecules interacts preferentially with the Pd atom and the other interacts also with an adjacent Mg^{2+} cation. Such a bonding configuration could originate from asymmetries in the surface electric field, due for example to the location of the F centers on step edges. It should be mentioned that an asymmetric $Pd(CO)_a(CO)_b$ complex formed on an F center has been recently found by first principle calculations.[38] In this structure one CO is on-top of Pd (more strongly bound), while the second one binds on the side of the Pd atom.[38] The existence of this minimum, not found in our calculations, could be due to an asymmetric relaxation of the substrate cluster which is not allowed in our model.

Table 2. Adsorption Properties of $Pd(CO)_2$ Complexes Adsorbed on O Anions and F and F^+ Terrace Centers of the MgO Surface

	free $Pd(CO)_2$	terrace		
		O_{5c}	F_{5c}	$F_{5c}{}^+$
cluster			O_9Mg_5	
symmetry			C_{2v}	
z(PdCO),[a] Å		2.374	1.943	1.956
d(Pd−C), Å	1.966	1.954	1.980	1.981
d(CO), Å	1.133	1.144	1.150	1.141
α(CPdC), deg	176.4	124.6	126.3	130.9
β(PdCO), deg	179.1	170.8	182.9	177.6
$D_e(CO)_1$,[b] eV	1.32	0.30	0.58	0.68
$D_e(CO)_2$,[c] eV	1.80	2.23	0.75	0.79
$\omega_1(^{12}CO)$,[d] cm^{-1}	2154	2059	1997	2059
$\Delta\omega_1(^{12}CO)$,[e] cm^{-1}	−16	−111	−173	−111
$\omega_2(^{12}CO)$,[d] cm^{-1}	2085	2018	1966	2029
$\Delta\omega_2(^{12}CO)$,[e] cm^{-1}	−85	−152	−204	−141

[a] Vertical distance between the Pd atom and the surface plane. [b] Computed as $E[MgO/Pd(CO)] + E(CO) - E[MgO/Pd(CO)_2]$; not corrected by the BSSE. [c] Computed as $E(MgO/Pd) + E(CO) - E[MgO/Pd/(CO)]$; not corrected by the BSSE. [d] All computed frequencies are multiplied by a scaling factor $f = \omega_0(^{12}CO \text{ exptl, } 2170 \text{ cm}^{-1})/\omega_0(^{12}CO \text{ theor, } 2221 \text{ cm}^{-1}) = 0.977$, which takes into account the small overestimate of the free CO ω_0. [e] Computed with respect to the CO harmonic gas-phase value, 2170 cm^{-1}.

We also tried to add three CO molecules to the same Pd atom; two of these molecules are tilted toward the surface, while one is normal to it. While the supported $Pd(CO)_3$ complex is stable toward dissociation of the three CO molecules, it is unstable with respect to the $Pd(CO)_2$ complex and gas-phase CO. Thus it is unlikely that a single supported Pd atom can bind more than two CO molecules.

5. Discussion and Conclusions

The results of the TDS experiments for CO on bare MgO(100), without Pd, clearly show the presence of one adsorption

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peak centered at around 150 K; this peak is due to the interaction of CO with defect sites of the MgO surface, most likely low-coordinated Mg^{2+} cations at steps and kinks.[53] In fact, on a single crystal MgO(100) surface with a low concentration of defects there is only one desorption peak at 57 K, which corresponds to CO weakly bound to terrace sites ($E_b = 0.14$ eV).[54] In the presence of deposited Pd atoms, a weak shoulder appears at around 260 K, Figure 2a. As evidenced by the difference spectrum, Figure 2c, this peak is due to the desorption of CO from the deposited Pd atoms and the corresponding binding energy is 0.7 ± 0.1 eV. The supported Pd−CO complexes exhibit a ^{12}CO ω_e of 2055 cm^{-1}, red-shifted with respect to gas-phase CO by 88 cm^{-1}.

