

A Surface Site as Polydentate Ligand of a Metal Complex: Density Functional Studies of Rhenium Subcarbonyls Supported on Magnesium Oxide

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Notwithstanding the importance of supported organometallic species as industrial catalysts,¹ most are nonuniform mixtures, with only a few being well-characterized at the atomic level. Rhenium subcarbonyls on MgO, in contrast, consist of nearly uniform surface species and are among the best-studied organometallic complexes on oxides.^{2–4} EXAFS² and infrared spectra³ showed that decomposition of the precursors [HRe(CO)₅],² [H₃Re₃(CO)₁₂],² and [Re₂(CO)₁₀]³ on MgO powder results in fragments, assigned as Re(CO)₃⁺, coordinated to surface ligands.⁵ The concept of a surface site as a polydentate ligand evokes the remarkable circumstance in which the adsorbate–substrate bonds are as strong as metal–ligand bonds in common transition metal complexes, as shown by the present investigation.

Depending on the degree of MgO surface hydroxylation, structural models of the supported complexes ranging from Re(CO)₃{OMg}₃ (three O anions of MgO as ligands) to Re(CO)₃{HOMg}₃ (three OH groups of MgO as ligands) have been invoked.^{2,3} Weakening of the adsorbate–substrate interactions with increasing surface hydroxylation was manifested from the C–O frequency shift.³ An important signature of the supported complexes is the sensitivity of their infrared band positions in the ω(C–O) region, from which the average number of surface oxide and hydroxide ligands coordinated to a Re atom was inferred.³ On the basis of ω(C–O) features, these two limiting complexes were assigned C_{3v} symmetry,³ implying a surface site with three O ligands, although interaction with a site offering four O centers would seemingly be more compatible with the most stable square (001) face of MgO. However, further structural insights could not be developed on the basis of spectroscopic data alone.³

Thus, we examined the structural model with the help of quantum chemical calculations to (i) justify the possibility of forming Re(CO)₃/MgO complexes, (ii) determine their structural and spectroscopic parameters in more detail, and (iii) investigate whether the Re–O_{surf} bonds are indeed sufficiently strong and similar to common coordination bonds to support the concept of a surface site as a polydentate ligand. To the best of our knowledge, this work is the first computational study of oxide-supported organometallic species bonded via the metal center.

Here, adsorption complexes of Re(CO)₃ and Re(CO)₃⁺ on cationic defect sites (V_s centers) of MgO were investigated with the aid of a model cluster density functional (DF) method. Adsorption sites were considered representing both dehydroxyl-

ated and hydroxylated MgO surfaces with three neighboring symmetry-equivalent oxygen atoms exposed. The supported complexes Re(CO)₃{OMg}₃ and Re(CO)₃{HOMg}₃ proposed earlier³ are shown to indeed correspond to stable configurations of the cluster models. The calculated geometric and vibrational parameters agree well with available experimental results. For instance, the calculated Re–O_{surf} bond length of Re(CO)₃{OMg}₃, 2.15 Å, coincides with the EXAFS value² of the complex assigned to Re(CO)₃{OMg}_x{HOMg}_{3–x} (x ≈ 2).³ The calculations reproduce the stronger red-shift of the frequency ω(C–O) of rhenium subcarbonyl measured on hydroxylated MgO sites relative to rhenium subcarbonyl on dehydroxylated sites. Especially important is the finding that the Re–{OMg} adsorption energy in Re(CO)₃{OMg}₃, 3.37–3.51 eV/bond, is significantly higher than the Re–CO binding energy in Re(CO)₃⁺, 2.51 eV/bond, and in Re(CO)₃, 2.39 eV/bond, thus substantiating the concept of surface ligands. Various combinations of conceivable electronic configurations of the adsorbate, Re(0) and Re(I) tricarbonyl moieties, and the substrate defect sites V_s and V_s[–] were considered.

