

Can the Three-Coordinated Mg Site of MgO Accommodate More Than One CO Molecule?

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Received: July 7, 2000; In Final Form: September 21, 2000

A new mechanism of CO adsorption at the three-coordinated (3c) Mg sites of MgO is proposed on the basis of a quantum chemical study of the phenomenon of gradual diminution of the 2202 cm^{-1} band of the $\text{OC}\cdot\text{Mg}_{3\text{c}}$ species upon increase of the CO pressure above 10^{-1} Torr [Coluccia, S., et al. *Spectrochim. Acta* **1993**, *49A*, 1289]. The MgO surface is modeled by bare $\text{Mg}_{10}\text{O}_{10}$ and $\text{Mg}_{16}\text{O}_{16}$ clusters at the HF and DFT (B3LYP) levels of theory. We examine the hypotheses that the intensity decrease may be due to (i) the static dipole–dipole or/and inductive interactions with the CO molecules at the neighboring $\text{Mg}_{4\text{c}}$ sites and (ii) the coadsorption of two or three CO molecules at the $\text{Mg}_{3\text{c}}$ sites. The computed frequency shifts and binding energies suggest that the discussed phenomenon is due to the coadsorption of two CO molecules at the $\text{Mg}_{3\text{c}}$ sites.

Introduction

The chemical reactivity of MgO is frequently related to the low-coordinated Mg and O surface sites of this oxide.^{1–5} Among the Mg species, the three-coordinated (3c) site raises particular interest as the Mg site of the lowest connectivity. According to the general dependence of chemical activity on the coordination number, one should expect this site to be the most active Lewis site of MgO in adsorption and catalysis.

Carbon monoxide is widely used as a probe molecule in IR spectroscopic characterization of Lewis sites of non-d oxides.^{6–8} CO coordinates to these sites exclusively via the C-end lone pair. The blue shift of the CO frequency induced by this interaction is commonly accepted as a measure of the acid strength for series of closely related sites: the larger the frequency shift the stronger the Lewis site. Experimental and theoretical studies have shown^{7,9–12} that the coordination of CO on the $\text{Mg}_{3\text{c}}$ site is associated with the largest frequency shift of CO on MgO, namely $\Delta\nu = 59 \text{ cm}^{-1}$. An interesting feature of the corresponding 2202 cm^{-1} band⁷ is that its intensity gradually decreases upon increase of the pressure from 10^{-1} Torr. Understanding of this effect should provide insight into the elementary mechanism of CO adsorption at MgO surface. In the present, combined IR and quantum chemical study we explain this behavior of the 2202 cm^{-1} band by the coadsorption of two CO molecules at the $\text{Mg}_{3\text{c}}$ sites. This adsorption mechanism has never been discussed before in the literature.

Experimental Section

MgO ex-hydroxide (MgO-h) was prepared by thermal decomposition of the parent $\text{Mg}(\text{OH})_2$.^{13,14} Prior to CO adsorption, the pellet was outgassed at 1123 K. The final surface area was 200 m^2/g .

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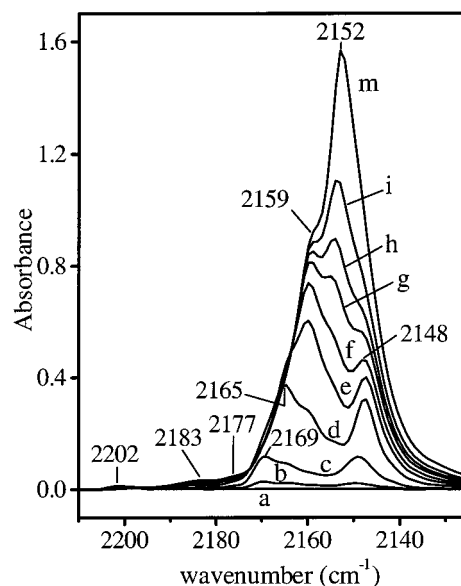


Figure 1. The 2210–2125 cm^{-1} region of the IR spectra of CO adsorbed at MgO-h surface at 77 K under progressively increased pressure: (a) 3×10^{-2} , (b) 5×10^{-2} , (c) 8×10^{-2} , (d) 10^{-1} , (e) 2×10^{-1} , (f) 4×10^{-1} , (g) 6×10^{-1} , (h) 8×10^{-1} , (i) 1, and (m) 2 Torr.

