Adsorption and Reaction of $[\text{Re}_2(\text{CO})_{10}]$ on Ultrathin MgO Films Grown on a Mo(110) Surface: Characterization by Infrared Reflection–Absorption Spectroscopy and Temperature-Programmed Desorption


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The decarbonylation of $[\text{Re}_2(\text{CO})_{10}]$ on ultrathin MgO(111) films (~50 Å) grown on a Mo(110) substrate was investigated with infrared reflection–absorption spectroscopy and temperature-programmed desorption/decomposition. When $[\text{Re}_2(\text{CO})_{10}]$ was adsorbed at 320 K, it reacted with the MgO(111) surface, forming a rhenium subcarbonyl, $[\text{Re}(\text{CO})_4\{\text{OMg}\}]_2$, where $\{\text{OMg}\}$ represents oxygen on the MgO(111) surface. Upon heating to temperatures >400 K, $[\text{Re}(\text{CO})_4\{\text{OMg}\}]_2$ was decarbonylated, forming $[\text{Re}(\text{CO})_3\{\text{OMg}\}]$. Further heating to temperatures >600 K induced the formation of rhenium metal clusters. When it was adsorbed at 110 K, $[\text{Re}_2(\text{CO})_{10}]$ condensed on MgO(111), with a fraction of the first layer decomposing to form $[\text{Re}(\text{CO})_4\{\text{OMg}\}]_2$. In temperature-programmed desorption experiments, $[\text{Re}_2(\text{CO})_{10}]$ multilayers desorbed at 295 K. An unidentified rhenium carbonyl species, probably rhenium pentacarbonyl, desorbed at 350 K. The CO stretching frequencies of the rhenium subcarbonyls are highly nonuniform, and the surfaces are heterogeneous because the metal clusters or crystallites are highly nonuniform in size and shape and the support surfaces are heterogeneous. In attempts to understand the structure of the metal–support interface better, experiments have been done with simple mononuclear (single-metal-atom) complexes bonded to the surfaces of metal oxide powders. Their structures have been characterized with a variety of techniques, including infrared spectroscopy, temperature-programmed desorption/decomposition (TPD), and extended X-ray absorption fine structure (EXAFS) spectroscopy. Models have been proposed for these structures, accounting for both metal–CO bonding and metal–support bonding. However, the surfaces of the metal oxide powders are highly nonuniform, and the available physical data provide only average structural information. Thus, the identities of the crystal planes on which the structures are bonded are unknown, and the possibility that the structures exist largely at defect sites has been virtually impossible to assess.

The goals of this work were to prepare rhenium subcarbonyls like those described above on a relatively well-defined metal oxide surface under ultrahigh-vacuum conditions. $[\text{Re}_2(\text{CO})_{10}]$ was chosen to be the organometallic precursor because it has been shown to lead to well-defined structures on MgO powders and has a vapor pressure high enough to allow for vapor deposition in ultrahigh-vacuum apparatus. The surface was chosen to be that of a MgO film because thin MgO films can be easily prepared and characterized with an array of surface science techniques. Thin films on metal single crystals are more attractive than bulk metal oxide single crystals because they are good conductors and can be more easily cleaned, cooled, and reheated than the bulk insulating materials, and they do not become charged as bulk metal oxides do in experiments carried out with impinging beams of charged particles. Because the aforementioned rhenium subcarbonyl has C$_{3v}$ symmetry, the MgO thin films were chosen to be MgO(111), which, fortunately, can be grown on a Mo(110) substrate.

The samples were characterized by temperature-programmed desorption/decomposition (TPD) and infrared reflection–absorption (IRAS) spectroscopy because the results allow a direct comparison with results characterizing the powder samples.

