

Structure of a mononuclear Rhenium catalyst supported on MgO: An ab initio study

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Abstract

A theoretical study of a mononuclear catalyst precursor, the $\text{HRe}(\text{CO})_5$ complex, both isolated and adsorbed on the MgO (100) surface is reported. Ab initio calculations have been performed at the RHF and CASSCF levels of theory using a basis set of at least double- ζ quality. To represent the surface three different clusters have been selected: OMg_5^{8+} , O_5Mg_5 and $\text{O}_9\text{Mg}_5^{8-}$. The environment effects are introduced by embedding these clusters in a set of total ion potentials and point charges. At the RHF level, the organorhenium complex does not bind to the surface due to an overestimation of its dipole moment while at the CASSCF level, a large adsorbate–surface interaction is found. Vibrational frequencies for the isolated complex have been computed and found to agree with the experiment.

Keywords: Rhenium; Magnesium oxide

1. Introduction

Catalysts made from organorhenium precursors supported on metal oxides are important in industrial processes such as the conversion of petroleum and petrochemicals [1–6]. Experimental kinetic results indicate that the active site in alkane hydrogenolysis involves more than one surface metal atom and that the C–C bond breaking is preceded of multiple dehydrogenation steps [1,3,7]. However, when mononuclear Re complexes are used, only dehydrogenation of cycloalkanes is observed [8]. Taken together these results suggest that metal atoms with labile ligands may catalyze dehydrogenation of

alkanes leading to the rupture of the C–C bond in nearby metal centers [9].

One important challenge of research in theoretical catalysis is the understanding of the relationships between surface structure and catalyst properties. The first step in meeting this challenge is the study of the structure and properties of mononuclear catalyst precursors supported on the surface of adequate metal oxides.

The simplest organorhenium catalyst precursor for which experimental data have been reported is $\text{HRe}(\text{CO})_5$. The properties of this compound supported on MgO have been studied from both kinetic and spectroscopic (IR, UV, XPS and EXAFS) techniques. These data reveal that in absence of dipolar solvents, $\text{HRe}(\text{CO})_5$ is adsorbed maintaining its identity. Thus, when the IR spectra of the isolated and supported

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species are compared, only small shifts in the bands are observed. However, when a dipolar solvent is added a cleavage of the Re–H bond is found [4,5].

In the present work we report on a theoretical study of $\text{HRe}(\text{CO})_5$, both isolated and MgO /supported, based on *ab initio* quantum mechanical calculations. The molecular structure and the vibrational spectrum of the isolated complex have been computed from both RHF and CASSCF wave functions. For the adsorbed system, embedded cluster calculations at the CASSCF level have been performed in which, the size of the cluster has been increased in order to analyze the goodness of the model.

2. Model and computational details

Ab initio embedded cluster calculations were undertaken using the effective core potential (ECP) reported by Stevens et al. [10,11] to describe inner electrons of Re, C and O atoms in the organometallic complex. For valence electrons of the Re atom (5s, 5p, 4d and 6s) the basis set was (7s7p5d) contracted to [4s4p3d]. For the C and O atoms of the carbonyl ligand only the 2s and 2p electrons were taken into account using a (4s4p)/[2s2p] basis set. The H atom was described using a standard DZV basis set [12]. The number of basis functions for the Re complex was then 116.

To model the MgO (100) surface embedded cluster calculations were performed in order to take into account the environment lattice effects. This is done by embedding the cluster representing the surface into a set of point charges at the crystal positions. This method has been widely used and very recently, the importance of the Madelung potential introduced by these point charges has been stressed [13]. Three models of the MgO (100) surface have been used (Fig. 1). The first one, model A, consists of a OMg_5^{8+} cluster embedded in an array of 670 point charges (four layers of 13×13 ions). In this cluster the oxide anion was described

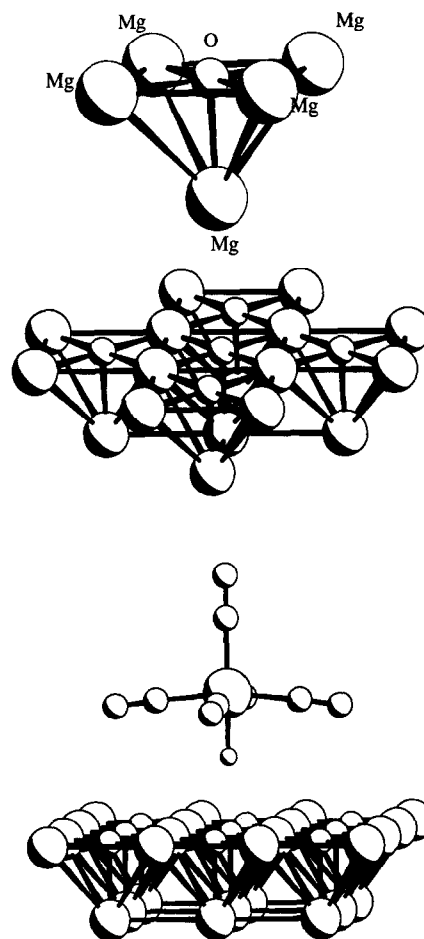


Fig. 1. Models of the MgO (100) surface. Top: model A, OMg_5^{8+} . Middle: model B, $\text{O}_5\text{Mg}_5 + 12$ Mg TIPs. Bottom: model C, $\text{O}_9\text{Mg}_5^{8-} + 20$ Mg TIPs. For model C the adsorbed $\text{HRe}(\text{CO})_5$ complex is also included.