IR spectra were obtained by a Bruker IFS 48 instrument; the resolution was 4 cm^{-1} . The IR cell, suitable for spectra at 77 K, was permanently connected to a standard vacuum system (residual pressure: 10^{-6} Torr) and allowed all thermal pretreatments and adsorption–desorption experiments to be carried out in situ.

Details of Calculation

Ab initio HF and DFT calculations were performed with the GAUSSIAN-94 package.¹⁵ For DFT calculations the hybrid

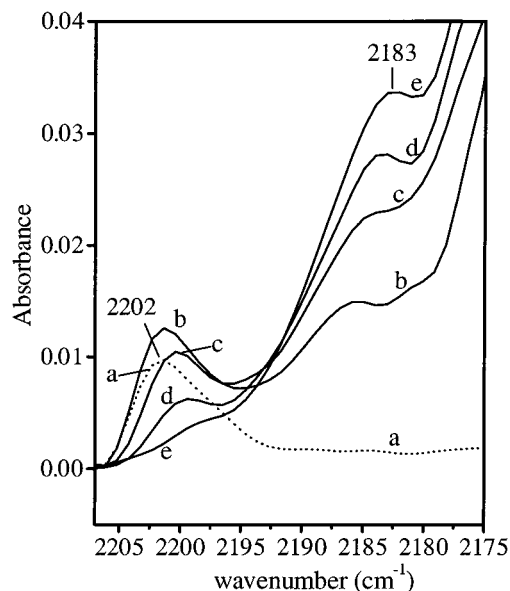


Figure 2. The detailed behavior of the IR bands of CO in the 2210–2175 cm^{-1} region upon increase of the CO pressure: (a) 3×10^{-2} , (b) 8×10^{-2} , (c) 2×10^{-1} , (d) 6×10^{-1} , and (e) 2 Torr.

TABLE 1: Total Binding Energies, E_b (kcal/mol), Binding Energies per Successively Adsorbed Molecule, ΔE_b (kcal/mol), and Frequency Shifts, $\Delta\nu$ (cm^{-1}), for CO Molecules at the Mg_{3c} Site of MgO Cluster Models

model	species	E_b^a [ΔE_b^b]			$\Delta\nu$	
		DFT/HF	DFT	DFT(zp) ^c	HF	expt
1a	OC·Mg _{3c}				64	59
1b	OC·Mg _{3c}				62	59
2a	OC·Mg _{3c}	8.2 [8.2]	8.2 [8.2]	7.1 [7.1]	64	59
2b	2OC·Mg _{3c}	10.8 [2.6]	10.1 [1.9]	8.0 [0.9]	35,38	40
2c	3OC·Mg _{3c}	12.6 [1.8]	10.2 [0.1]	6.8 [−1.2]	30,30,35	

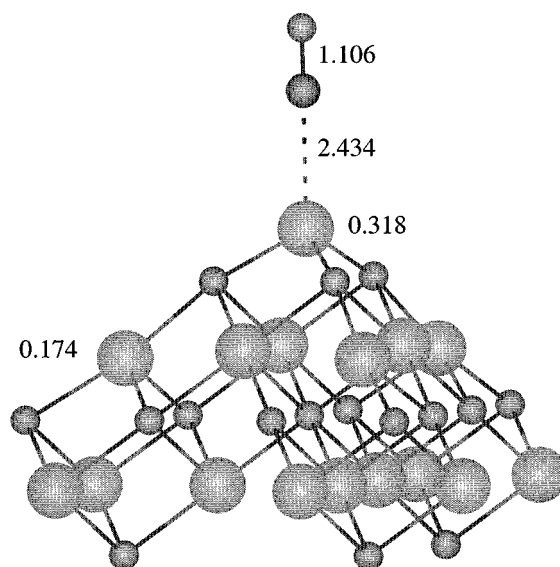
^a BSSE corrected; $E_b = [E(\text{free CO molecules}) + E(\text{substrate})] - E(\text{complex})$. ^b For the adsorption of the n th CO molecule, $\Delta E_b = [E(\text{free CO molecule}) + E(\text{complex with } (n-1) \text{ CO molecules}) - E(\text{complex with } n \text{ CO molecules})]$. ^c Zero point corrected.