Experimental Methods

The TPD and IRAS experiments were performed in an ultrahigh-vacuum chamber described previously. This chamber is equipped with Auger electron spectroscopy, a UTI mass spectrometer, and a Mattson Cygnus 100 FTIR spectrometer. The characterization of the MgO films was done in a separate chamber equipped with X-ray photoelectron (XPS), Auger electron (AES), and ion scattering (ISS) spectroscopies and low-energy electron diffraction (LEED). Identical procedures were used to prepare the MgO films in the two chambers. The base pressure of each chamber was <10$^{-9}$ Torr.

Preparation and Characterization of Ultrathin MgO(111) Film on a Mo(110) Substrate

Thin MgO films were prepared by evaporating pure metallic magnesium in 5 × 10$^{-7}$ Torr of oxygen (O$_2$) onto a clean Mo(110) substrate at room temperature; the samples were subsequently annealed to 800 K. This method is similar to that used to prepare MgO(100) on Mo(100). Mo(110) was cleaned by heating in oxygen at 1200 K and flashing to 2000 K in vacuo. The MgO films were characterized by LEED and He$^+$ ISS. LEED exhibited a good (1 × 1) hexagonal pattern, demonstrating (111) orientation of the MgO films. XPS and AES showed the film to have the stoichiometry of MgO and the absence of the Mg$_2$O$_3$ state. ISS showed the surface to be composed of both oxygen and magnesium. The stability of the MgO films was investigated with temperature-programmed desorption; the films were found to be stable at temperatures <1400 K, and at higher temperatures the MgO was reduced by the Mo substrate, forming volatile MoO$_3$ and Mg vapor. The MgO films used in this investigation were approximately 50 Å thick.

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Small CO desorption features were also observed at 300-400 K of the \([\text{Re}^*(\text{CO})_6]\) precursor (-5 monolayers) at 110 K. The intensities of the Re(CO)_2+ rhenium-containing fragments by using the same mass spectrometer. Adsorption of \([\text{Re}_2(\text{CO})_{10}]\) at 110 K. The identity of the \([\text{Re}_2(\text{CO})_{10}]\) was verified by mass spectrometry.

The 350 K peak, with a tail extending to 450 K, includes a rhenium-containing component other than \([\text{Re}_2(\text{CO})_{10}]\). The relative intensities of the five rhenium-containing fragments associated with the 350 K peak do not agree with those found for the 295 K sublimation peak. The intensities of the Re(CO)_5^+ and Re(CO)_4^+ fragments associated with the 350 K peak are higher than those associated with the 295 K peak. The identity of the species desorbing at 350 K is not known, however, because of the insufficient range of the mass spectrometer.

The major CO evolution was observed at 465 K (Figure 1B). Small CO desorption features were also observed at 300-400 K and at temperatures >700 K. The evolution of CO during the TPD of \([\text{Re}_2(\text{CO})_{10}]\) was monitored at \(m/q = 12\) (C^+). \(\text{C}^+ (m/q = 12)\) was chosen instead of CO^+ (\(m/q = 28\)) to allow simultaneous monitoring of CO at \(m/q = 12\) (C^+) and the rhenium-containing fragments by using the same mass spectrometer sensitivity scale.

Infrared Reflection–Absorption Spectra of Samples Prepared by Adsorption of \([\text{Re}_2(\text{CO})_{10}]\) at 110 K. After the initial adsorption of the \([\text{Re}_2(\text{CO})_{10}]\) precursor (~5 monolayers) at 110 K, bands in the v_CO region of the infrared spectrum were observed at 2130, 2110, 2083, 2052, and 2025 (sh), and 1970 cm\(^{-1}\) (Figure 2A). Heating the sample to temperatures <250 K did not change the spectrum. As the temperature increased to >250 K, these bands decreased in intensity (Figures 2A,B), because of the desorption of \([\text{Re}_2(\text{CO})_{10}]\). When the temperature was in the range between 310 and 330 K (between the temperatures at which the two rhenium carbonyl desorption peaks were observed in the TPD spectra), the spectrum was quite complicated. Peaks at ~2108, 2058, 2045, 2008, and 1960 cm\(^{-1}\) were observed (Figure 2B). After the sample had been heated to 500 K, ReCO bands remained only at 2054 and 1933 cm\(^{-1}\) (Figure 2B). Continued heating to 600 K resulted in an apparent shifting of the higher-wavenumber band to 2036 cm\(^{-1}\) (Figure 2B).

