Adsorption and Reaction of [HRe(CO)₅] on Ultrathin MgO(111) and Amorphous SiO₂ Films Grown on a Mo(110) Surface: Characterization by Infrared Reflection–Absorption Spectroscopy and Temperature-Programmed Desorption

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The adsorption and reaction of [HRe(CO)₅] on ultrathin MgO(111) and on amorphous SiO₂ films grown on a Mo(110) substrate were investigated with infrared reflection–absorption spectroscopy and temperature-programmed desorption. Similar adsorption and reaction chemistry were observed for samples prepared on both MgO(111) and SiO₂ surfaces. [HRe(CO)₅] was physisorbed in multilayers at 100 K. A fraction of the [HRe(CO)₅] present in multilayer desorbed at 200 K, and as the temperature was raised, more strongly bound species were formed, which desorbed at 340 K. Heating of the sample in the range 100–300 K produced rhenium pentacarbonyls such as [Re(CO)₅(OM)] (M = Mg, Si), as indicated by the infrared spectra. Species suggested to be [Re(CO)₄(OM)]₂ (M = Mg, Si) were formed in the temperature range 100–350 K, as indicated by the infrared spectra and a comparison of the spectra with those observed for samples prepared similarly from [Re(CO)₅]. Heating to 400–500 K resulted in significant decarbonylation. The major species formed on both surfaces during this decarbonylation were surface-bound rhenium tricarbonyls, identified by infrared spectroscopy as [Re(CO)₃(OM)] (M = Mg, Si). These results demonstrate strong parallels between the chemistry of rhenium carbonyls adsorbed on metal oxide thin films and those adsorbed on metal oxide powders.

Introduction

Notwithstanding the importance of supported metals as industrial catalysts, their structures are not well understood because the metal clusters (crystallites) in them are highly nonuniform in size and shape, and the support surfaces are heterogeneous. In particular, much remains to be learned about the structure of the metal-support interfaces in these materials. Thus experiments have been done with mononuclear (single-metal-atom) complexes bonded to the surfaces of metal oxide powders, since the metal-support bonding in these relatively simple materials may provide some insight into the metal-support interface in supported metal catalysts. The results of a variety of techniques, including extended X-ray absorption fine structure (EXAFS) spectroscopy, have shown that the metal-oxygen bonding in metal-oxide-supported mononuclear metal complexes is characterized by metal-oxygen distances (2.1–2.2 Å) that are also found for almost all the metal oxide-supported metal clusters that have been characterized by EXAFS spectroscopy.¹ Thus, to a degree, the mononuclear metal complexes are models of supported metal clusters on metal oxide surfaces; however, the models are limited in their validity, because the metal-support interface in metal oxide-supported metal catalysts is typically characterized by both short metal–oxygen distance and a longer distance of about 2.7 Å.¹

The goals of this work were to understand the nature of the metal–metal oxide bonding better by investigating relatively well-defined and stable adsorbed species (rhenium subcarbonyls) on relatively well-defined metal oxide surfaces under ultrahigh vacuum conditions. [HRe(CO)₅] was chosen to be the precursor of the adsorbed species because it has been shown to lead to well-defined structures on MgO powder surfaces²–⁴ and has a vapor pressure high enough to allow vapor deposition in ultrahigh vacuum apparatus. The surfaces were chosen to be those of MgO and SiO₂ thin films because they can be easily prepared and characterized with an array of surface science techniques.⁵–⁹ 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.¹⁰ This chamber is equipped with a UTI mass spectrometer and a Mattson Cygnus 100 FTIR spectrometer; it was also possible to characterize the samples by Auger electron spectroscopy. The characterization of the MgO and SiO₂ films was done in a separate chamber equipped with X-ray photoelectron (XPS), Auger electron (AES), and ion scattering (ISS) spectroscopies as well as low-energy electron diffraction (LEED). The procedures used to prepare the MgO films in the two chambers were identical; likewise, the...
procedures used to make the SiO₂ films in the two chambers were identical. The base pressure in each chamber was <10⁻⁶ Torr.