B3LYP functional¹⁶ was employed which is a parametrized combination of the Becke exchange functional,¹⁷ the Lee, Yang, and Parr correlation functional,¹⁸ and the exact Hartree–Fock exchange.

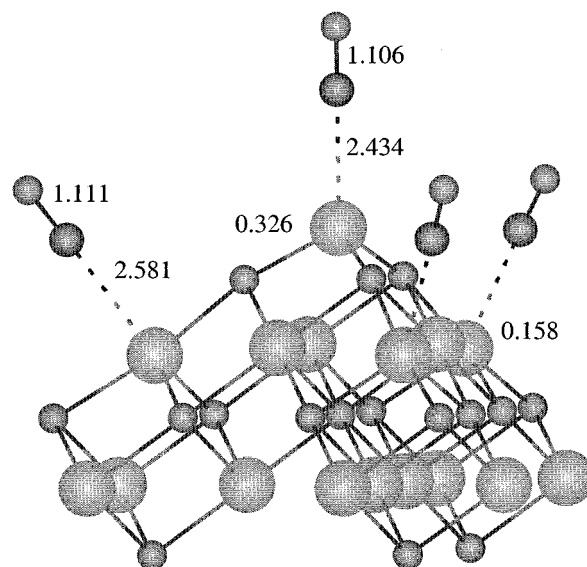
The CO bond and the CO position with respect to MgO models were fully optimized within the adopted symmetry constraints. In the MgO models only the position of the adsorbing Mg atoms was optimized; the positions of all the other Mg and O atoms correspond to those of the MgO lattice ($R_{\text{MgO}} = 2.1 \text{ \AA}$). This is in line with the generally accepted methodology of molecular modeling for ionic oxides.^{5,9–12,19,20}

The employed methodology of calculation of the frequency shift and binding energy of CO using small, bare MgO clusters has been validated and described elsewhere.^{9,11,12} The Mg_{3c} site was modeled by $\text{Mg}_{10}\text{O}_{10}$ and $\text{Mg}_{16}\text{O}_{16}$ clusters. A combined basis set was used: the 6-31G(d) basis set for CO molecule and the 3-21G basis set for MgO clusters. According to previous checks^{9,11} of the bare cluster models of the OC·Mg_{3c} and OC·Mg_{4c} species against experimental IR and TPD data and results of AIMP¹⁰ embedded cluster calculations, one should not expect an improvement of the accuracy in increasing either cluster size or basis set.

The frequency shifts were calculated at the HF level.^{9,11} Since for the CO complexes the C–O oscillator is kinematically independent to a high accuracy,^{11,21} the correction to the harmonic HF frequency shifts $\Delta\nu^{\text{HF}}$ for the basis set incomplete-



1a



1b

Figure 3. Cluster models used for examining the influence of the CO molecules at the neighboring Mg_{4c} sites on the frequency of the CO adsorbed at the Mg_{3c} site. HF/6-31G(d) bond lengths and inward displacements (in \AA) of the adsorbing Mg_{3c} and Mg_{4c} sites.

ness and the electron correlation neglect was performed by the scaling procedure¹¹

$$\Delta\nu = k\Delta\nu^{\text{HF}} \quad (1)$$

where $k = 0.8897$ is the scaling factor, being defined as that fitting the computed HF/6-31G(d) harmonic frequency of free CO, 2439 cm^{-1} , to the experimental value, 2170 cm^{-1} .²² The errors due to BSSE and anharmonicity have been shown to be negligible ($\sim 1\text{--}2 \text{ cm}^{-1}$ ^{11,23}).