Figure 3 shows IRAS spectra for a sample prepared by dosing ~2 monolayers of \([\text{Re}_2(\text{CO})_{10}]\) on a MgO film heated to the indicated temperatures. The spectra are similar to those of Figures 1A and B.
2A,B, but they are slightly simpler. At 120 K, two major bands were observed, at 2081 and 2050 cm$^{-1}$. Upon heating to temperatures $>$250 K, additional bands were observed at 2110 and 2008 cm$^{-1}$. Heating to temperatures $>$400 K resulted in two major bands at 2058 and 1942 cm$^{-1}$.

**Temperature-Programmed Desorption of Samples Prepared by Adsorption of $[\text{Re}_2(\text{CO})_{10}]$ at 320 K.** Figure 4 shows the CO evolution during temperature-programmed desorption following saturation exposure of $[\text{Re}_2(\text{CO})_{10}]$ at room temperature. CO desorbed at 550 K, $\sim$70 K higher than the temperature of desorption of CO when the $[\text{Re}_2(\text{CO})_{10}]$ had been adsorbed at 110 K.

**Infrared Reflection-Absorption Spectra of Samples Prepared by Adsorption of $[\text{Re}_2(\text{CO})_{10}]$ at 320 K.** After exposing the MgO film to $[\text{Re}_2(\text{CO})_{10}]$ vapor (exposure $\sim$5 monolayers) at 320 K, the infrared spectra exhibited four well-resolved bands, at 2108, 2043, 2004, and 1958 cm$^{-1}$ (Figure 5). When the sample was heated to 400 K, the bands at 2108, 2043, and 2004 cm$^{-1}$ disappeared, and a new band emerged at 2052 cm$^{-1}$. Further increases in the temperature led to decreased intensities of the bands at 2052 and 1935 cm$^{-1}$ and also led to shifts of these bands to lower frequencies.

**Preadsorption of Water.** Approximately 2 monolayers of water was introduced onto the MgO thin film at 110 K, followed by the adsorption of $[\text{Re}_2(\text{CO})_{10}]$. Both the TPD and infrared data were nearly identical to the data characterizing samples prepared by adsorption of $[\text{Re}_2(\text{CO})_{10}]$ in the absence of water (data not shown). However, the final rhenium coverage following $[\text{Re}_2(\text{CO})_{10}]$ decomposition on the water-precovered surface was only approximately half of that observed following decomposition of $[\text{Re}_2(\text{CO})_{10}]$ adsorbed onto a clean MgO film. Multilayer water
Water. After the sample had been heated to 300 K, the band positions were nearly identical to those observed prior to adsorption of water.

Reversibility of Decarbonylation. After the sample prepared from $[\text{Re}_2(\text{CO})_{10}]$ adsorbed on MgO at 100 K had been decarbonylated by heating to 1000 K, it was exposed to 20 langmuirs of CO (20 μTorr·s). The infrared spectrum exhibited a single νCO band at 2040 cm$^{-1}$, and the subsequent temperature-programmed desorption spectrum included a CO evolution peak at 430 K (data not shown).

Discussion

Multilayers of $[\text{Re}_2(\text{CO})_{10}]$ on MgO. Both the TPD and the infrared data show that exposure of the MgO film to $[\text{Re}_2(\text{CO})_{10}]$ at 110 K led to formation of rhenium carbonyl multilayers. The formation of these bulklike $[\text{Re}_2(\text{CO})_{10}]$ multilayers resulting from the condensation of the $[\text{Re}_2(\text{CO})_{10}]$ on the cold MgO surface was not unexpected. For example, $[\text{Re}_2(\text{CO})_{10}]$ crystals have been produced by sublimation onto a cold finger. The TPD experiments showed that the multilayers are stable at temperatures <250 K, and the corresponding desorption energy is nearly the same as the heat of sublimation of $[\text{Re}_2(\text{CO})_{10}]$.

