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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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Carbonyl Complexes with Alumina and Magnesia

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DEGREE OF..... Bachelor of Science

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**An Infrared Spectroscopic Study of the Interaction of
Rhenium Carbonyl Complexes with Alumina and Magnesia.**

By

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Thesis

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I. INTRODUCTION

Most metallic heterogenous catalysts currently in practical use consist of transition metal species dispersed on oxide supports. Recent results indicate that activation of carbon-carbon bonds and carbon-oxygen bonds depends on the microstructure of supported metal particles.¹ Despite recent efforts the exact nature of that dependency remains unknown.

Supporting metal complexes is a method which has been extensively investigated in producing heterogenous catalysts. One area of intense research involves the possible dependency of supported metal microstructures on the nuclearity of the molecular precursor.²

The catalytic properties of a polynuclear rhenium complex $\text{H}_3\text{Re}_3(\text{CO})_{12}$, and a mononuclear complex $\text{HRe}(\text{CO})_5$ on MgO have been investigated for the hydrogenation of propene and the isomerization/hydrogenolysis of cyclopropane.² Both supported rhenium complexes catalyze the propene hydrogenation, while in contrast, only the sample prepared with $\text{H}_3\text{Re}_3(\text{CO})_{12}$ catalyzes the cyclopropane hydrogenolysis. These results were interpreted with the proposal that the $\text{H}_3\text{Re}_3(\text{CO})_{12}/\text{MgO}$ sample has ensembles of Re centers while the $\text{HRe}(\text{CO})_5/\text{MgO}$ sample has only isolated Re atoms from each other. Only the former sample could catalyze the hydrogenolysis of cyclopropane because this reaction requires several

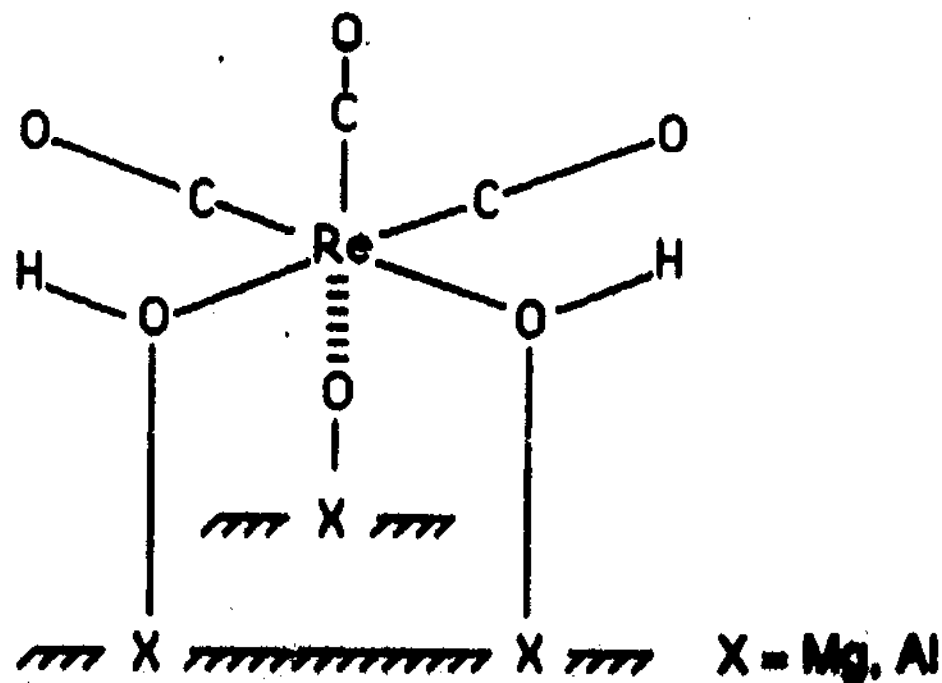


FIGURE 1. Proposed structure of the oxide supported rhenium subcarbonyl, a catalyst precursor.¹

metal centers in close proximity. The hydrogenation of propene is less demanding, apparently requiring only one metal center for conversion to propane.¹