The binding energies for OC·Mg_{3c} and OC·Mg_{4c} complexes computed by the HF method¹¹ and those computed by the

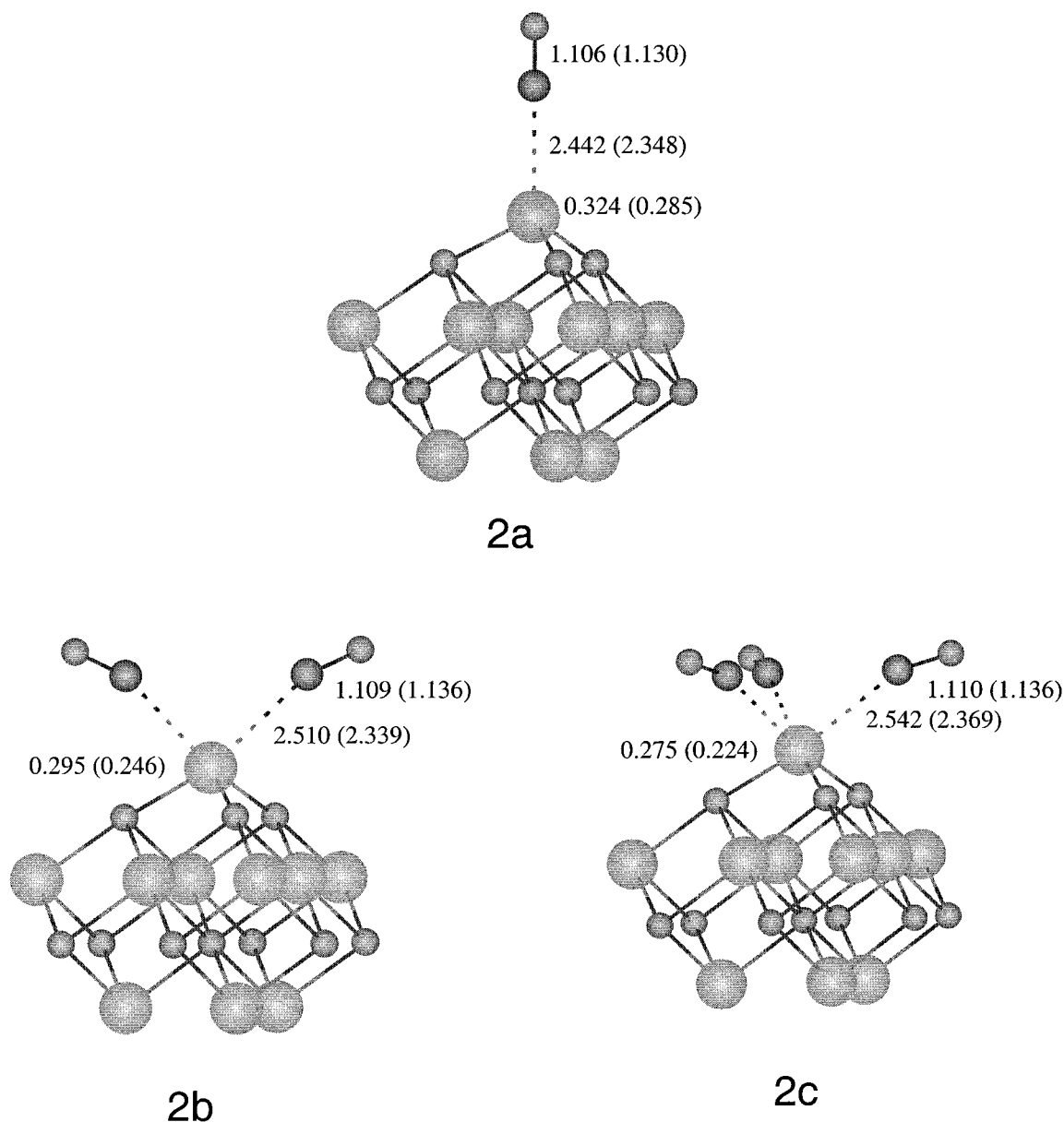


Figure 4. Cluster models mimicking the increase of the number of CO molecules adsorbed at the Mg_{3c} site upon increase of the CO pressure. HF/6-31G(d) and B3LYP/6-31G(d) (in parentheses) bond lengths and inward displacements (in Å) of the adsorbing Mg_{3c} sites.