The infrared spectra characteristic of the multilayers (Figure 2A), which exhibited major νCO bands at 2083, 2052, 2025 (sh), and 1970 cm$^{-1}$, agree with those reported for $[\text{Re}_2(\text{CO})_{10}]$. Solvated $[\text{Re}_2(\text{CO})_{10}]$ (which has $D_{4h}$ symmetry) has three infrared-active νCO bands, $b_2(e = \text{equatorial}), b_1(a = \text{axial})$, and $a_1$, with frequencies of 2070, 1976, and 2014 cm$^{-1}$, respectively (Table 1). In the infrared spectrum of single-crystal $[\text{Re}_2(\text{CO})_{10}]$, these bands are split into longitudinal (LO) and transverse-optical (TO) branches with frequencies shown in Table 1. Since only the LO modes are active because of the selection rules of infrared reflection–absorption, the three bands at 2083, 2051, and 1970 cm$^{-1}$ are assigned to the LO of $b_2(e), a_1$, and $b_1(a)$, respectively. In the infrared spectrum of single-crystal $[\text{Re}_2(\text{CO})_{10}]$, the positions of these LO bands are 2086, 2048, and 1970 cm$^{-1}$. The intensities of these three bands in the solution spectrum of $[\text{Re}_2(\text{CO})_{10}]$ are all roughly the same, but the $b_1(a)$ band is much weaker than the other two bands in the spectrum of the multilayers of $[\text{Re}_2(\text{CO})_{10}]$ on MgO (Figure 2A). This comparison suggests that the Re–Re bond is nearly parallel to the MgO surface, since the CO stretch of the $b_1(a)$ band has a dipole moment along the Re–Re bond.

The weak band at 2130 cm$^{-1}$ and the shoulder at 2025 cm$^{-1}$ observed for the multilayers of $[\text{Re}_2(\text{CO})_{10}]$ are attributed to νCO bands corresponding to $a_1(e = \text{equatorial})$ and $e_2$ molecular symmetry, which have values of 2125 and 2025 cm$^{-1}$ for $[\text{Re}_{20}(\text{CO})]_2$ single crystals. These two bands are Raman-active and infrared-inactive. However, the data are consistent with the suggestion that the molecular symmetry of the first several monolayers of $[\text{Re}_2(\text{CO})_{10}]$ on the MgO surface is distorted, so that the $a_1(e)$ and $e_2$ modes are infrared-active in the IRAS experiments.

The weak band at 2110 cm$^{-1}$ does not correspond to any bands reported for $[\text{Re}_2(\text{CO})_{10}]$ single crystals or in solution, and thus this band is attributed to other surface rhenium carbonyl species. The intensity of this band increased upon heating of the sample from 100 to 250 K (Figure 2A), in which temperature region no $[\text{Re}_2(\text{CO})_{10}]$ desorption was observed. The identity of the rhenium carbonyl species characterized by the 2110 cm$^{-1}$ band is discussed below.

Decarbonylation of $[\text{Re}_2(\text{CO})_{10}]$ on MgO(111). In each of the temperature-programmed desorption experiments with the samples prepared by adsorption of $[\text{Re}_2(\text{CO})_{10}]$ on MgO at <200 and 320 K, there was only one major CO evolution peak, observed at 465 and 550 K, respectively (Figures 1B and 4). This CO evolution occurred at temperatures higher than those at which rhenium-containing fragments desorbed (Figure 1A). Since CO
lignards were lost from the Re, other ligands may have replaced them. If the other ligands were rhenium, the surface species would be metallic rhenium clusters, and if the ligands were oxygen, the surface species would be rhenium subcarbonyls bound to the surface by Re-O bonds. The infrared spectra (Figures 2B and 5) demonstrate the presence of several rhenium subcarbonyl species in the temperature range 300–500 K resulting from the heating of [Re2(CO)10] multilayers on the MgO film. The infrared and TPD results taken together suggest that these rhenium subcarbonyl species have similar thermal stabilities. The evidence for these surface species is discussed in the following sections.