**Preparation and Characterization of Ultrathin MgO(111) Films on a Mo(110) Substrate.** Thin Mo films were prepared by evaporating pure metallic magnesium in 5 × 10⁻⁴ Torr of oxygen 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 annealing 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 (111) 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 Mg²⁺ 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 MgO and Mg vapor. The MgO films were approximately 50 Å thick.

**Preparation and Characterization of Ultrathin SiO₂ Films on a Mo(110) Substrate.** The ultrathin SiO₂ films were prepared by evaporating silicon in ~10⁻⁵ Torr of oxygen by a reported method. After being annealed to 1400 K, the stoichiometric SiO₂ films exhibited the electronic and bonding structures of vitreous silica. The SiO₂ films are stable at temperatures >1500 K. They were approximately 50 Å thick.

**Materials.** [HRe(CO)₅] was prepared at the University of California by a literature method. [Zn(CO)₄]Br₂, Zn powder (Fisher), and H₃PO₄ (Fisher) were used as received for this preparation. The synthesis of the air-sensitive [HRe(CO)₅] was done with the exclusion of air on a double-manifold Schlenk chamber at ambient temperature. The flux was monitored by mass spectrometry. The temperature of the sample was ramped at a rate of 1 K/s. The contribution of the fragmentation of desorbed rheniumcontaining species because the relative intensities of the five rhenium-containing fragments associated with the peak at 340 K (namely, 100:50:140:100:45) are nearly identical to those observed when gas-phase [HRe(CO)₅] was admitted to the same vacuum chamber (namely, 100:50:130:100:45).

**Temperature-Programmed Desorption/Decomposition.** The temperature of the sample was ramped at a rate of 5 K/s in the range 100–1000 K, and the products were monitored with the mass spectrometer. The temperature was measured with a W-5% Re/W-26%Re thermocouple that was spot-welded to the back of the Mo(110) crystal. The upper limit of detectability of the mass spectrometer was m/q = 300.

**Fourier Transform Infrared Reflection–Absorption Spectroscopy.** The crystal was lowered into the infrared beam path and aligned. The incident angle of the infrared beam with respect to the surface normal was 85°. Spectra with a resolution of 4 cm⁻¹ were recorded after each cycle in which the sample was heated at a rate of 5 K/s to a particular temperature and immediately cooled to about 110–120 K. The temperatures to which the sample was heated ranged from 150 to 1000 K.

**Results**

**Temperature-Programmed Desorption of Samples Prepared by Adsorption of [HRe(CO)₅] on SiO₂ Films.** Figure 1 shows typical TPD spectra characterizing a sample prepared from [HRe(CO)₅] on a SiO₂ thin film. Because of the limitation of our mass spectrometer, which has a range of 0–300 amu, the parent ion of [HRe(CO)₅] could not be monitored. Five rhenium-containing fragments were monitored, with m/q = 186, 214, 242, 270, and 298, corresponding to Re⁺, Re(CO)⁺, Re(CO)₂⁺, Re(CO)₃⁺, and Re(CO)₄⁺, respectively. Each of the TPD spectra (Figure 1) characteristic of rhenium-containing fragments includes two distinct peaks centered at 200 and 340 K. When the exposure of the films to [HRe(CO)₅] was increased, the intensity of the peak centered at 200 K increased without saturation. Therefore, the peak at 200 K is attributed to the sublimation of [HRe(CO)₅]. In contrast, the peak at 340 K reached saturation; i.e., beyond a certain level of exposure to [HRe(CO)₅] the peak intensity did not increase. The peak at 340 K, with a tail extending to 400 K, is also attributed to a mononuclear (single-metal-atom) rhenium pentacarbonyl species because the relative intensities of the five rhenium-containing fragments associated with the peak at 340 K (namely, 100:50:140:100:45) are nearly identical to those observed when gas-phase [HRe(CO)₅] was admitted to the same vacuum chamber (namely, 100:50:130:100:45).