Extensive spectroscopic characterization by Gates and co-workers of these samples have shown the presence of the $\text{Re}(\text{CO})_3$ fragment bound to three surface oxides (Figure 1). The species was proposed to be the catalyst precursor in the conversion of propene and cyclopropane.³ Dr. Michael Keyes at the University of Illinois has shown that the $\text{Re}(\text{CO})_3$ surface species were also present with other rhenium complexes, $\text{Re}_2(\text{CO})_{10}$ and $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$, supported on Al_2O_3 -- samples which were shown to be catalysts for the hydrogenolysis of ethane.

This thesis describes an effort to measure quantitatively by infrared spectroscopy the percent of $\text{Re}(\text{CO})_3$ surface species attained upon decomposition of $\text{Re}_2(\text{CO})_{10}$ and $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$ on alumina. This was accomplished by employment of a model compound, $[\text{Re}(\text{CO})_3\text{OH}]_4$ (Figure 2), where the $\text{Re}(\text{CO})_3$ entities occupy four corners of a cubane structure and are bonded to three oxides -- analogous to the proposed surface structure. The work was expanded to include MgO as a support, in order to determine if conversion of the parent carbonyl to $\text{Re}(\text{CO})_3$ species may be generalized for other oxide supports.

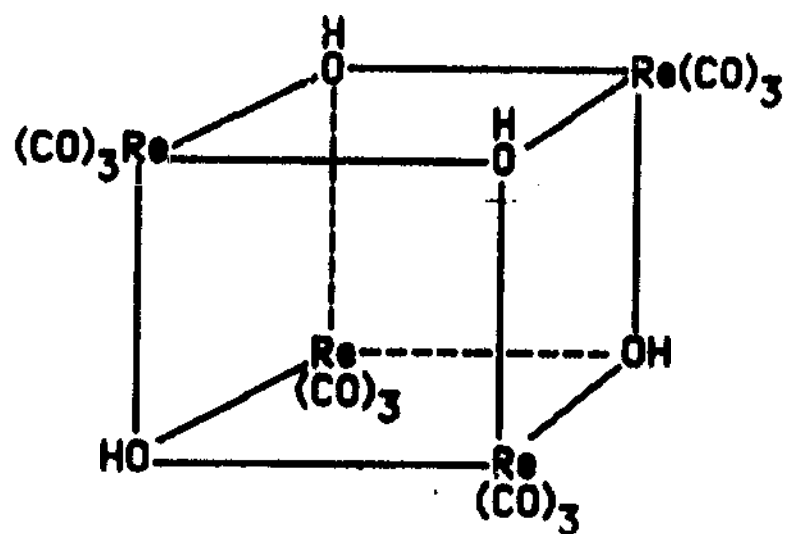


FIGURE 2. Distorted cubane structure of $[\text{Re}(\text{CO})_3\text{OH}]_4$.

The data collected in this thesis is expected to complement results obtained from other techniques, e.g., temperature programmed reaction (TPR). TPR is a technique in which the gases produced by the reaction of supported metal complexes with H_2 are monitored as a function of temperature. The infrared spectra recorded for the samples, when coupled with the data from TPR studies extends the present understanding of the chemical properties of supported rhenium complexes.

II. EXPERIMENTAL

$\text{Re}_2(\text{CO})_{10}$ was purchased from Pressure Chemical and used as received. $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$ was synthesized by a literature method⁴ and kindly provided by Dr. Chi-Mi Tai Hayward. Diethyl ether (Aldrich) was freshly distilled from sodium/benzophenone ketyl before use. Pentane was purchased from Aldrich and used as received. Acetone was purchased from Fisher and used as received. $[\text{Re}(\text{CO})_3\text{OH}]_4$ was synthesized according to a literature method⁵ as described below.

