**SUMMARY OF ACCOMPLISHMENTS IN DOE-SPONSORED
PROJECT ENTITLED
METAL-SUPPORT BONDS IN SUPPORTED METAL CATALYSTS**

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This research project, now in its third year, is an investigation of the synthesis, structure, and bonding of a family of metal complexes, clusters, and particles on the surfaces of high-area metal oxide supports. The focus is the structure of the metal-support interface. Surface species have been prepared by synthetic organometallic chemistry on the support surfaces. The organometallic precursors are complexes of W, Re, Os, Ir, and Pt, including $\text{W}(\text{CO})_6$, $\text{HRe}(\text{CO})_5$, $\text{Re}_2(\text{CO})_{10}$, $\text{H}_3\text{Re}_3(\text{CO})_{12}$, $\text{H}_2\text{Os}(\text{CO})_4$, $\text{Ir}(\eta^3\text{-C}_3\text{H}_5)_3$, and $\text{Pt}(\eta^3\text{-C}_3\text{H}_5)_2$. The supports are primarily MgO and $\gamma\text{-Al}_2\text{O}_3$. The surface species have been characterized by infrared and EXAFS spectroscopies, among other techniques (Table 1).

The major results have been obtained for Re and Ir. A significant fraction of the effort has been devoted to finding conditions for preparation of nearly unique ("molecular") organometallic and metallic species on the support surfaces. We have found conditions for preparation of apparently unique subcarbonyls of W, Re, Os on support surfaces (Table 1). Iridium and platinum are more difficult to prepare in the form of stable subcarbonyls, being easily converted into the metallic form, giving structurally nonuniform crystallites on the supports; our results with iridium and platinum subcarbonyls are still preliminary (Table 1).

Table 1. Subcarbonyls formed from Organometallic Precursors

Precursor	Support	Symmetry indicated by carbonyl infrared spectrum	Structural formulation
W(CO) ₆	γ-Al ₂ O ₃	C _{3v}	W(CO) ₃ {OAl} ₃ ^a
	MgO	variable	mixture—no single species has been formed
W(¹³ CO) ₆	γ-Al ₂ O ₃	{experiments still in progress to determine ¹³ C and ¹⁸³ W NMR spectra}	
¹⁸³ W(CO) ₆	γ-Al ₂ O ₃		
{ HRe(CO) ₅ Re ₂ (CO) ₁₀ H ₃ Re ₃ (CO) ₁₂ }	MgO	C _{3v}	Re(CO) ₃ {OMg}{HOMg} ₂ ^b
Os ₃ (CO) ₁₂	γ-Al ₂ O ₃	C _{3v}	Os(CO) ₃ {OAl} ₃ ^a
Ir(CO) ₂ (acac)	γ-Al ₂ O ₃	C _{2v}	Ir(CO) ₂ {OAl} ₂ ^{a,c}
	MgO	C _{2v}	Ir(CO) ₂ {OMg} ₂ ^{a,c}
Pt(CH ₃) ₂ (COD)	γ-Al ₂ O ₃	C _{2v}	Pt(COD){HOAl} ₂ ^c

^a Oxo ligands not identified: may be O and/or OH.

^b Among others. See text and Table 2.

^c Preliminary results; interpretation tentative; experiments still in progress.

Some surface syntheses take place straightforwardly as a result of acid-base chemistry; for example, when the hydridorhenium precursors [H₃Re₃(CO)₁₂ and HRe(CO)₅] react with the basic MgO surface from organic solutions, they are chemisorbed. The former is deprotonated to give surface ion pairs involving [H₂Re₃(CO)₁₂]⁻ and surface Mg²⁺ ions, and the latter (a much weaker acid) gives a strongly bonded but undissociated surface species.

Other syntheses have been carried out with organometallic precursors that are not Brønsted acids, e.g., W(CO)₆ and Re₂(CO)₁₀. A family of rhenium carbonyls has been prepared on MgO. Simple physisorbed Re₂(CO)₁₀ has been formed at very low temperatures. When Re₂(CO)₁₀ is brought in contact with the MgO surface after it has been hydrated—and the contacting is carried out at -50°C, the organometallic is weakly adsorbed, with infrared spectra measured at low temperature

suggesting that the surface species is $\text{Re}_2(\text{CO})_9(\text{H}_2\text{O})$, hydrogen-bonded to the surface. When a solution of $\text{Re}_2(\text{CO})_{10}$ in an organic solvent is brought in contact with MgO powder at higher temperatures, it is chemisorbed and converted into $[\text{Re}_2(\text{CO})_9]^{2-}$ (which can be extracted into solution by ion exchange, e.g., with a solution of $[\text{PPN}]\text{Cl}$). The surface chemistry in this preparation mimics that occurring in basic solutions. The dianions are inferred to be ion-paired to the surface.