The major CO evolution was observed in a narrow peak at 430 K (Figure 1). Small CO desorption features were also observed at 200–400 K. The evolution of CO during the TPD of the sample prepared from [HRe(CO)₅] was monitored at m/q = 12 (C⁺) and m/q = 12 (C²⁺). 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 with the same mass spectrometer sensitivity scale. The contribution of the fragmentation of desorbed rhenium carbonyls to the C⁺ signal was negligible.

**Temperature-Programmed Desorption of Samples Prepared by Adsorption of [HRe(CO)₅] on MgO(111) Films.** The TPD spectra of the samples formed from [HRe(CO)₅] on MgO(111) thin films were observed to be identical to those characterizing the samples formed from [HRe(CO)₅] on SiO₂ films. Rhenium carbonyls desorbed at 200 and 340 K. The principal CO evolution peak was observed at 430 K.

**Infrared Reflection–Absorption Spectroscopy of Samples Prepared by Adsorption of [HRe(CO)₅] on MgO(111) Films.** Figure 2 shows IRAS spectra characterizing samples prepared by adsorption of [HRe(CO)₅] on MgO films; the samples had been heated to the indicated temperatures prior to the measurement of the spectra. The initial coverage of the film by [HRe(CO)₅] was...
Adsorption and Reaction of \([\text{HRe(CO)}_5]\)

Langmuir, Vol. 10, No. 9, 1994

Figure 2. Fourier transform infrared reflection-absorption spectra for samples prepared by the adsorption of 4 monolayers of \([\text{HRe(CO)}_5]\) on MgO(111)/Mo(110). The spectra were recorded after the surface had been briefly heated to the indicated temperatures. \([\text{HRe(CO)}_5]\) was adsorbed at about 100 K.

Estimated to be 4 monolayers, where one monolayer is taken to be the coverage at which the 200 K desorption peak appeared in the TPD spectrum. After adsorption of \([\text{HRe(CO)}_5]\) on the MgO films at 100 K, a very strong, broad band was observed in the \(\nu_{\text{CO}}\) region of the spectrum at 2068 cm\(^{-1}\), and weak bands were evident at 2138 and 1950 cm\(^{-1}\) (Figure 2A). After the sample had been heated to 250 K, the intensity of the 2068 cm\(^{-1}\) band decreased, the weak band at 2138 cm\(^{-1}\) disappeared, and two low-intensity bands appeared, at 2155 and 2102 cm\(^{-1}\). After the sample had been heated to 300 K, resolved peaks at 2158, 2104, 2066, and 2027 cm\(^{-1}\), as well as an unresolved shoulder at about 2000 cm\(^{-1}\), were observed (Figure 2B). Heating to 350–400 K resulted in the disappearance of the band at 2158 cm\(^{-1}\) and a decrease in intensity of the band at 2066 cm\(^{-1}\). After the sample had been heated further to 450 K, only two bands were observed, at about 2066 and 1960 cm\(^{-1}\). No \(\nu_{\text{CO}}\) bands were observed after the sample had been heated to temperatures > 600 K.

Infrared Reflection–Absorption Spectroscopy of Samples Prepared by Adsorption of \([\text{HRe(CO)}_5]\) on SiO\(_2\) Films. The IRAS spectrum recorded after the initial adsorption of \([\text{HRe(CO)}_5]\) on SiO\(_2\) films was identical to that observed for samples prepared on MgO(111) films. The spectra characterizing the species formed from \([\text{HRe(CO)}_5]\) on SiO\(_2\) films, recorded after the samples had been heated to temperatures > 100 K, were observed to be slightly different from those characterizing samples prepared from \([\text{HRe(CO)}_5]\) on MgO films. Figure 3 shows IRAS spectra for a sample prepared by adsorption of ~1 monolayer of \([\text{HRe(CO)}_5]\) on a SiO\(_2\) thin film which had been heated to the indicated temperatures. At 100 K, a principal band at 2069 cm\(^{-1}\) was observed in addition to several weak shoulders, at ~2135, 2100, 2020, and 1950 cm\(^{-1}\). When the sample was heated to 200 K, two bands became resolved, at 2153 and 2029 cm\(^{-1}\). After the sample had been heated to 350 K, the band at 2153 cm\(^{-1}\) disappeared and \(\nu_{\text{CO}}\) bands were observed at 2101, 2070, 2033, and 1990 cm\(^{-1}\). After the sample was further heated to 400–500 K, only two broad bands were observed, at about 2050 and 1980 cm\(^{-1}\). No \(\nu_{\text{CO}}\) bands were observed after the sample had been heated to temperatures > 600 K.