Preparation of $[\text{Re}(\text{CO})_3\text{OH}]_4$. Water (10 mL) was added to a solution of $\text{Re}_2(\text{CO})_{10}$ (0.33g, 0.50 mmol) in diethyl ether (200 mL), contained in a pyrex round bottom flask, capped with a rubber septum and vented with a syringe needle. The mixture was stirred at room temperature and irradiated for 15 hours with a 400 W medium pressure mercury lamp. The mixture was evaporated, and the solid was washed with pentane (100 mL) to remove any unreacted $\text{Re}_2(\text{CO})_{10}$. The remaining residue was dissolved in ether and the solution was passed through an alumina (acidic) column. $[\text{Re}(\text{CO})_3\text{OH}]_4$ was recovered from the colorless eluate, recrystallized from ether/pentane (1:2), and dried in vacuum. Anal. Calcd. for

$[\text{Re}(\text{CO})_3\text{OH}]_4$: C, 12.54; H, 0.35. Found: C, 12.70; H, 0.33. IR (diethyl ether): ν_{CO} 2023(s), 1920(vs) cm^{-1} ; lit⁵ ν_{CO} 2021(s), 1919(vs) cm^{-1} .

Preparation of IR samples. Preparation of all supported samples was done by incipient wetness. Typically 0.8 g samples were made. In each case, the parent carbonyl was dissolved in 1.2 mL acetone for alumina, and 2.0 mL acetone for magnesia. The solution was then added to the support, stirred, and left to dry overnight. A 40 mg sample size was used to insure a uniform and self-supporting wafer. Also, because of this sample size we were able to maintain a consistent path width in our wafer, since a varying wafer thickness effects the intensity of the absorbance. This was accomplished by placing 40 mg of the supported sample on a retaining ring, 12 mm in diameter, in between two pieces of glassine paper. An anvil was then placed on top of the glassine paper, and pressed in wafers using a Beckman pellet press (8 tons pressure). The wafer was then placed in between two pieces of circular discs and placed in an IR cell. Under typical conditions the sample was, after heating in flowing hydrogen, allowed to cool to room temperature before an infrared spectra was taken. An Omega Model CN2011 temperature controller was used to raise the temperature 4 $^{\circ}\text{C}/\text{min}$ and an MKS Model 247C Mass flow controller was used to set the H_2 flow rate at 20cc/min.

Calculations. To calculate the number of $\text{Re}(\text{CO})_3$ groups/40 mg of sample the following was done. Sample #1 in Table 1 will be used to illustrate the calculations. The number of moles of $[\text{Re}(\text{CO})_3\text{OH}]_4$, 6.7×10^{-6} , was determined. The moles of $[\text{Re}(\text{CO})_3\text{OH}]_4$ were then multiplied by four, since there are four $\text{Re}(\text{CO})_3$ groups present in the tetramer, to yield 2.69×10^{-5} moles of $\text{Re}(\text{CO})_3$ in one gram of sample. Since our sample size was fixed at 40 mg, the number of moles of $\text{Re}(\text{CO})_3$ groups per sample was 1.07×10^{-6} . IR spectra were then recorded and the absorbance at 2027 cm^{-1} (Figure 3) was measured for each standard sample. Table 1 shows the data that was obtained.

Table 1. Calibration Curve Data for Alumina

<u>SAMPLE</u>	<u>Wt. $[\text{Re}(\text{CO})_3\text{OH}]_4$ (g)</u>	<u>Wt. Al_2O_3 (g)</u>	<u>%Re</u>	<u>#$\text{Re}(\text{CO})_3$ groups/40mg</u>	<u>Abs 2027cm^{-1}</u>
1	0.00772	1.00379	0.501	1.07×10^{-6}	0.84
2	0.00623	1.00194	0.406	8.66×10^{-7}	0.713
3	0.00561	1.00165	0.365	7.80×10^{-7}	0.629
4	0.00704	1.99946	0.229	4.90×10^{-7}	0.404
5	0.00524	2.01250	0.160	3.54×10^{-7}	0.335
6	0.00390	3.00129	0.085	1.81×10^{-7}	0.179