MCPF¹⁰ method including electron correlation are equal within 1 kcal/mol. However, since the adsorption of CO at Mg sites of MgO is mainly governed by electrostatics^{11,20,24} and the inclusion of electron correlation may only improve the description of the electron density for CO molecule, the binding energy is computed at the B3LYP/HF and B3LYP levels. Corrections to the binding energies for the basis set superposition error (BSSE) are estimated by the counterpoise method.²⁵

Results and Discussion

1. IR Data. Figure 1 shows the 2210–2125 cm^{-1} spectral region of CO adsorbed on MgO-h under progressively increased pressure from 10^{-2} to 2 Torr. The low-frequency region of the spectra associated with chemisorbed CO species⁷ is not presented. At least eight IR bands can be distinguished at 2202, 2183, 2177, 2169, 2165, 2159, 2152, and 2148 cm^{-1} . As commonly assumed, the 2202, 2159, and 2152 cm^{-1} bands correspond to the CO on Mg_{3c} , Mg_{4c} , and Mg_{5c} sites, respectively.^{7,9–12} The 2148 cm^{-1} band has been recently assigned¹² to the CO molecules interacting with the Mg_{4c} and

Mg_{5c} sites at the stepped MgO-h surface. The interpretation of the other bands is missing in the literature. The relative intensity of the 2202 cm^{-1} band is very small. This conforms to the general trend of the heterogeneous catalysis on defect oxides surfaces that the more active is a site the less is its surface concentration.

Figure 2 shows the detailed behavior of the 2202 cm^{-1} band. The most interesting observation is that this band gradually diminishes upon increase of the pressure from 10^{-1} Torr and nearly disappears at 1 Torr. One might suggest only two physically plausible interpretations for this phenomenon:

1. The 2202 cm^{-1} band is affected by the static dipole–dipole interaction and/or the inductive interaction through the surface between the CO at Mg_{3c} sites and the CO at the neighboring Mg_{4c} sites. The dynamic dipole–dipole interaction⁶ can be excluded considering the difference in CO frequency (43 cm^{-1}) between the $\text{OC}\cdot\text{Mg}_{3c}$ and $\text{OC}\cdot\text{Mg}_{4c}$ species. The effect of the CO adsorption at the neighboring Mg_{5c} sites can be neglected to a first approximation since the corresponding adsorption interaction is much weaker.

2. When increasing the CO pressure the coadsorption of two or three CO molecules takes place at the low-coordinated Mg_{3c} sites.

To discriminate between these two interpretations we examine them by quantum chemical calculations of cluster models.

2. Calculation Results. Table 1 reports the results of calculations for models $\text{CO}\cdot\text{Mg}_{16}\text{O}_{16}$ (**1a**) and $4\text{CO}\cdot\text{Mg}_{16}\text{O}_{16}$ (**1b**) (Figure 3). Model **1a** mimics the adsorption of CO at a very low coverage, when the coordination at the strongest Mg_{3c} sites should preferentially occur. Model **1b** corresponds to a higher coverage when the adsorption at Mg_{4c} sites should also take place. The difference in CO frequency between the $\text{OC}\cdot\text{Mg}_{3c}$ complexes of these models is 2 cm^{-1} only. These results suggest that the overall effect of the neighboring $\text{OC}\cdot\text{Mg}_{4c}$ species on the CO frequency of $\text{OC}\cdot\text{Mg}_{3c}$ is negligible. This disproves the hypothesis that the decrease of the 2202 cm^{-1} band of CO at Mg_{3c} sites may be due to the dipole–dipole and/or inductive interactions with the CO molecules at the neighboring Mg_{4c} sites. The predicted shift $\Delta\nu = 64\text{--}62\text{ cm}^{-1}$ of CO at the Mg_{3c} sites is very close to the corresponding experimental value (59 cm^{-1}).