Identification of Rhenium Subcarbonyls. Samples Formed by Adsorption of [Re2(CO)10] at 320 K. After the adsorption of [Re2(CO)10] onto the MgO thin film at 320 K, the infrared spectrum exhibited four peaks, at 2108, 2043, 2004, and 1958 cm⁻¹. The 2108-cm⁻¹ peak is characteristic of the rhenium tetracarbonyl dimer [Re(CO)4X2] (X = Cl, Br, I). 17 The other three bands also agree with the bands of rhenium tetracarbonyldimer. For example, [Re(CO)4Cl2] exhibits four νCO bands, at 2114, 2032, 2000, and 1959 cm⁻¹ (Table 1). 17 McKenna et al. 1 reported a band at 2101 cm⁻¹ to be characteristic of the surface-bound rhenium tetracarbonyldimer with a Re-Re bond, [Re2(CO)4(OSi)], where the braces represent groups terminating SiO2. Thus, the infrared results are consistent with the inference that the species formed on MgO was [Re(CO)4(OMg)], or possibly a mononuclear rhenium subcarbonyl such as [Re(CO)4(OMg)], which was formed during the adsorption of [Re2(CO)10] on the MgO film at 320 K.

Heating of the sample caused further decarbonylation and transformation of the tetracarbonyl species as evidence by the infrared spectra of Figure 5. After heating to 400–500 K, only two νCO bands were observed in the infrared spectrum, at 2052 and 1935 cm⁻¹. These bands are attributed to rhenium subcarbonyls, and not to CO chemisorbed on rhenium clusters, because CO chemisorbed on rhenium crystallites exhibits 18 a single band at ~2035 cm⁻¹ and desorbs at ~430 K. The spectra resemble those reported for rhenium tricarbonyls on MgO powder. 5,4,6 These surface-bound subcarbonyls have been formulated on the basis of infrared, TPD, extended X-ray absorption fine structure, and other data as [Re(CO)3(OMg)(HOMg)], where 0 ≤ x ≤ 3. 2,4,6

A variety of rhenium carbonyl precursors have been used to prepare rhenium subcarbonyls on metal oxide powders. They include [HRe(CO)5], [Re2(CO)10], 1,1,4 and [H3Re2(CO)12] 2,4 (Table 1). The formation of the rhenium tricarbonyls from the latter two implies that fragmentation reactions (Re-Re bond breaking) took place on the metal oxide surfaces, consistent with the postulated formation of mononuclear rhenium subcarbonyls on the MgO film.

The bands characterizing the rhenium tricarbonyls on the MgO film were observed at slightly higher wavenumbers than those characterizing rhenium tricarbonyls on MgO powders. The carbonyl stretching frequencies characterizing the latter samples have been reported to increase with the degree of dehydroxylation. 5,6 The MgO powders contained hydroxyl groups, even after treatment at high temperatures, whereas the MgO films gave no indication in the infrared spectra of such groups. Thus, the difference in the infrared spectra of the supported rhenium subcarbonyls is attributed to the different ligands offered by the two surfaces; these were O on the MgO film and O and OH on the MgO powders. Thus, we infer that the species supported on the MgO film were [Re(CO)4(OMg)]. The MgO powder-supported species [Re(CO)4(OMg)] has been inferred from the infrared spectra to have pseudo-C3v symmetry. 5,4 Therefore, we assign the bands at 2052 and 1935 cm⁻¹ characterizing the MgO film-supported sample to the symmetric and antisymmetric carbonyl stretching vibrations in [Re(CO)4(OMg)], respectively.