Discussion

Multilayers of \([\text{HRe(CO)}_5]\) on MgO(111) and SiO\(_2\) Films. The TPD data are consistent with the inference that exposure of both the MgO and the SiO\(_2\) films to \([\text{HRe(CO)}_5]\) at 100 K led to the formation of \([\text{HRe(CO)}_5]\) multilayers. The TPD spectra in Figure 1 show a peak at 200 K associated with rhenium-containing fragments that increased without saturation with increasing exposure of the surface to \([\text{HRe(CO)}_5]\). This peak is attributed to the sublimation of \([\text{HRe(CO)}_5]\) multilayers.

The infrared spectra (Figures 2A and 3) are consistent with the formation of \([\text{HRe(CO)}_5]\) multilayers after adsorption on the MgO and SiO\(_2\) films at 100 K. A very strong, broad band was observed in the \(\nu_{\text{CO}}\) region of the spectrum at 2068 cm\(^{-1}\), and weak bands were evident at 2138 and 1950 cm\(^{-1}\) (Figure 2A). Solvated \([\text{HRe(CO)}_5]\) (which has \(C_4h\) symmetry) exhibits three principal infrared-active \(\nu_{\text{CO}}\) bands, \(\nu_1\)(a;equatorial), \(\epsilon\), and \(\nu_2\)(a;axial), with frequencies of 2014 (vs), 2007 (s), and 1982 cm\(^{-1}\), respectively.\(^{14}\) The infrared bands characteristic of molecules in solution are different from those of the compound in
the crystalline state, which are usually split into the longitudinal-(LO) and transverse-optical (TO) branches. The selection rules of infrared reflection-absorption spectroscopy allow only bands of the LO branch to be detected. No infrared data have been reported for solid [HRe(CO)5Br]; however, single-crystal infrared data for a similar compound, [Re(CO)5Br], have been reported. Three principal \(v_{\text{CO}}\) bands have been reported for solvated [Re(CO)5Br], at 2151 (w), 2044 (s), and 1985 (m) cm\(^{-1}\), which correspond to the \(a_1\)(e), \(e\), and \(a_1\)(a) bands, respectively. The LO branches of the \(a_1\)(e), \(e\), and \(a_1\)(a) bands for [Re(CO)5Br] single crystals exhibit frequencies of 2153, 2061, and 1974 cm\(^{-1}\), respectively. By comparison, we assign the band at 2068 cm\(^{-1}\) (Figure 2A) to the LO branch of the \(e\) vibration, the weak band at 2138 cm\(^{-1}\) to \(a_1\)(e)-LO, and the shoulder at 1950-2000 cm\(^{-1}\) to \(a_1\)(a)-LO. The locations of these infrared bands for [HRe(CO)5] multilayers at lower energies than those reported for [Re(CO)5Br] single crystals can be explained by the different ligands on the rhenium pentacarbonyl moiety. The hydrate ligand would be expected to withdraw less electron density from the rhenium atom than would the Br ligand. Thus the greater electron density on the rhenium atom in [HRe(CO)5] would result in more efficient \(\pi\)-back-bonding, which in turn would result in the appearance of the \(v_{\text{CO}}\) bands at lower energies, consistent with the observations.