When any of these surface species is oxidized, in O_2 or by treatment under vacuum (the surface OH groups being sufficient oxidizing agents), robust rhenium subcarbonyls are formed; these are formulated as $[\text{Re}(\text{CO})_3 \{ \text{OMg} \}_x \{ \text{HOMg} \}_{3-x}]$, on the basis of infrared and EXAFS spectra, among other data. (Here the braces denote groups (ligands) terminating the MgO support.) Since the subcarbonyls involve covalent bonding of the metal to the support, they were of primary interest in the research.

To begin to clarify the issue of just what surface ligands provided by the MgO are part of the rhenium subcarbonyls, experiments were done with rhenium subcarbonyls on MgO supports having controlled degrees of hydroxylation and methoxylation. Infrared spectra in the range near 3700 cm^{-1} gave evidence of the surface hydroxyl ligands, for example, and changes in the carbonyl spectrum with surface composition led to identification of a family of subcarbonyls including $\text{Re}(\text{CO})_3 \{ \text{OMg} \}_3$, $\text{Re}(\text{CO})_3 \{ \text{HOMg} \}_3$ (as well as mixtures of the two), and $\text{Re}(\text{CO})_3 \{ \text{CH}_3\text{OMg} \}_3$ (Table 2).

Table 2. Family of Rhenium Subcarbonyls prepared from $\text{Re}_2(\text{CO})_{10}$

Support	Symmetry indicated by carbonyl infrared spectrum ^a	Structural formulation
Dehydroxylated MgO	C_{3v}	$\text{Re}(\text{CO})_3 \{ \text{OMg} \}_3$
Fully hydroxylated MgO	C_{3v}	$\text{Re}(\text{CO})_3 \{ \text{HOMg} \}_3$
Methoxylated MgO	C_{3v}	$\text{Re}(\text{CO})_3 \{ \text{CH}_3\text{OMg} \}_3$
Partially dehydroxylated MgO	C_{3v}	$\text{Re}(\text{CO})_3 \{ \text{OMg} \}_x \{ \text{HOMg} \}_{3-x}$

We have made substantial progress in characterizing the rhenium subcarbonyls by EXAFS spectroscopy and temperature-programmed decomposition (TPDE) as well. The EXAFS data provide quantitative structural information; a model of the rhenium subcarbonyl is illustrated in Figure 1.

Figure 1. Structural model of rhenium subcarbonyl on MgO. The distances were estimated from EXAFS data.

EXAFS results for several metal subcarbonyls are summarized in Table 3. The average metal-support oxygen, metal-carbon, and metal-carbonyl oxygen (O*) distances are similar for each member of the family for these third-row metals. The characteristic metal cation-surface oxygen distance is about 0.21 nm.

This same approximate distance has been reported by Koningsberger, Prins, and coworkers for a number of highly dispersed supported metal aggregates (or crystallites) on Al_2O_3 and TiO_2 supports [Van't Blik et al., 1985; Martens et al., 1988; Koningsberger et al., 1985], following evacuation of the samples. These workers have consistently also reported a longer metal-support oxygen distance (typically, about 0.27 nm) for the same samples after reduction by H_2 (and in the presence of H_2). The comparison with the subcarbonyl data is intriguing and suggests that the shorter distances characteristic of the supported metals might be indicative of

Table 3. Metal Subcarbonyls: Structural Characterization by EXAFS Spectroscopy

Precursor	Support	Structural Formulation	EXAFS					
			M-O ^a		M-C ^b		M-O ^{*c}	
			CN	distance, nm	CN	distance, nm	CN	distance, nm
Re ₂ (CO) ₁₀	MgO	Re(CO) ₃ (OMg)(HOMg) ₂	3.1	0.214	2.6	0.189	2.6	0.307
H ₃ Re ₃ (CO) ₁₂	MgO	Re(CO) ₃ (OMg)(HOMg) ₂	2.7	0.215	3.0	0.188	3.0	0.309
Os ₃ (CO) ₁₂	γ-Al ₂ O ₃	Os(CO) ₃ (OAl) ₃ ^{d*}	3	0.217	2.8	0.191	—	0.305
Re ₂ Pt(CO) ₁₂	γ-Al ₂ O ₃	Re(CO) ₃ (OAl)(HOAl) ₂ ^e	3.0 ^e	0.212 ^e	2.9 ^e	0.185 ^e	2.5	0.304
		Pt(CO) ₂ (OAl) ₃ ^d		0.21 ^f		0.18 ^f		0.30 ^f

^a Metal-oxygen parameters; CN is coordination number

^b Metal-carbonyl carbon parameters.