Samples Formed by Adsorption of [Re2(CO)10] at 110 K. After the adsorption of [Re2(CO)10] multilayers at 110 K and the subsequent heating to 300–400 K, the infrared bands were not well resolved, indicating that several different species may have coexisted on the surface. A weak band appeared at 2110 cm⁻¹ immediately upon adsorption of [Re2(CO)10] at 110 K and increased in intensity as the sample was heated in the range 120–310 K (Figure 3). This band is characteristic of dimeric rhenium tetracarbonyls, as stated above. Thus, we suggest that a surface-bound rhenium tetracarbonyldimer, [Re(CO)4(OMg)], had been formed at 110 K. This species is inferred to have been present with the multilayers of [Re2(CO)10] on the MgO surface at 110 K.

After heating to 330 K, a temperature greater than that at which multilayer [Re2(CO)10] desorbed, the corresponding infrared bands were much broader than those observed for [Re2(CO)10] adsorbed at 320 K. The infrared bands at 2108, 2045, and 2008 cm⁻¹ (Figure 2B) suggest that [Re(CO)4(OMg)] was still present on the surface under these conditions. Other unidentified rhenium carbonyls may also have been present.

Temperature-programmed desorption data show that rhenium carbonyl species other than [Re2(CO)10] desorbed in the temperature range 300–400 K (Figure 1A). The relative intensities of the five rhenium-containing ions, Re(CO)₅⁺ (x = 0–4), associated with the peak at 350 K (100:55:120:75:45) do not agree with those observed for [Re₂(CO)₁₀] (100:55:34:45:45). The small temperature difference (350 K for the product and 295 K for [Re₂(CO)₁₀]) would not be expected to cause a large change in the fragmentation pattern. We were unable to identify the gas-phase carbonyl product(s) associated with the peak at 350 K because of the limited range of the mass spectrometer. The observed fragmentation pattern is similar to that measured for [HRe(CO)₅] (100:50:30:100:45). The similarity of the two fragmentation patterns suggests that a rhenium pentacarbonyl species may have been produced.

After heating to 500 K, the sample prepared by adsorption of [Re₂(CO)₁₀] on MgO at 110 K, only two νCO bands were observed in the infrared spectrum (Figure 2B), at 2054 and 1933 cm⁻¹.
These bands are again attributed to rhenium subcarbonyls formulated as \([\text{Re}(\text{CO})_3(\text{OMg})_3]\) because the observed band locations are nearly identical to those observed for the sample prepared by adsorption of \([\text{Re}_2(\text{CO})_{10}]\) at 320 K after it had been heated to 400–500 K. The broadness of the spectral features at 2054 and 1933 cm\(^{-1}\) may be an indication of the presence of other minor surface species.

Evidence of Metallic Rhenium Clusters. When the samples prepared from \([\text{Re}_2(\text{CO})_{10}]\) on MgO films were heated to temperatures >700 K, nearly all the CO had been desorbed from the surface, as evidenced by temperature-programmed desorption and infrared spectra. The broad feature in the TPD spectrum (Figure 1B) in the temperature range 700–1000 K suggests that small amounts of CO dissociated on the surface and eventually recombined. The amount of CO dissociation increased with rhenium coverage (data not shown). The total amount of rhenium metal on the MgO surface depended on the initial \([\text{Re}_2(\text{CO})_{10}]\) coverage, with a maximum of \(\sim 1 \times 10^{15}\) atoms/cm\(^2\).