**Table 1. CO Stretching Frequencies in Rhenium Carbonyls**

<table>
<thead>
<tr>
<th>precursor</th>
<th>solvent or support/treatment</th>
<th>(v_{\text{CO}}) bands, cm(^{-1})</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HRe(CO)5]</td>
<td>cyclohexane solution</td>
<td>2014 (vs), 2007 (s), 1982 (w)</td>
<td>14</td>
</tr>
<tr>
<td>[Re(CO)5Br]</td>
<td>cyclohexane solution</td>
<td>2151 (w), 2044 (s), 1985 (m)</td>
<td>16</td>
</tr>
<tr>
<td>[Re(CO)5Br]</td>
<td>none (single crystal)</td>
<td>LO: 2153, 2076, 2074, 2002, 1970</td>
<td>15</td>
</tr>
<tr>
<td>[Re(CO)5Cl]</td>
<td>CCl4 solution</td>
<td>2114 (w), 2031 (s), 2000 (m), 1959 (m)</td>
<td>18</td>
</tr>
<tr>
<td>[Re(CO)5Cl]</td>
<td>CCl4 solution</td>
<td>2106 (w), 2029 (s), 2001 (m), 1965 (m)</td>
<td>18</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 663 K/dosed with methanol at 473 K</td>
<td>2008 (s), 1885 (vs)</td>
<td>19</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 673 K</td>
<td>2011 (vs), 1895 (vs), 1862 (sh)</td>
<td>3</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 665 K/dosed with water at 473 K</td>
<td>2014 (s), 1994 (vs)</td>
<td>19</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 973 K</td>
<td>2017 (vs), 1908 (vs), 1867 (sh)</td>
<td>3</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 665 K, spectrum at 668 K in vacuo</td>
<td>2022 (s), 1905 (s)</td>
<td>19</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 973 K</td>
<td>2026 (s), 1905 (s)</td>
<td>19</td>
</tr>
<tr>
<td>[HRe(CO)5]</td>
<td>MgO calcined at 973 K, spectrum at 373 K, in vacuo</td>
<td>2026 (s), 1921 (s)</td>
<td>19</td>
</tr>
</tbody>
</table>


pentacarbonyl species, [Re(CO)5(O)(Mg)]. The spectrum recorded after the initial adsorption of [HRe(CO)5] on the MgO films includes a very weak shoulder at 2153-2155 cm\(^{-1}\) (Figure 2A), which suggests that some of the [HRe(CO)5] reacted with the metal oxide surface to form the surface-bound rhenium pentacarbonyl even at 100 K.

The 2014 cm\(^{-1}\) peak (Figure 2B) is suggestive of species with structures related to those of the rhenium tetracarbonyl dimers [Re(CO)4X2] (X = Cl, Br, I). The other two bands, at 2027 and 2000 cm\(^{-1}\), are similar to those observed for these rhenium tetracarbonyl dimers. For example, [Re(CO)5Cl2] is characterized by four \(v_{\text{CO}}\) bands at 2114, 2032, 2000, and 1959 cm\(^{-1}\) (Table 1). McKenna et al. reported a band at 2101 cm\(^{-1}\) to be characteristic of the surface-bound rhenium tetracarbonyl dimer with a Re-Re bond, formed from [Re(CO)5]2, i.e., [Re2(CO)4(OSi)]2. Thus the bands at 2110, 2027, and 2000 cm\(^{-1}\), observed after the sample had been heated to 300 K (Figure 2B), are suggested to be an indication of a surface-bound rhenium tetracarbonyl dimer, [Re(CO)4-(OMg)]2. Alternatively, the spectrum might be attributed to an analogous mononuclear rhenium subcarbonyl, [Re(CO)4(OMg)]2, but there is a lack of molecular analogues for a comparison of spectra.