using the all electron (9s5p)/[4s3p] basis set optimized for O^- by Pacchioni et al. [14] while Mg^{2+} ions were described using the ECP reported by Stevens et al. [10] including a (4s4p)/[2s2p] valence basis set. The second model for the surface, model 13, is obtained by adding the nearest four surface oxygens to cluster A. These oxygens are described using an all electron (4s4p)/[2s2p] basis set proposed by Huzinaga [15] and are surrounded by a set of twelve Mg^{2+} total ion potentials (TIPs) to avoid the strong polarization of the oxide electronic clouds induced by the point charges. Finally, model C arises from the addition of the next

nearest four surface oxygens also surrounded by TIPs. The number of basis functions for clusters A, B and C are 54, 94 and 134.

In the CASSCF calculations [16,17], the active space included the Re *d* occupied orbitals (d_{xz} , d_{yz} , d_{xy}) that represent the bond between the Re atom and the carbonyl ligands and the MO representing the σ_{ReH} bond as well as their antibonding partners. This gives place to an active space consisting of 8 electrons distributed in all possible ways in 8 orbitals (468 CSF in C_{2v} symmetry, 1764 CSF in C_1 symmetry).

Geometries were optimized by standard analytical gradient techniques. Stationary points were characterized by computation and further diagonalization of the second derivative matrix of the energy obtained by finite differences of analytically computed gradients. All calculations were performed using the HONDO-8.5 program [18] in its serial and parallel versions running on IBM RS6000 and HP/735 workstations.

3. Results

3.1. The $\text{HRe}(\text{CO})_5$ complex

The structural parameters optimized at the RHF and CASSCF levels of theory for the $\text{HRe}(\text{CO})_5$ complex are summarized in Table 1 and the geometry and atomic labelling is sketched in Fig. 2. The complex has C_{4v} symmetry with a Re–H bond distance of 1.743 Å at

Table 1
Structural parameters of the $\text{HRe}(\text{CO})_5$ complex computed at the RHF and CASSCF levels (Å and degrees)

	RHF	CASSCF
H–Re	1.743	1.755
Re–C _{eq}	2.032	2.042
Re–C _{ax}	2.016	2.040
(CO) _{eq}	1.148	1.149
(CO) _{ax}	1.154	1.156
< H–Re–C _{eq}	84.7	84.8
< Re–C _{eq} O _{eq}	177.4	177.6
μ (debyes)	0.5618	$9.845 \cdot 10^{-2}$

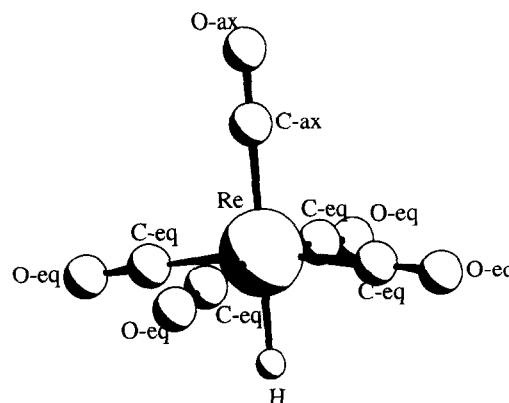


Fig. 2. Optimized geometry and atmo labels for the $\text{HRe}(\text{CO})_5$ complex.

the RHF level which increases by 0.012 Å when non-dynamical correlation is included. At the RHF level, the Re–carbonyl distance for the equatorial ligand appears to be somewhat larger than that for the axial one, although they are found to be similar at the CASSCF level. The lengthening observed in the bond distances at this level agrees with the fact that in the wave function some mix involving excitations to anti-bonding MOs are incorporated. Finally, as observed in most of these complexes, the molecular structure is found to feature an umbrella-type distortion of the equatorial carbonyl ligands towards the Re–H axis with a HRe–C bond angle of 84.7°. Another interesting electronic property of this compound reported in Table 1 is its dipole moment μ . At the RHF

Table 2
Selected computed diagonal force constants ($\text{mdyn}/\text{Å}$) and vibrational frequencies (cm^{-1}) for $\text{HRe}(\text{CO})_5$

	RHF		CASSCF		Exp ⁵
	<i>f</i>	ν	<i>f</i>	ν	
H–Re	2.2	1919	2.1	1870	1983
Re–CO _{eq}	2.5	385	2.4	370	
		424		426	
		430		421	
Re–CO _{ax}	2.8	436	2.4	408	
C–O _{eq}	19.0	2270	18.8	2267	
		2185		2174	
		2152		2120	
C–O _{ax}	18.3	2126	17.9	2089	2015
				2005	

Table 3

GGeometries and adsorption energies obtained from CASSCF calculations for $\text{HRe}(\text{CO})_5$ adsorbed on the MgO (100) surface (Å and kcal/mol)

	Model A	Model B	Model C
d(O–H)	2.783	2.646	2.117
E_{ads}	2.7	12.4	20.5

level its value is 0.5618 debye with the negative end pointing towards the hydrogen. As can be seen, the value of μ dramatically decreases at the CASSCF level and as we will see shortly, this effect will be of the most importance in the interpretation of the adsorption process. In Table 2 vibrational frequencies and diagonal force constants computed at both calculation levels are reported. As expected the RHF frequencies are larger than that obtained from the CASSCF calculations in agreement with the trends observed for the bond distances. These frequencies, on the other hand, are found in reasonably agreement with the experiment [5] supporting thus the reliability of the CASSCF wave functions.