^c Metal-carbonyl oxygen parameters.

^d Oxo ligands not identified (O and/or OH)

^e Preliminary results

^f Preliminary and tentative; analysis of data in progress.

*Ref.: Duivenvoorden, F. B. M., Koningsberger, D. C., Uh, Y. S., and Gates, B. C., *J. Am. Chem. Soc.*, **108**, 6254 (1986).

cation-oxygen interactions; these are not evident in reduced catalysts containing larger aggregates (crystallites), and a question is raised about whether the metal was fully reduced to the metallic state in the highly dispersed supported metals after evacuation. Further, for all these samples it is still not known just what the surface groups (e.g., O or OH) are.

When H₃Re₃(CO)₁₂ was adsorbed from organic solution onto γ-Al₂O₃, a chemisorbed species was formed. When this sample was treated in H₂ at 400°C, a new structure was formed, which has been characterized by various spectroscopies. The metal is cationic, as indicated by XPS and XANES, and the EXAFS data are consistent with a simple structure: the Re-Re coordination number is 2, indicating that the surface structure is still predominantly trirhenium, even after the high-temperature treatment in H₂. Further, the average Re-Re distance is 0.267 nm, which is substantially less than the Re-Re distance in bulk Re metal, 0.274 nm.

Figure 2. Model of a trirhenium structure on the alumina surface. The structure is formulated on the basis of EXAFS data, the surface is assumed to be the (111) surface.

These results have been used to formulate a model of the surface structure, shown in Figure 2. The short Re-Re distance suggests that the surface species has Re-Re multiple bonds; in this sense, it is roughly comparable to some molecular structures with multiple metal-metal bonds, such as that shown in Figure 3. The supported metal species is new and remarkable for its structural simplicity and uniformity; it is apparently more akin to the "molecular" subcarbonyls than to supported metallic species.

Figure 3. A metal cluster with multiple metal-metal bonds, $\text{Re}_3(\mu\text{-O-}i\text{Pr})_3(\text{O-}i\text{Pr})_6$. (Hoffman et al., *J. Am. Chem. Soc.*, **111**, 1531 (1989).

To broaden the comparison and include structures characteristic of more conventional supported metal catalysts, some samples incorporating the rhenium subcarbonyls were treated in H_2 to give metallic particles on the MgO support. However, the subcarbonyl of this relatively oxophilic metal is highly resistant to reduction (at least on a partially hydroxylated surface), and temperatures well in excess of $400^\circ C$ were required for substantial metal crystallite formation. Samples incorporating Re metal particles formed by treatment in H_2 at $500^\circ C$ have been characterized by EXAFS spectroscopy. The average Re-Re coordination number was found to be 6.3. However, only a fraction of the Re was reduced to metal; the rest remained in difficult-to-characterize structures having cationic Re.

Since one of the goals was to characterize the metal-support interface in supported metals with the metal fully reduced and the metal structure quite uniform, we made efforts with a $\gamma-Al_2O_3$ -supported sample prepared by deposition of $Os_3(CO)_{12}$, followed by oxidation to form the subcarbonyl (apparently in the form of triosmium ensembles [Schwank et al., 1983; Dossi et al., 1989]). These samples were treated in H_2 in an attempt to form supported metallic species. The EXAFS results showed that the supported Os structures were always highly dispersed (and the Os-Os coordination numbers indicated that most were not much larger than Os_3), but we could not obtain fully consistent and reproducible EXAFS results from one sample to the next. The causes of the inconsistency are not understood; we speculate that the degree of reduction and aggregation of the Os may be quite sensitive to surface properties such as the degree of hydroxylation (although we attempted to control it carefully); we speculate that Os is too oxophilic to allow easy reduction to the metallic form without substantial sintering, at least on $\gamma-Al_2O_3$.