As the sample was heated from 300 to 400 K, the peaks in the \(v_{\text{CO}}\) region generally decreased in intensity. The peak at 340 K, with a tail extending to 400 K, observed in the TPD data, has been attributed above to the decomposition of [Re(CO)5(O)(Mg)] on MgO. The near absence of desorbed CO is consistent with the inference that [Re(CO)4(OMg)] and [Re(CO)4(OMg)]2 (or related species) had been formed on the MgO surface at these temperatures, because formation of [Re(CO)5(OMg)] from [HRe(CO)5] on MgO requires no loss of CO, and formation of [Re(CO)4(OMg)]2 from [HRe(CO)5] on MgO involves loss of only one CO ligand per rhenium atom.

The TPD data show that significant decarbonylation occurred in the range 400-500 K. Since no rhenium-containing fragments were observed to desorb in this temperature range, the decarbonylation is attributed to surface reactions leading to CO evolution without the desorption of rhenium. After the sample had been heated to 450 K, two \(v_{\text{CO}}\) bands were observed, a strong band at 2066 cm\(^{-1}\) and a broad, weak band at about 1960 cm\(^{-1}\). These bands are attributed to rhenium subcarbonyls because the bands resemble those reported for rhenium tricarbonyl on MgO powder.23,19,30 (Presumably, metallic...
Adsorption and Reaction of [HRe(CO)$_5$] on MgO(111/Mo(110))

These surface-bound rhenium subcarbonyls have been prepared from a variety of rhenium carbonyl precursors, including [HRe(CO)$_5$]$_2$ [2,3]. These surface-bound rhenium subcarbonyls have been formulated on the basis of infrared, TPD, extended X-ray absorption fine structure, and other data as [Re(CO)$_3$(OMg)$_3$]$_2$ [2,3,19]. The bands were not attributed to CO chemisorbed on rhenium metal clusters, because CO chemisorbed on rhenium crystallites exhibits a single band at 2035 cm$^{-1}$ [21].

Figure 4. Reaction scheme proposed for [HRe(CO)$_5$] on MgO(111)/Mo(110).

The v$_{CO}$ frequencies characterizing MgO powder-supported rhenium tricarbonyls have been reported to increase with the degree of dehydroxylation of the support [3,19]. The bands characterizing the MgO film-supported rhenium tricarbonyls were observed at higher frequencies than those characterizing the powder-supported samples, consistent with the negligible degree of hydroxylation of the MgO(111) surface as indicated by the lack of evidence of surface hydroxyl groups in the infrared spectrum [22]. Thus we infer that the species supported on the MgO(111) surface species temp, K | v$_{CO}$, cm$^{-1}$

<table>
<thead>
<tr>
<th>[HRe(CO)$_5$]</th>
<th>multilayers on MgO</th>
<th>[HRe(CO)$_5$(OMg)]$_2$</th>
<th>[HRe(CO)$_5$(OMg)]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2158 (w), 2066 (va)</td>
<td>2104 (m), 2027 (s), 2000 (sh)</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2066 (s), 1960 (w,br)</td>
<td>350, 2101 (w), 2070 (s), 2033 (m), 1990 (w)</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>2153 (w), 2070 (s)</td>
<td>350, 2050 (s), 1900 (m,br)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Summary of Infrared Band Assignments

ascribed above, this band is characteristic of the [HRe(CO)$_5$] moiety [15,17]. McKenna et al. [17] observed a band at 2150 cm$^{-1}$ for a sample prepared by adsorption of [Re$_2$(CO)$_6$] on SiO$_2$ powder, followed by photolysis in tetrahydrofuran. They attributed this band to surface-bound rhenium pentacarbonyls, formulated as [Re(CO)$_5$(OSi)$_2$]. Thus we suggest that the band observed at 2153 cm$^{-1}$ is characteristic of the SiO$_2$-bound rhenium pentacarbonyl formed by reaction of [HRe(CO)$_5$] with the SiO$_2$ surface.