3.2. Adsorption of the $\text{HRe}(\text{CO})_5$ complex

Preliminary attempts to obtain an adsorbate–surface equilibrium structure at the RHF level failed. Examination of the potential energy curve for the system showed that the interaction was always repulsive in disagreement with the ex-

periment. The reason for this repulsive behavior arises from the interaction between the dipole moment of the complex and the electrostatic field of the surface. These results prompted us to use a better wave function to describe the complex, namely the CASSCF approach. Effectively, with this level of theory the computed dipole moment is nearly zero as stated above and the interaction with the surface becomes now attractive. This result clearly shows that care has to be taken when RHF wave functions are used to describe the adsorption process of an organometallic since erroneous conclusions can be obtained.

Adsorbate–substrate distances and adsorption energies for the three models here considered are reported in Table 3. These distances have been determined numerically with the complex geometry frozen, however a full optimization for model A showed no significant changes. As can be seen in the Table 3 there is a noticeably lowering in the adsorbate–substrate distance when the size of the cluster modelling the surface increases. The same trend is observed for the adsorption energies. Thus, going from model A to model B, E_{ads} increases from 2.7 to 12.4 kcal/mol and to 20.5 kcal/mol when going to model C. These energies are not corrected for the basis set superposition error although such corrections are expected to be small since the distances between the surface oxides and the carbonyl ligands are rather large (about 4 Å). In

Table 4

Mulliken population analysis obtained from CASSCF calculations for $\text{HRe}(\text{CO})_5$ and relevant surface atoms ^a

	$\text{HRe}(\text{CO})_5$	Model A		Model B		Model C	
H	0.880	0.860		0.818		0.782	
Re	16.367	16.465		16.541		16.534	
C_{ax}	3.765	3.763		3.761		3.746	
O_{ax}	6.032	6.028		6.031		6.032	
C_{eq}	3.738	3.737		3.739		3.743	
O_{eq}	6.001	5.999		6.001		6.000	
O		10.004	(9.929)	9.846	(9.712)	9.958	(9.803)
Mg_1		–0.017	(0.017)	–0.101	(–0.046)	–0.184	(–0.022)
Mg_2		0.006	(0.003)	0.463	(0.255)	0.696	(0.567)

^a See Fig. 2 for atomic labels. Mg_1 and Mg_2 refers to surface and apical Mg^{2+} cations, respectively. Values between parentheses correspond to isolated surface.

any case, these results make clear that in the problem at hand, an extended model of the adsorption site is needed.

With the aim to understand these trends a Mulliken population analysis has been performed. As shown in Table 4, whatever the model is, the Mulliken populations for the C and O carbonyl atoms appear to be almost the same to that of the isolated complex. Likewise the hydrogen population decreases while that of Re raises showing that upon adsorption there is an electron density shift from the hydrogen atom towards the Re which appears to be more efficient as the size of the cluster increases. This increment in the net charge of the hydrogen atom would lead to a stronger interaction with the surface oxide in agreement with the observed trend. In order to understand the origin of the H–Re electron density shift we can examine the Mulliken populations of the surface atoms. As reported in Table 4, upon adsorption there is a small change in the populations of the oxygen and the four first layer magnesium ions (labelled as Mg₁). However when the cluster grows the population of the apical magnesium ion (Mg₂) features a noticeable increment. This electron density pushes the oxide electronic cloud away from the surface inducing a repolarization of the H–Re bond.

4. Concluding remarks

Although it has not been proven, the interaction between the HRe(CO)₅ complex and the MgO surface is mainly of electrostatic nature. To deal with this kind of interaction it is compulsory to correctly estimate the dipole moment of the adsorbate. As shown in this paper, a plain RHF wave function is not suitable to describe the dipole moment of the complex and leads to a repulsive interaction with the surface in disagreement with the experiment. However, when at least some of the non-dynamical correlation contributions are included in the wave function, the computed electronic properties become good

enough to overcome this problem. We have shown that for the system at hand it is enough to incorporate these contributions through a CASSCF wave function to obtain an adsorbate–substrate bound system.

On the other hand, we have shown that increasing the size of the cluster used to model the surface leads to larger adsorption energies. We have argued that this trend is due to an increment in the electron density at the surface which in turn polarizes the H–Re bond giving rise to a larger surface–hydrogen interaction. Obviously, the convergency of the cluster size versus the interaction energy has to be examined and further work in this direction is now in progress.

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