Scalar-relativistic⁶ all-electron density DF calculations were carried out employing the code ParaGauss for parallel computers⁷ and a generalized-gradient exchange–correlation approximation.^{8,9} The Gaussian-type basis sets were: Re (21s,17p,12d,7f) → [9s,8p,5d,2f],^{10a} C and O (of CO) (9s,5p,1d) → [5s,4p,1d],^{10b} H (6s,2p) → [3s,2p],^{10b} Mg (15s,10p,1d) → [6s,5p,1d],^{10c} O (13s,8p,1d) → [5s,4p,1d].^{10c}

A probable adsorption site on MgO is inferred to expose three surface O ligands in C_{3v} arrangement available for bonding with a Re center of subcarbonyl species.³ Adsorption sites each exposing an equilateral triangle of oxygen atoms are formed by removal of a three-coordinated Mg atom at the corner position of a cubic (MgO)_n particle. The high stretching frequency of a CO probe, 2194 cm^{–1},³ is indicative of a considerable concentration of defects on powder MgO samples, in particular, of low-coordinated Mg sites.¹¹ Depending on the state of the removed Mg species, Mg⁰, Mg⁺, or Mg²⁺, the adsorption site will be created as either a neutral or charged vacancy, V_s, V_s[–], or V_s^{2–}, respectively. The formation energies of the former two defects are 15.3 eV (15e²) and 17.6 eV (15e³). Formation of a singlet V_s^{2–} (15e⁴) is estimated to require 33.9 eV and is therefore less probable. The electron affinity (EA) of V_s, 4.44 eV, favors the formation of V_s[–], but addition of a further electron is not supported, EA(V_s[–]) = –0.13 eV.

Models of Re(CO)₃ adsorbed on V_s and V_s[–] sites obtained by Re substituting for a three-coordinated Mg atom are shown in Figure 1A. To account for long-range electrostatic interactions, the substrate cluster models O₃Mg₆ⁿ⁺ (n = 8 for V_s, n = 7 for V_s[–]) were embedded into an array of 10 × 10 × 10 point charges (PCs) of ±2 au to arrive at an electroneutral model of a V_s site. Care was taken to avoid contact of easily polarizable oxygen anions of the substrate cluster with positive embedding PCs.¹² The model of hydroxylated MgO was derived from that of dehydroxylated MgO by formal dissociation of three water

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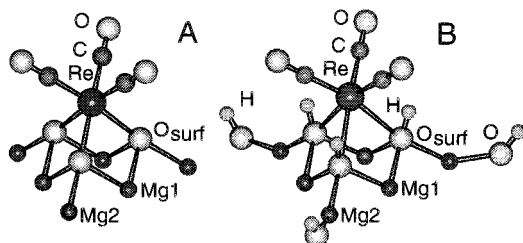
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Table 1. Calculated Observables of Various $\text{Re}(\text{CO})_3/\text{MgO}$ Models in Comparison with Available Experimental Results^{a,b} (in parentheses)

system	$r(\text{Re}-\text{O})$	$r(\text{Re}-\text{C})$	$r(\text{C}-\text{O})$	$\alpha(\text{Re}-\text{C}-\text{O})$	$\alpha(\text{C}-\text{Re}-\text{C})$	$r(\text{O}-\text{Mg1})$	$r(\text{O}-\text{Mg2})$	E_b	$\omega(\text{Re}-\text{MgO})$	$\omega(\text{Re}-\text{CO})$	$\Delta\omega(\text{C}-\text{O})^c$
$\text{Re}(\text{CO})_3\{\text{OMg}\}_3$											
$\text{Re}(\text{O})(\text{CO})_3/\text{V}_s^-$	2.26	1.90	1.18	179.4	90.1	2.03	2.02	2.79	528	510	-153
$\text{Re}(\text{I})(\text{CO})_3/\text{V}_s^-^d$	2.15 (2.15)	1.95 (1.88)	1.16	177.5	88.6	2.04	2.09	3.51	552	479	-93 (-107)
$\text{Re}(\text{I})(\text{CO})_3/\text{V}_s$	2.05	2.02	1.15	179.8	87.7	2.05	2.15	2.74	551	439	-29
$\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$											
$\text{Re}(\text{I})(\text{CO})_3/\text{V}_s(\text{OH})$	2.55	1.91	1.17	177.4	91.5	2.03	2.07	0.67	417	523	-123 (-129)