After the SiO$_2$-supported sample had been heated to 350 K, four v$_{CO}$ bands were observed, at 2101, 2070, 2033, and 1990 cm$^{-1}$ (Figure 3). McKenna et al. [17] attributed a band at 2101 cm$^{-1}$ to a surface-bound rhenium tetracarbonyl dimer, [Re(CO)$_4$(OSi)$_2$]. An identical band was observed for our SiO$_2$ film-supported sample. The bands at 2033 and 1990 cm$^{-1}$ can also be attributed to [Re(CO)$_5$(OSi)$_2$]. Hileman et al. [18] reported similar bands for [Re(CO)$_4$Cl]$_2$ at 2032 and 2000 cm$^{-1}$ (Table 1). As for the MgO film-supported sample, we again recognize that the spectrum might be attributed to an analogous mononuclear rhenium subcarbonyl, [Re(CO)$_4$(OSi)$_2$].

We attribute the v$_{CO}$ band at 2070 cm$^{-1}$ observed for samples heated in the temperature range 100–350 K to physisorbed [HRe(CO)$_5$] or to [Re(CO)$_5$(OSi)$_2$].

The overall infrared absorbance decreased significantly as the temperature of treatment was increased from 100 to 400 K, and no significant CO evolution was observed. By reasoning analogously to that stated above for the MgO-supported samples, we infer that these results are consistent with the formation of [Re(CO)$_5$(OSi)$_2$] and [Re(CO)$_4$(OSi)$_2$]$_4$ (or related mononuclear species).

When the sample had been heated to temperatures in the range 400–500 K, in which significant CO evolution occurred as evidenced by the TPD data, the sample was characterized by two broad v$_{CO}$ bands, at approximately 2050 and 1990 cm$^{-1}$. By reasoning analogously to that stated above for samples prepared on MgO films, we assign these two bands to the surface-bound rhenium tricarbonyl [Re(O)(CO)$_4$(OSi)$_2$]. McKenna et al. [17] reported bands at 2032 and 1935 cm$^{-1}$ for this rhenium tricarbonyl bound to SiO$_2$ powder. The appearance of the thin-film bands at higher frequencies than those observed by McKenna et al. [17] for rhenium subcarbonyls on SiO$_2$ powders is consistent with the presence of hydroxyl groups on the SiO$_2$ powder surfaces, but not on the SiO$_2$ films. The relative intensities of the bands at 2050 and 1990 cm$^{-1}$ are not the same as those observed for the rhenium tricarbonyls on MgO(111) films. Other species in addition to the rhenium tricarbonyl may have been present.

Comparison of the Chemistry of [HRe(CO)$_5$] on MgO(111) and on SiO$_2$ Films. On both surfaces, [HRe(CO)$_5$] reacted to form [Re(CO)$_5$(OM)] and [Re(CO)$_5$(OM)]$_2$ (or related species) (M = Mg, Si). [Re(CO)$_5$(OM)] was observed to be stable at temperatures <300 K on both surfaces. The lack of exact agreement between the v$_{CO}$ spectra of the MgO- and SiO$_2$-supported species in the temperature range of 350–400 K (Table 2) suggests...
the presence of a variety of structures on the SiO₂ surface, which, in contrast to the MgO(111) surface, lacks rigorous threefold symmetry.

When the sample temperature was increased to 350 K, a fraction of these surface-bound rhenium pentacarbonyls desorbed as volatile rhenium pentacarbonyls (as evidenced by the TPD data), and the remainder reacted to form other surface-bound rhenium carbonyls. The inferred formation of molecularly adsorbed rhenium pentacarbonyl, [Re(CO)₅{OMg}]{M} (M = Mg, Si), is consistent with the chemistry of rhenium carbonyls on metal oxide powder surfaces. [HRe(CO)₅] is a weak proton donor and has been reported to react with the basic surface of MgO, leading to partial deprotonation by O²⁻ groups to form ion pairs such as {MgO}H⁺{Re(CO)₅}⁻. Such a species, upon dissociation of the proton, would give a chemisorbed species analogous to [Re(CO)₅{OMg}]. Furthermore, the formation of [Re(CO)₅{OMg}][MgO·H⁺] has been reported to result from the photolysis of [Re₂(CO)₁₀] adsorbed on SiO₂ powder.¹⁷