Proposed Reaction Schemes. In summary, a reaction scheme that accounts for the observations for \([\text{Re}_2(\text{CO})_{10}]\) on MgO following adsorption at 320 K is shown in Figure 7. There is no evidence of intermediates in the decarbonylation of \([\text{Re}(\text{CO})_3(\text{OMg})_3]\). A scheme representing the observations for the samples prepared by adsorption of \([\text{Re}_2(\text{CO})_{10}]\) at 110 K is more complicated. When \([\text{Re}_2(\text{CO})_{10}]\) was adsorbed on MgO at 110 K, only a fraction of the molecules were decarbonylated, forming \([\text{Re}(\text{CO})_4(\text{OMg})_2]\). The degree of decarbonylation increased with temperature. Multilayers of \([\text{Re}_2(\text{CO})_{10}]\) desorbed at \(\sim 295\) K as other rhenium carbonyl species formed. Upon further heating to temperatures >300 K, \([\text{Re}(\text{CO})_4(\text{OMg})_2]\) and other unidentified species reacted to yield volatile rhenium carbonyls and surface-bound rhenium subcarbonyls such as \([\text{Re}(\text{CO})_3(\text{OMg})_3]\). When the sample was heated to temperatures >600 K, metallic rhenium formed on the MgO surface.

Effect of Pretreated Water. Since most powder metal oxide supports contain surface hydroxyl groups, whereas the MgO thin film did not, we pretreated water on the MgO film to examine its effect on the chemistry of the rhenium carbonyls. Both the TPD and infrared data characteristic of a sample prepared by adsorption of \([\text{Re}_2(\text{CO})_{10}]\) on a MgO thin film that was precovered with water (\(\sim 2\) monolayers) were observed to be nearly the same as the corresponding data characterizing samples prepared by adsorption of \([\text{Re}_2(\text{CO})_{10}]\) on a MgO thin film in the absence of water. The similarity of the data suggests that samples prepared by adsorption of water before the adsorption of \([\text{Re}_2(\text{CO})_{10}]\) underwent surface reactions similar to those observed for samples without water. However, the final rhenium coverage following decomposition of \([\text{Re}_2(\text{CO})_{10}]\) on the water-precovered surface was only approximately half of the that observed for the sample without water. We speculate that the water (and possibly surface hydroxyl groups formed from it by reaction with the MgO) inhibited the adsorption of \([\text{Re}_2(\text{CO})_{10}]\) and its reaction with the MgO film.

Effect of Postadsorbed Water. Since the locations of the \(\nu_{\text{CO}}\) bands of the surface-bound rhenium tricarbonyl have been reported to be sensitive to the degree of hydroxylation of the metal oxide powder surfaces,\(6,6\) experiments were done to investigate the effects of water adsorbed on the MgO film. Water was adsorbed after the adsorption of \([\text{Re}_2(\text{CO})_{10}]\) and its subsequent conversion into surface-bound rhenium subcarbonyl species \([\text{Re}(\text{CO})_3(\text{OMg})_3]\) by heating to 500 K. Prior to the adsorption of water, two \(\nu_{\text{CO}}\) bands were observed, at 2054 and 1934 cm\(^{-1}\) (Figure 6A). After adsorption of \(\sim 2\) monolayers of water at 100 K, the \(\nu_{\text{CO}}\) bands shifted to lower energies, 2024 and 1906 cm\(^{-1}\) (Figure 6B). These bands are close in their positions to the bands characterizing the rhenium subcarbonyls supported on MgO powder, the surface of which was estimated to be 93% dehydroxylated.\(6\)

Nature of the Bonding of the Rhenium Subcarbonyls to the MgO Surface. All the results are consistent with the formation of rhenium subcarbonyls having the composition \([\text{Re}(\text{CO})_3(\text{OMg})_3]\) as a result of heating the samples to temperatures >400 K. The MgO film was epitaxially grown on Mo(110) and had the hexagonal orientation of MgO(111). Thus, the surface oxygen atoms were arranged in triangular arrays so that each of the three oxygen atoms in a triangle could readily bond as a ligand to a single rhenium atom in a metal complex such as \([\text{Re}(\text{CO})_3(\text{OMg})_3]\), which is expected to have \(C_3\) symmetry and be analogous to numerous known molecular complexes.\(19\)