The results indicate that W, Re, and, likely, Os are too oxophilic to allow clean, simple reduction of the subcarbonyls to form highly dispersed particles of metal without substantial aggregation on the supports. Therefore, to meet our goal to investigate the metal-support interface in supported catalysts with highly dispersed metallic structures, we have also worked with the more noble Ir and Pt. The results for Pt are all consistent with the interpretation that the surface species formed from the organometallic precursors $Pt(CH_3)(COD)$ and $Pt(\eta^3-C_3H_5)_2$ were readily

converted on the oxide supports to rather large particles of metallic Pt. These are unremarkable samples and have not been characterized in detail.

Success was achieved with Ir: with the basic support MgO, we have been able to use $\text{Ir}(\eta^3\text{-C}_3\text{H}_5)_3$ and $\text{H}_4\text{Ir}_4(\text{CO})_{12}$ to form high yields of $[\text{HIr}_4(\text{CO})_{11}]^-$ and $[\text{Ir}_6(\text{CO})_{15}]^{2-}$, which were identified by their surface IR and EXAFS spectra and which could be extracted into solution by cation metathesis with $[\text{PPN}]\text{Cl}$. This surface synthetic chemistry mimics the organometallic chemistry in basic solutions.

We have identified conditions to decarbonylate these surface-bound carbonyl anions without substantially changing the nuclearity (the number of metal atoms) in the clusters and characterized the surface-bound decarbonylated Ir_4 and Ir_6 clusters with EXAFS spectroscopy [Maloney et al., in press; Maloney et al., to be published]. The data were compared with data for a sample made from $\text{Ir}_4(\text{CO})_{12}$ and treated with H_2 under forcing conditions to give larger particles of Ir having, on average, substantially more than 6 Ir atoms (these samples are structurally nonuniform, being characteristic of more typical supported metal catalysts).

The EXAFS data of Figure 4 show how valuable the supported Ir_4 and Ir_6 samples are for characterization of the metal-support interface; much of the EXAFS signal is characteristic of this interface, whereas in the sample that was reduced more vigorously, the Ir-Ir interactions begin to dominate, making characterization of the metal-support interface less accurate. The structural uniformity of the supported Ir_4 and Ir_6 samples contributes to the exactness of the EXAFS characterizations; these samples are excellently suited to this method.

Structural parameters determined from the EXAFS analysis are summarized in Table 4. The longer metal-oxygen distances are close to the values determined for other highly dispersed oxide-supported metals by Koningsberger and Prins, as mentioned above. Remaining questions include the following: what are the oxygen-containing surface ligands? Are they O and OH? Where is the hydrogen in the metal-support interface? These questions provide part of the motivation for the proposed continuation of this research.

Figure 4. Relative contributions of the Ir-Ir, Ir-O, and Ir-Mg contribution in the Fourier transform of the EXAFS signals for Ir₄/MgO (A) and Ir₆/MgO (B).

There is a clear pattern in the results (consistent with broad experience): the relatively oxophilic metals (W, Re) form stable subcarbonyls and are difficult to reduce to the metallic forms of supported metal catalysts. On the other hand, the more noble metals to the right of the third row of the periodic table (Ir, Pt) are easily reduced to the metallic form, and formation and stabilization of the subcarbonyls is not so easy. The implication is that there may be only a few (if any) metals that allow formation of structurally simple surface species ranging from subcarbonyls to metals; we have come closest to meeting this goal with iridium, which is therefore chosen for more thorough characterizations proposed in the next phase of the research.

These generalizations about the metals raise some intriguing questions (which have been recognized before): what structures can be formed when a pair of metals is used, one oxophilic and one noble? We have begun to answer the questions with experiments done with Re-Pt samples formed from Re₂Pt(CO)₁₂. When deposited from organic solution onto the surface of γ -Al₂O₃, this cluster breaks apart, forming rhenium subcarbonyl (characterized by infrared and

Table 4.