The suggested formation of dinuclear rhenium subcarbonyls ([Re(CO)₅{OMg}]{M} = Mg, Si) from the mononuclear precursor is consistent with the solution chemistry of rhenium carbonyls. Rhenium pentacarbonyl halides {e.g., [Re(CO)₅{X}] (X = Cl, Br, I)} are readily converted into rhenium tetracarbonyl halide dimers in solution at 100–120 °C.²³ We suggest that analogous, presumably bimolecular, reactions occurred on the MgO(111) and SiO₂ surfaces, with [HRe(CO)₅] or [Re(CO)₅{OMg}] (M = Mg, Si) reacting to form the surface-bound rhenium tetracarbonyl dimer, [Re(CO)₅{OMg}]{M} (M = Mg, Si).

The principal species formed on each surface in the range 400–500 K were rhenium tricarbonyls, inferred from the infrared reflection-absorption spectra to be [Re(CO)₃{OMg}]{M} on MgO(111) films (Figure 2B) and [Re(CO)₃{OSi}]{M} on SiO₂ films (Figure 3). Other surface species may also have been present.

Comparison of the Chemistry of [HRe(CO)₅] and [Re₂(CO)₁₀] on MgO(111) Films. The adsorption and reaction of [Re₂(CO)₁₀] on MgO(111) films has already been reported.²² The two rhenium carbonyl precursors show very similar chemistry on the MgO surface. Both precursors have been suggested to react to form rhenium tetracarbonyl dimers, [Re(CO)₄{OMg}]{M}, and the stable surface-bound rhenium tricarbonyl, [Re(CO)₃{OMg}]{M}. The observations that (1) the dimeric precursor [Re₂(CO)₁₀] reacted on the MgO(111) surface to give dimeric rhenium tetracarbonyls and that (2) the infrared spectrum attributed to the latter is nearly the same as that suggested here to be indicative of the dimeric rhenium tetracarbonyl formed from the mononuclear precursor [HRe(CO)₅] lend support to the suggestion that the mononuclear precursor was converted into a dimeric surface species.

No infrared evidence of surface-bound rhenium pentacarbonyls such as [Re(CO)₅{OMg}] was observed for the reaction of [Re₂(CO)₁₀] on MgO.²² However, the TPD data suggested the presence of rhenium pentacarbonyls on the MgO(111) surface.²² Thus the chemistry of rhenium carbonyls on MgO(111) is almost the same, irrespective of whether the precursor is [HRe(CO)₅] or [Re₂(CO)₁₀].

Nature of the Bonding of the Rhenium Tricarbonyls to the Surface. As discussed separately, the results are consistent with the bonding of Re(I) in the rhenium subcarbonyl to three oxygen atoms on the hexagonal MgO(111) surface.²² The data presented here indicate similar bonding on the surface of SiO₂. We infer that the amorphous SiO₂ offered the appropriate surface bonding sites.

Conclusions

Similar adsorption and reaction chemistry were observed for samples prepared on both MgO(111) and SiO₂ surfaces. [HRe(CO)₅] was physisorbed in multilayers at 100 K. A fraction of the [HRe(CO)₅] present in multilayers desorbed at 200 K, and as the temperature was raised, more strongly bound species were formed, which desorbed at 340 K. Heating of the sample in the range 100–300 K produced rhenium pentacarbonyls such as [Re(CO)₅{OMg}]{M} = Mg, Si, as indicated by the infrared spectra. Species suggested to be [Re(CO)₅{OMg}]{M} (M = Mg, Si) were formed in the temperature range 100–350 K, as indicated by the infrared spectra and a comparison of the spectra with those observed for samples prepared similarly from [Re₂(CO)₁₀]. Heating to 400–500 K resulted in significant decarbonylation. The major species formed on both surfaces during this decarbonylation were surface-bound rhenium tricarbonyls, identified by infrared spectroscopy as [Re(CO)₅{OMg}]{M} (M = Mg, Si). The infrared assignments are summarized in Table 2.

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