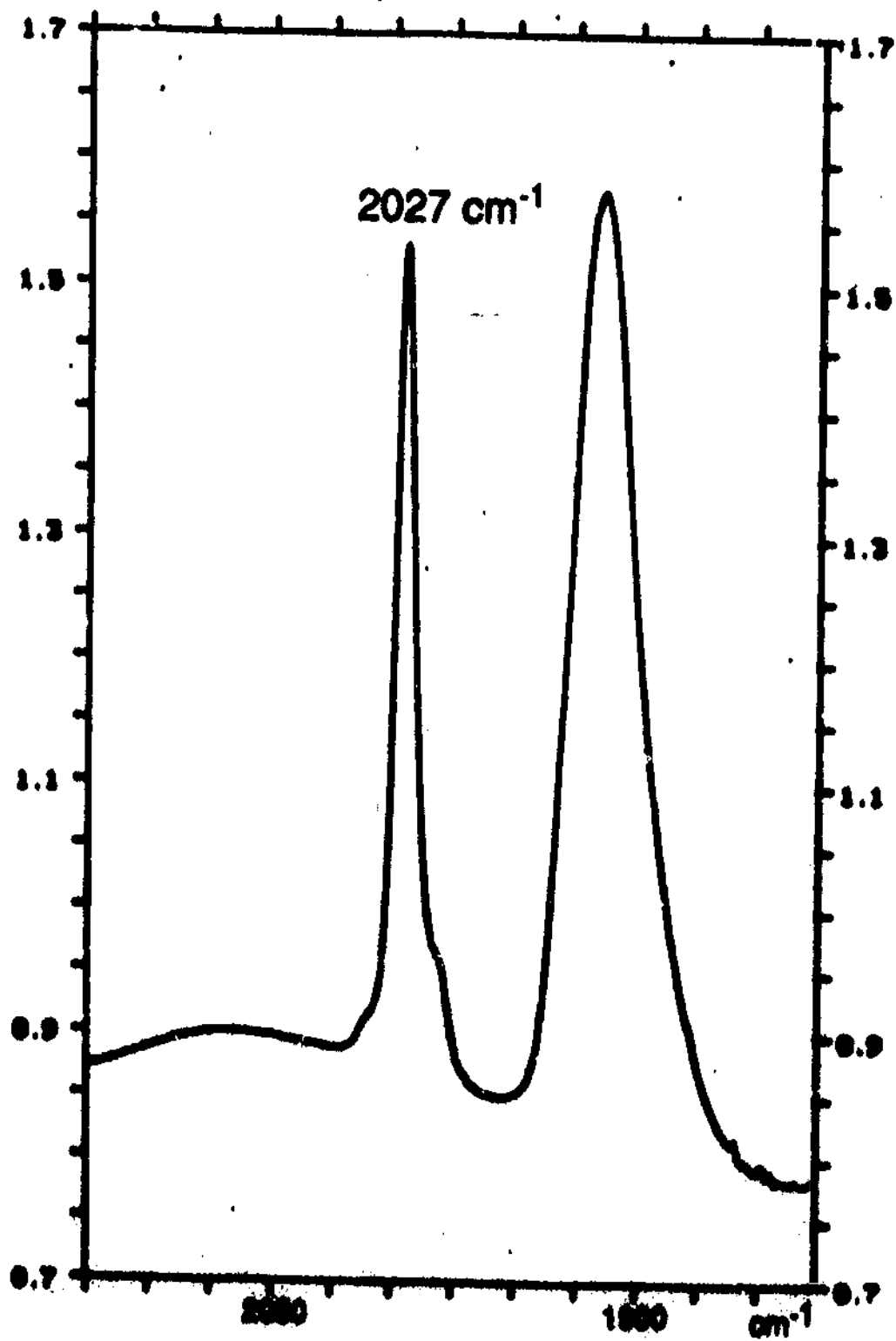


FIGURE 3. $\text{Fe}(\text{CO})_5\text{O}(\text{H})/\text{Al}_2\text{O}_3$ (0.801% Fe) used to obtain absorbance at 2027 cm^{-1} for calibration curve.