These data provide important information for the identification of the surface sites where the Pd atoms are likely to be trapped. Cluster models of regular and defect sites at the MgO surface with adsorbed Pd−CO complexes have been considered and the corresponding properties have been determined by first principle gradient corrected DFT calculations. The defect sites considered can be classified in three groups: the surface O anion sites, the neutral oxygen vacancies or F centers, and the charged oxygen vacancies or F^+ centers. Each of these defects can be found in the material in various environments, at terraces, steps, and kinks. Actually, it has been shown by total energy calculations that oxygen vacancies form preferentially at low-coordinated sites[11,55] so that a thermal treatment of a polycrystalline material at high temperatures should result in the diffusion of the vacancies from the subsurface to the low-coordinated surface sites.

The Pd−CO complexes bound to surface O_{nc} anions exhibit similar characteristics, independent of the anion coordination. The Pd−CO bond is strong, >2 eV, and the CO frequency shift is large, almost twice the experimental one. This rules out the O anions as the sites where Pd is bound. This is also consistent with the fact that the binding energy of Pd atoms on-top of the O anions is not very high, 1−1.5 eV. The diffusion of the Pd atoms through the O−O channels on the surface can imply barriers of 0.5 eV or less,[56] suggesting that the Pd atoms are likely to diffuse on the surface until they become trapped by some active defects. The neutral F centers are very good candidates from this point of view since the binding of Pd to these centers is of the order of 3.5 eV. This means that to detrap a Pd atom from one of these sites a temperature of about 900 K is required. The Pd−CO units bound to the F centers exhibit a much weaker Pd−CO bond, of the order of 0.3−0.5 eV. This is close to the experimental estimate, 0.7 ± 0.1 eV, and suggests that the F centers could be possible adsorption sites for Pd atoms. However, the computed C−O frequencies exhibit ω shifts, which are somewhat too large: on a terrace F_{5c} center $\Delta\omega$ are −156 (CO axis normal to the surface plane) and −217 cm^{-1} (bent orientation), respectively.

The last group of defects considered is the paramagnetic F^+ centers. On these defects Pd is bound more strongly than on the O sites but not as strongly as on the F centers; the binding energy of Pd on F^+ centers is consistent with a temperature-induced diffusion of 400 K. The Pd−CO complexes at $F_{nc}{}^+$ sites have bonding characteristics very close to the measured ones. The Pd−CO dissociation energy is in fact 0.6−0.7 eV depending on the location of the defect, terrace, edge, or corner. The vibrational shift goes from −46 (corner) to −78 (terrace) cm^{-1} and is 98 cm^{-1} for bent PdCO on $F_{5c}{}^+$. The difference in CO ω_0 for the different sites is not large enough to allow for a further distinction between $F_{5c}{}^+$, $F_{4c}{}^+$, and $F_{3c}{}^+$ centers although the computed value for the terrace $F_{5c}{}^+$ defect is very close to the experimental one.

The existence of F^+ centers on a MgO film grown on a metal substrate is likely when electron tunneling through the film is possible. The positions of the valence band, conduction band, and F and F^+ impurity levels of the MgO surface have been determined recently.[57] The surface valence band lies 6.7 eV below the vacuum; an F center gives rise to a level about 3.7 eV below the vacuum. The Fermi level of a metal is usually around 4.5−5 eV; thus, if the MgO film is in contact with a metal substrate the F centers will release an electron to the metal conduction band with formation of an F^+ center. On the other hand the F^+ centers lie only about 1 eV above the MgO valence band and should be stable even in the presence of the metal substrate. If the film thickness increases, insulating properties should develop and prevent the charge transfer from F centers to the metal conduction band to occur. In addition, F^+ centers are known to exist also on the surface of polycrystalline MgO where their presence is demonstrated by a characteristic EPR signal.[10,52] These centers are responsible for a rich surface chemistry, which leads to the formation of stable and metastable radical anions by exposure to O_2, CO, or even N_2 molecules.[6,58]

To summarize, we have presented theoretical and experimental evidence that the adsorption properties of Pd−CO complexes formed on MgO thin films cannot be reconciled with the picture of Pd atoms bound to the surface O anions, located either on terraces or on low-coordinated sites. Much more consistent with the observation is the hypothesis that the Pd atoms are bound to the oxygen vacancies. Preliminary results indicate that Pd atoms bound to these sites are active in promoting the cyclization reaction of acetylene to benzene.[59]

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