The intensity of the 2050-cm\(^{-1}\) band was observed to be much stronger than that of the 1930-cm\(^{-1}\) band for \([\text{Re}(\text{CO})_3(\text{OMg})_3]\) on the MgO thin film, whereas the opposite was true on MgO powder.\(2\) Assuming \(C_3\) symmetry, the 2050-cm\(^{-1}\) band is attributed to the symmetric stretching of the \([\text{Re}(\text{CO})_3]\) group and has a dipole moment nearly perpendicular to the plane in which the three lattice oxygens lie, whereas the 1930-cm\(^{-1}\) band is attributed to the antisymmetric motion and has its dipole moment nearly parallel to the MgO(111) surface. Since IRAS can only probe vibrational modes having a perpendicular component because of the selection rule, the relative intensities of the bands at 2050 and 1930 cm\(^{-1}\) further support the postulated structure of \([\text{Re}(\text{CO})_3(\text{OMg})_3]\) in which the \([\text{Re}(\text{CO})_3]\) moiety is coordinated by three lattice oxygens and has \(C_3\) symmetry.

This inference about the symmetry of the surface-bound rhenium subcarbonyls is in agreement with the conclusions based on EXAFS, infrared, and other evidence for rhenium tricarbonyls on the surface of MgO powder. However, the predominant face on MgO powder is the square (100) face, and the simplified structural models suggested for rhenium subcarbonyls on the MgO powder\(2,6,19\) are constrained by the incorporation of three surface oxygen atoms arranged in a square array. The misfit in these simplified models has led to the suggestion that the rhenium subcarbonyls were actually bonded at surface defect sites where their 3-fold symmetry could be accommodated in an energetically more favorable way.\(3\) The present results add support to this suggestion and demonstrate the value of structurally characterized supports such as that used in the present work for elucidation of the nature of the metal–support interface.

Conclusions

\([\text{Re}_2(\text{CO})_{10}]\) reacted with the MgO(111) surface upon adsorption at 320 K, forming a surface-bound rhenium tetracarbonyl species, \([\text{Re}(\text{CO})_4(\text{OMg})_2]\). When the sample was heated to temperatures >400 K, \([\text{Re}(\text{CO})_4(\text{OMg})_2]\) was decarbonylated, forming a surface-bound rhenium tricarbonyl, \([\text{Re}(\text{CO})_3(\text{OMg})_3]\). Further heating to temperatures >600 K induced the formation of rhenium metal clusters. Rhenium subcarbonyls were not formed when the rhenium metal clusters were exposed to low-pressure CO at room temperature. When adsorbed at 110 K, \([\text{Re}(\text{CO})_{10}]\) formed multilayers on MgO(111) with a fraction of the first layer decomposing to form \([\text{Re}(\text{CO})_4(\text{OMg})_2]\). \(\text{Re}-\)
(CO)_{10} \text{ multilayers desorbed at 295 K. An unidentified rhenium carbonyl species, probably rhenium pentacarbonyl, was also desorbed at 350 K during temperature-programmed desorption experiments. Heating of the sample to 400–500 K resulted in the formation of surface-bound rhenium tricarbonyls, } [\text{Re(CO)}_3\text{-}[\text{OMg}_3]]. \text{ The } \nu\text{CO band frequencies of the rhenium subcarbonyl species were found to be dependent on the coadsorption of water. The infrared spectra show that the symmetry of the surface-bound rhenium tricarbonyls is } C_{3v}. \text{ The conclusion is in agreement with the evidence characterizing rhenium tricarbonyls on } \text{MgO powder surfaces, which are predominantly MgO(100). The results suggest that the rhenium subcarbonyls are bonded to defect sites or faces other than the (100) face on the powders. The results demonstrate the value of structurally characterized supports such as that used in the present work for elucidation of the nature of the metal–support interface.}

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References and Notes