III. RESULTS

A. Alumina

When $\text{Re}_2(\text{CO})_{10}$ was deposited by incipient wetness on alumina (0.5% Re), the structural integrity of the parent carbonyl was maintained. This was evident by examining the IR bands of $\text{Re}_2(\text{CO})_{10}$ in acetone versus after deposition on alumina. As displayed in Tables 2 and 3, the IR bands for the supported $\text{Re}_2(\text{CO})_{10}$ (2072(vs), 2019(s), 1970(s,sh) cm^{-1}) match closely for those of $\text{Re}_2(\text{CO})_{10}$ in solution (2072(s), 2011(vs), and 1969(sh) cm^{-1}).

The alumina supported $\text{Re}_2(\text{CO})_{10}$ was heated to 220°C and 320°C in flowing hydrogen (20 cc/min). At both temperatures carbonyl bands at 2025(s) and 1921(vs) cm^{-1} were observed (Figure 4). These bands matched closely with bands at 2027(s) and 1924(vs) cm^{-1} of the molecular tetramer, $[\text{Re}(\text{CO})_3\text{OH}]_4$ (Table 2). The tetramer contains four $\text{Re}(\text{CO})_3$ groups, each of which is bonded to three oxides. We propose that the bands at 2025(s), and 1921(vs) cm^{-1} are from a $\text{Re}(\text{CO})_3$ surface species, which has the same local environment around the metal center, as the Re centers in the tetramer, i.e. $\text{Re}(\text{CO})_3$ bonded to three surface oxides. In addition to the IR bands for the $\text{Re}(\text{CO})_3$ surface species, there is a weak band at 2070 cm^{-1} which

TABLE 2. Carbonyl Frequencies of Rhenium Carbonyl Complexes

<u>Molecular Complex</u>	<u>$\nu(\text{CO}) \text{ cm}^{-1}$</u>	<u>Reference</u>
$[\text{Re}(\text{CO})_3\text{OH}]_4$	2021(s) 1919(s) ^a	5
$\text{Re}_2(\text{CO})_{10}$	2072(s) 2011(vs) 1969(s) ^b	8
$[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$	2011(s,sh) 2004(s) 1951(w) 1932(w) 1893(w) ^b	4
$[\text{Re}(\text{CO})_5]^-$	1910(s) 1864(s) ^a	6, 7

a: in THF

b: in acetone

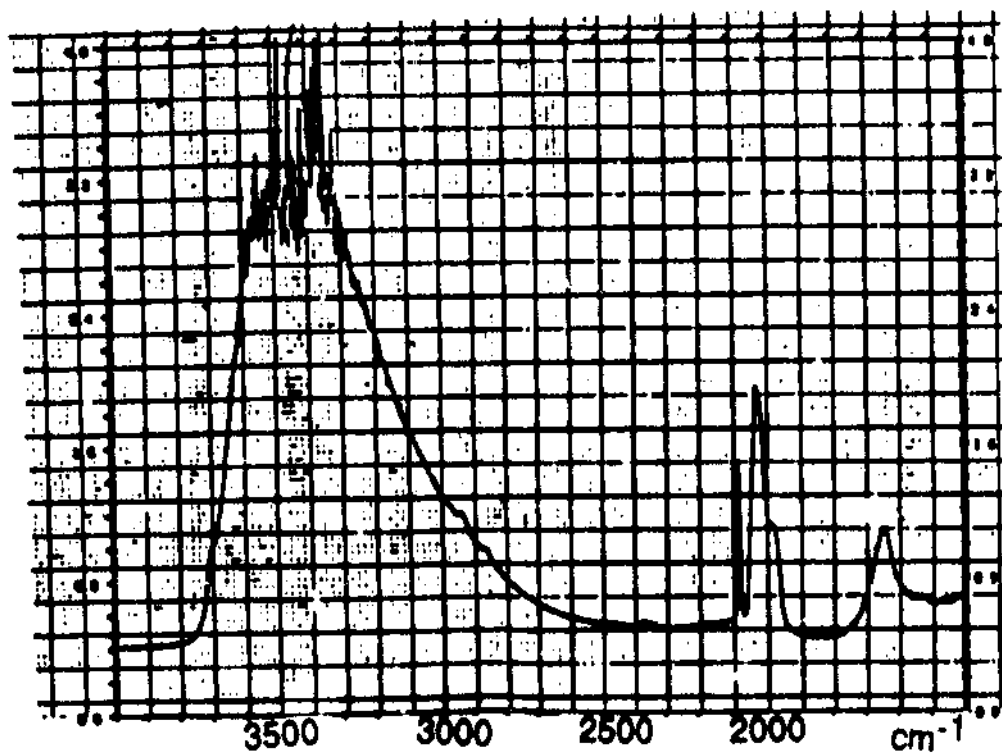
TABLE 3. Carbonyl Frequencies Obtained in this work of Supported Rhenium Carbonyl Species