^a Distances r in Å, angles α in degrees, binding energy E_b of $\text{Re}(\text{CO})_3$ species to MgO in eV per Re-O bond (three bonds), vibrational frequencies ω in cm^{-1} . ^b EXAFS distances from ref 2, vibrational frequencies from ref 3. ^c Frequency shift with respect to free CO: expt 2143 cm^{-1} ; calcd 2120 cm^{-1} . ^d Also represents $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s$, where $E_b = 3.37$ eV per Re-O bond with respect to $\text{Re}(\text{CO})_3$ and $\{\text{OMg}\}_3(\text{V}_s)$.

**Figure 1.** Cluster models of rhenium subcarbonyl adsorption complexes on dehydroxylated (A) $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ and hydroxylated (B) $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ cationic defects of MgO (point charges not shown).

molecules, giving three surface OH groups interacting with $\text{Re}(\text{CO})_3$ and three charge-balancing OH groups (with fixed geometry) attached to the boundary Mg cations (Figure 1B). The geometries of the cluster models were optimized under C_{3v} or C_3 symmetry constraints keeping the Mg cations fixed at the bulk-terminated positions. Although the oxidation state $\text{Re}(\text{I})$ is more common for $\text{XRe}(\text{CO})_3$ complexes (e.g., $\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3^{13}$), and $\text{Re}(\text{CO})_3^+$ species exhibit a closed-shell electron configuration $20a_1^2 2a_2^2 18e^4$, the $\text{Re}(\text{O})$ fragment $\text{Re}(\text{CO})_3$ exhibiting the open-shell ground state $20a_1^2 2a_2^2 19e^1$ has also been considered as possible product of $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ and $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ dissociation.

It is not straightforward to conclude which of the $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ models adequately represent the observed adsorption complexes. $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s^-$, $33e^4$ or 1A_1 , is the most stable (on the absolute energy scale) of the three $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ systems considered, being favored by 5.12 eV over the doublet complex, $33e^3$ or 2E , which represents both $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s$ and $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s^-$ systems. This energy difference may be rationalized by the EA of the V_s center, 4.44 eV, or the ionization potential of $\text{Re}(\text{O})(\text{CO})_3$, 6.97 eV. Adsorption energy is highest for the $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s^-$ moiety, 10.53 or 3.51 eV per $\text{Re}-\{\text{OMg}\}$ bond (Table 1), followed by 10.11 or 3.37 eV/bond in $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s$. Alternative triplet $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s$, $33e^2$ or 3A_2 , and singlet $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s^-$ are characterized by energies, 2.74 and 2.79 eV/bond, respectively (Table 1). These Re-O bond energies may be compared with the bond enthalpy measured for $\eta^5\text{-}(\text{C}_5\text{Me}_5)\text{ReO}_3$,¹⁴ 5.07 eV, and calculated with the same DF method for $\eta^5\text{-}(\text{C}_5\text{H}_5)\text{ReO}_3$,¹⁵ 5.29 eV, where the $\text{Re}=\text{O}$ double bond is somewhat stronger than in the present surface complex.