A. Structural parameters determined by EXAFS for the MgO-supported sample modeled as Ir₄/MgO.

Contribution	CN	distance, nm	Debye-Waller factor, $\Delta\sigma^2, \text{\AA}^{-2}$	Inner potential correction, E_0, eV
Ir-O	3.2	0.261	0.0066	-1.52
Ir-Ir	3.0	0.269	0.0011	1.22

B. Structural parameters determined by EXAFS for the MgO-supported sample modeled as Ir₆/MgO.

Contribution	CN	distance, nm	Debye-Waller factor, $\Delta\sigma^2, \text{\AA}^{-2}$	Inner potential correction, E_0, eV
Ir-O	2.1	0.254	0.0018	1.37
Ir-Ir	3.7	0.269	0.0001	4.94
Ir-O	1.3	0.322	0.0020	5.39

EXAFS spectra) and less-well characterized Pt structures, possibly also subcarbonyls. Under carefully chosen treatment conditions (H_2 at 400°C), the sample is converted into a bimetallic characterized by infrared, XPS, EXAFS, and XANES. The data show that Re is in a low positive oxidation state interacting with oxygen of the support but not present at the surface (no Re carbonyls are formed). Pt, on the other hand, is present at the surface, but has hardly any near-neighbor oxygens. The surface structure is modeled as shown in Figure 5. The Re is inferred to be inside the supported bilayer structure. The oxophilic character of the Re accounts for its role anchoring the Pt and, we speculate, helping to maintain its dispersion on the alumina support. This may be one of the roles of Re in the industrial Re-Pt/ Al_2O_3 reforming catalysts.

Figure 5. Structural model of a supported Re-Pt "bilayer" formed from $\text{Re}_2\text{Pt}(\text{CO})_{12}$ on $\gamma\text{-Al}_2\text{O}_3$. The structural parameters were determined by EXAFS spectroscopy; the surface of the support is assumed to be the (111) face of $\gamma\text{-Al}_2\text{O}_3$.

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PUBLICATIONS RESULTING FROM THIS RESEARCH

1. "Catalyst Design: Multicenter Surface Sites," Y. Iwasawa and B. C. Gates, *CHEMTECH*, **19**, 173 (1989).
2. "Supported Metals and Supported Organometallics," B. C. Gates and H. H. Lamb, *J. Mol. Catal.*, **52**, 1 (1989).

3. "Surface Catalytic Sites Prepared from $\text{HRe}(\text{CO})_5$ and $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$: Mononuclear, Trinuclear, and Metallic Rhenium Catalysts Supported on MgO ," P. S. Kirlin, F. B. M. van Zon, D. C. Koningsberger, and B. C. Gates, *J. Phys. Chem.*, accepted for publication.
4. "Cationic Trirhenium Rafts on γ -Alumina: Characterization by X-ray Absorption Spectroscopy," A. S. Fung, P. A. Tooley, D. C. Koningsberger, M. J. Kelley, and B. C. Gates, *J. Phys. Chem.*, accepted for publication.

PUBLICATIONS IN PREPARATION

1. "Characterization of the Metal-Support Interface in Supported Metal Catalysts by EXAFS Spectroscopy: Highly dispersed Iridium Clusters and Rafts on MgO ," F. B. M. van Zon, S. D. Maloney, B. C. Gates, and D. C. Koningsberger, *J. Am. Chem. Soc.*, to be submitted.
2. "Rhenium Subcarbonyls on MgO : Identification of the Surface Oxo Ligands by Infrared Spectroscopy," C. J. Papile and B. C. Gates, *Langmuir*, to be submitted.
3. "Rhenium Subcarbonyls on MgO : Characterization of the Metal-Support Interface by Infrared and Extended X-Ray Absorption Fine Structure Spectroscopies," C. J. Papile, J. R. Chang, and B. C. Gates, *J. Phys. Chem.*, to be submitted.
4. "Reaction of $\text{Re}_2\text{Pt}(\text{CO})_{12}$ with $\gamma\text{-Al}_2\text{O}_3$: Breakup of the Clusters and Formation of Rhenium Subcarbonyls," J. R. Chang, A. S. Fung, and B. C. Gates, to be published.
5. "An Alumina-Supported Catalyst Prepared from $[\text{Re}_2\text{Pt}(\text{CO})_{12}]$: Evidence of a Surface Bilayer Structure from Extended X-Ray Absorption Fine Structure and other Spectroscopies," A. S. Fung, M. J. Kelley, D. C. Koningsberger, and B. C. Gates, to be published.
6. "Structural Characterization of Tungsten Subcarbonyls on $\gamma\text{-Al}_2\text{O}_3$," L. Gron, N. Triantafyllou, K. M. Sanchez, M. Wolfer, and B. C. Gates, to be published.
7. "Highly Dispersed Osmium on γ -Alumina: Characterization by Extended X-Ray Absorption Fine Structure Spectroscopy," H. H. Lamb, D. C. Koningsberger, and B. C. Gates, to be published.

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