<u>Supported Complex</u>	<u>$\nu(\text{CO}) \text{ cm}^{-1}$</u>	<u>Conditions</u>
$[\text{Re}(\text{CO})_3\text{OH}]_4/\text{Al}_2\text{O}_3$	2027(s) 1924(s)	a
$\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$	2072(vs) 2019(s) 1970(s,sh)	a
$\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$	2070(w) 2027(s) 1914(vs)	b
$\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$	2072(w) 2025(s) 1915(vs)	c
$[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$	2062(w) 2010(s) 1950(w) 1932(w) 1896(w)	a
$[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$	2028(s)	c

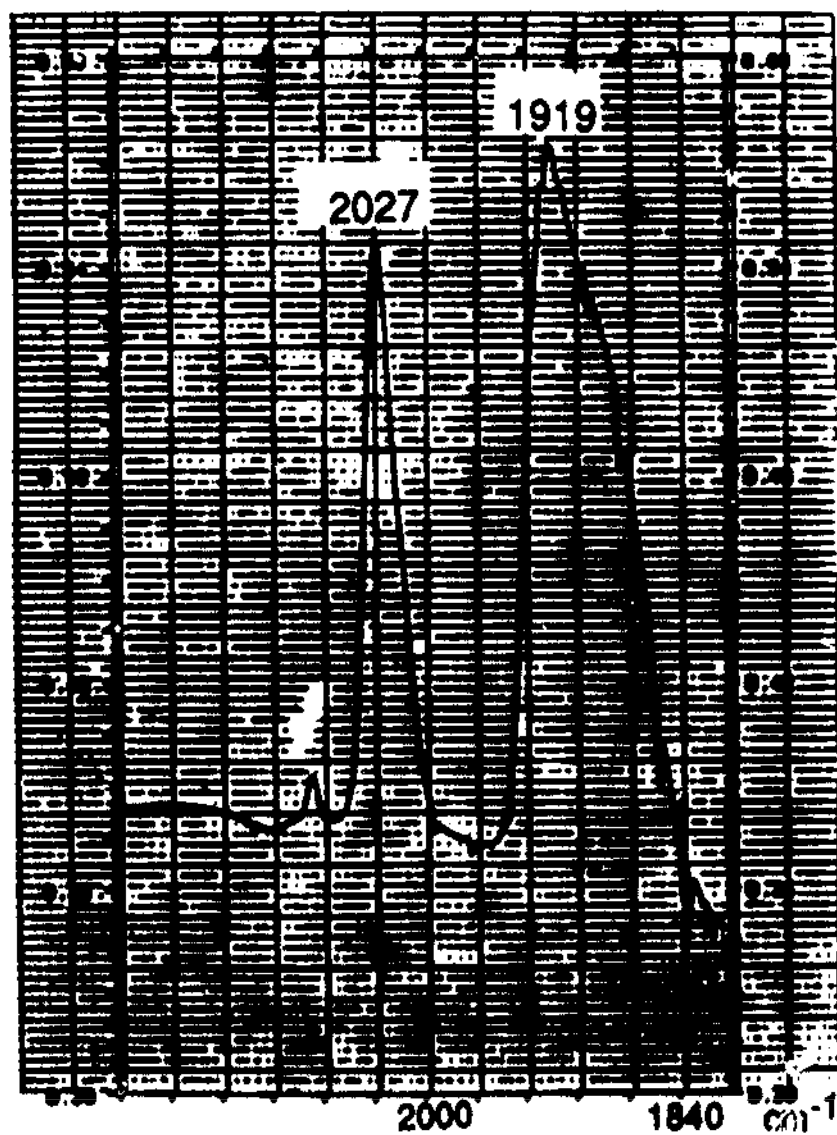
a: room temperature

b: heated to 220 °C in flowing hydrogen (20 cc/min)

c: heated to 320 °C in flowing hydrogen (20 cc/min)

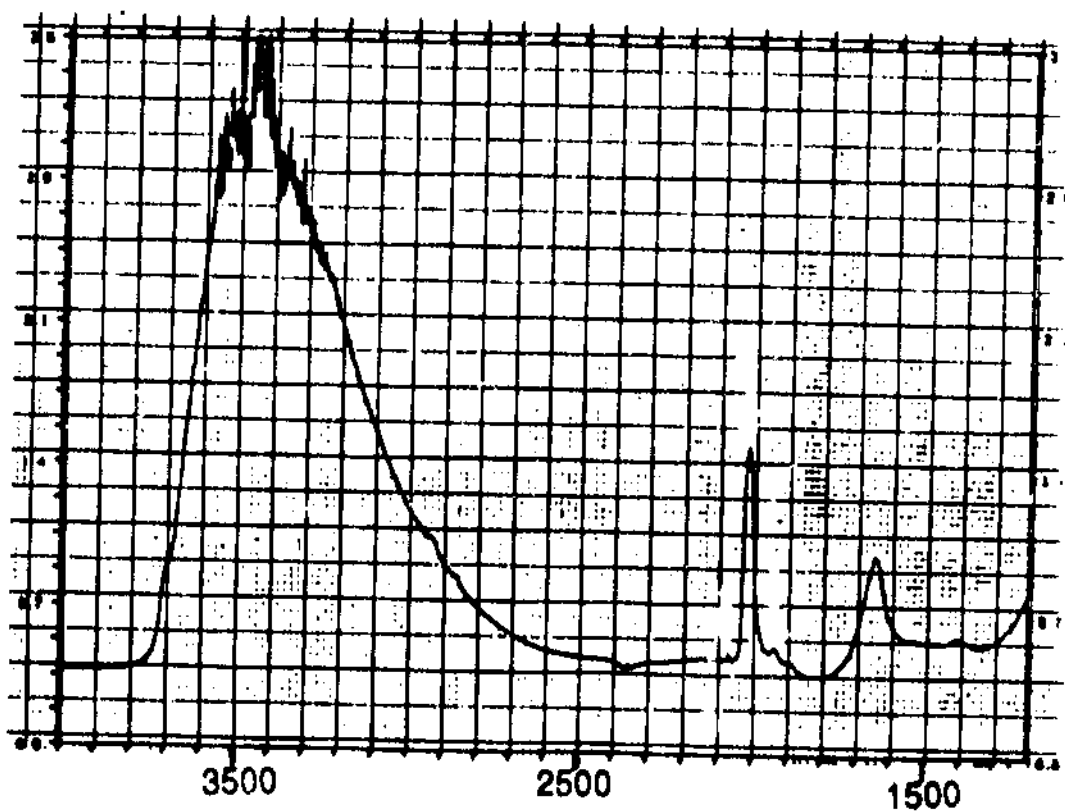


(a)