Table 1 presents also the results of calculations for clusters $\text{CO}\cdot\text{Mg}_{10}\text{O}_{10}$ (**2a**), $2\text{CO}\cdot\text{Mg}_{10}\text{O}_{10}$ (**2b**), and $3\text{CO}\cdot\text{Mg}_{10}\text{O}_{10}$ (**2c**) (Figure 4). They model the successive increase of the number of CO molecules at a Mg_{3c} site upon increase of the pressure. At the B3LYP (B3LYP//HF) level the total electronic binding energy increases in the series $\text{OC}\cdot\text{Mg}_{3c} < 2\text{OC}\cdot\text{Mg}_{3c} < 3\text{OC}\cdot\text{Mg}_{3c}$, with the binding energies for the coordination of the first, the second, and the third molecule being equal 8.2(8.2), 1.9(2.6), and 0.1(1.8) kcal/mol, respectively. When correcting the B3LYP values for the zero-point energy, the coadsorption of the second CO molecule remains energetically favorable by 0.9 kcal/mol while the coordination of the third CO molecule becomes energetically unfavorable by 1.2 kcal/mol (Table 1). The related decrease in binding energy is mainly due to the formation of five new vibrational levels upon coordination of a CO molecule, namely two hindered translational, one intermolecular stretching, and two hindered rotational CO vibrations. For the $\text{OC}\cdot\text{Mg}_{3c}$ species the corresponding B3LYP frequencies are 44(x2), 143, and 209(x2) cm^{-1} . For comparison, the best theoretical estimates for the electronic binding energy of CO at the Mg_{5c} sites of the (001) plane is 1.8¹⁰ and 2.5²⁹ kcal/mol which are very close to the predicted B3LYP electronic binding energy for the adsorption of the second CO molecule (1.9 kcal/mol). This result suggests that at a certain CO pressure, comparable to the pressure when the CO adsorption at the (001) plane starts ($\sim 10^{-1}$ Torr, cf. Figure 1), the coadsorption of the second CO molecule at the Mg_{3c} sites should take place.

The computed CO frequency shifts for $2\text{OC}\cdot\text{Mg}_{3c}$ (35 and 38 cm^{-1})²⁷ are close to the experimental shift of 40 cm^{-1} for the 2183 cm^{-1} band (Figures 1 and 2). The appearance of this band, the 2152 cm^{-1} band of the $\text{OC}\cdot\text{Mg}_{5c}$ species, and the disappearance of the 2202 cm^{-1} band start at approximately the same pressure of 10^{-1} Torr. This fact and the results of energy and frequency calculations suggest that at about 10^{-1} Torr the adsorption of the second CO molecules at the Mg_{3c} sites occurs forming the new $2\text{OC}\cdot\text{Mg}_{3c}$ species. This adsorption mechanism explains the phenomenon in question.

Conclusion

The IR spectra of CO adsorption at the MgO -h surface show that the 2202 cm^{-1} band of the CO at the Mg_{3c} sites gradually decreases upon increase of the pressure from 10^{-1} Torr. Quantum chemical calculations suggest that this effect is due to the coadsorption of two CO molecules at these sites. The

coadsorption of three CO molecules at the Mg_{3c} appears to be energetically unfavorable. The predicted CO frequency shifts of the $2\text{OC}\cdot\text{Mg}_{3c}$ species allow to associate these complexes with the 2183 cm^{-1} band in the IR spectra. The calculations disprove the hypothesis that the decrease in intensity of the 2202 cm^{-1} band may be accounted for by the static dipole–dipole interaction or/and the inductive interaction through the surface with the neighboring $\text{OC}\cdot\text{Mg}_{4c}$ species.

Acknowledgment. A.G.P. thanks the Swedish Foundation for International Cooperation in Research and Higher Education (STINT) for funding. Grants of computer time from the PDC and NSC supercomputer centers are gratefully acknowledged.

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- The difference in frequency between the coadsorbed molecules is due to their vibrational coupling through the adsorbing Mg atom. This difference is too small for the molecules to manifest themselves by two separate bands in the IR spectra.