An additional argument favoring $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s^-$ and $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s$ moieties can be gleaned from a comparison with the measured $\text{Re}-\text{O}_{\text{surf}}$ distance that according to the calculations should be most sensitive to the electronic structure of adsorption complexes. The experimental value characterizing the complex $\text{Re}(\text{CO})_3\{\text{OMg}\}_x\{\text{HOMg}\}_{3-x}$ ($x \approx 2$),³ 2.15 Å, is reproduced by the calculation. Other calculated bond lengths and angles of the species $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s^-$ and $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s$, are less sensitive to electronic features of the cluster models, but all fall in the range expected for $\text{XRe}(\text{CO})_3$ complexes (Table 1).¹³

The issue of possible electronic states of models $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ of the subcarbonyl on hydroxylated MgO is clearer because only one complex is bound: $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s(\text{OH})$ ($36a_1^1 38e^3$ or 3E); others do not even exhibit a local minimum at $\text{Re}-\text{O}_{\text{surf}}$ distances that would indicate significant adsorbate-substrate interaction. All calculated parameters of $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ reflect considerably weaker adsorption than for the dehydroxylated $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ congeners (Table 1). Upon hydroxylation, the $\text{Re}-\text{O}_{\text{surf}}$ bond strength is dramatically reduced, to 0.67 eV, concomitant with a significant bond elongation by 0.4 Å. The much smaller elongation measured for partially hydroxylated surfaces, at most 0.04 Å,¹³ shows that the complexes $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ with three weak $\text{Re}-\{\text{HOMg}\}$ bonds are probably only minority species in the samples with various degrees of hydroxylation investigated by EXAFS.⁴ Clearly, shorter, stronger $\text{Re}-\{\text{OMg}\}$ bonds form preferentially over $\text{Re}-\{\text{HOMg}\}$ bonds.

The $\omega(\text{C}-\text{O})$ spectra furnish signatures of the $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ and $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ complexes. The measured red-shifts of the high-frequency A_1 C-O bands are -107 and -129 cm^{-1} (relative to free CO), respectively.³ This frequency range is typical of related Re compounds, e.g., $\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3$.¹³ The calculated $\Delta\omega(\text{C}-\text{O})$ values characterizing $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s^-$ and $\text{Re}(\text{O})(\text{CO})_3/\text{V}_s$, -93 and -123 cm^{-1} , respectively, support the conclusion that they represent $\text{Re}(\text{CO})_3/\text{MgO}$ and $\text{Re}(\text{I})(\text{CO})_3/\text{V}_s(\text{OH})$ species, respectively. Other $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ models (Table 1) yield values of the vibrational frequency shift that differ considerably from experiment. Thus, the accurate reproduction of measured C-O frequencies and their shifts is a further important finding supporting the present theoretical and previous experimentally derived structural models of $\text{Re}(\text{CO})_3$ on MgO.³ The $\Delta\omega(\text{C}-\text{O})$ values calculated for free $\text{Re}(\text{CO})_3$ and $\text{Re}(\text{CO})_3^+$ species, -35 and -19 cm^{-1} , respectively, are significantly smaller than those of the complexes $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$ and $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$, wherein the substrate-to-adsorbate π back-donation acts to red-shift the C-O band. This picture is consistent with stronger π Re-to-carbonyl back-donation in more weakly bound adsorption complexes on hydroxylated MgO than in complexes at dehydroxylated sites and also agrees with the trend in the calculated Re-CO frequencies, indicating stronger (and shorter) Re-CO bonds in $\text{Re}(\text{CO})_3\{\text{HOMg}\}_3$ than in $\text{Re}(\text{CO})_3\{\text{OMg}\}_3$.

These DF calculations provide the first direct validation of the structural models of rhenium subcarbonyls adsorbed on powder MgO. The $\text{Re}-\text{O}_{\text{surf}}$ bonds are shown to be as strong as other common coordination bonds, thus justifying the concept of surface sites as polydentate ligands able to anchor organometallic fragments to supports.^{2-4,16} Surface hydroxylation can dramatically reduce the strength of such adsorption bonds. This conclusion implies possibilities for tuning of adsorptive and catalytic properties of supported organometallic species by modification of the surface stoichiometry of even such inert oxide supports as MgO.

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