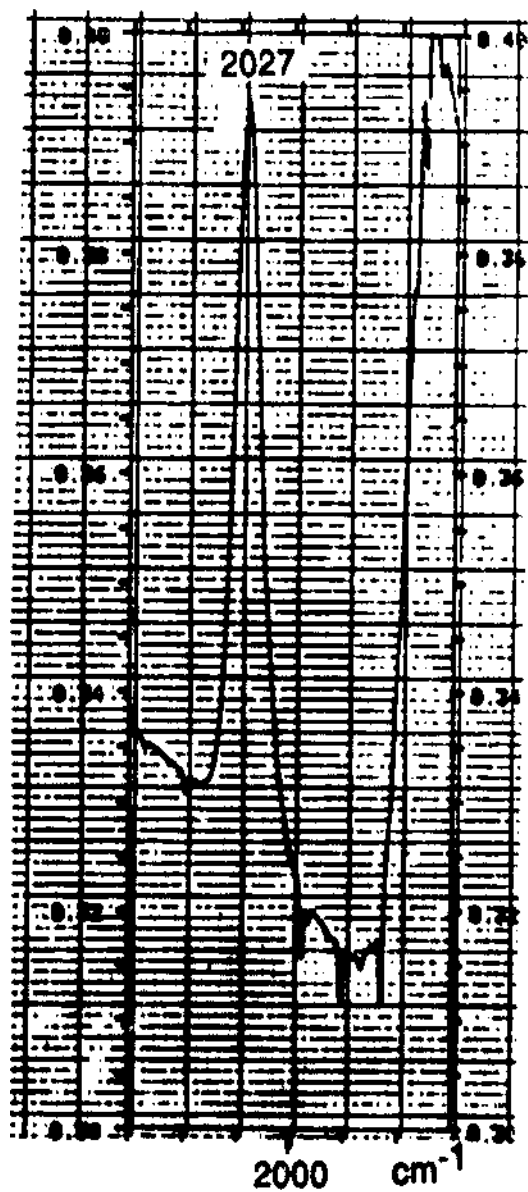


(b)

FIGURE 4. $\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$ before (a) and after heating to 220°C in flowing H_2 (b).



(a)



(b)

FIGURE 5. $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$ before (a) and after heating to 320°C (b).

may be indicative of residual $\text{Re}_2(\text{CO})_{10}$ which may not have reacted on the surface (Figure 3).

When $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$ was deposited on alumina (0.5% Re) and examined by infrared spectroscopy, bands in the carbonyl region at 2062(w), 2010(s), \approx 1950(w), 1932(w), and 1896(w) cm^{-1} were observed (Table 3). Four of these bands matched closely with those of the molecular complex in solution (Table 2). The band at 2010(s) cm^{-1} , probably was a composite of the bands at 2004(s) and 2011(s,sh) cm^{-1} , of the molecular complex because infrared bands generally tend to be broader for supported complexes as opposed to complexes in solution. Upon heating the supported $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$ to 320 $^\circ\text{C}$ in flowing hydrogen, bands at 2028(s) and 1920(m) cm^{-1} were observed, which suggests conversion to the $\text{Re}(\text{CO})_3$ species as was observed with the $\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$ samples.

In order to quantify the number of $\text{Re}(\text{CO})_3$ surface species present in each sample, the IR $\nu(\text{CO})$ intensities were compared with those of standard samples prepared with $[\text{Re}(\text{CO})_3\text{OH}]_4$. The number of $\text{Re}(\text{CO})_3$ groups in the standard samples was varied by decreasing the ratio of $[\text{Re}(\text{CO})_3\text{OH}]_4/\text{Al}_2\text{O}_3$. The following loadings of %Re were used: 0.501%, 0.406%, 0.365%, 0.229%, 0.169%, 0.085% (Table 1) The band at 2027 cm^{-1} was chosen for comparison amongst the samples since

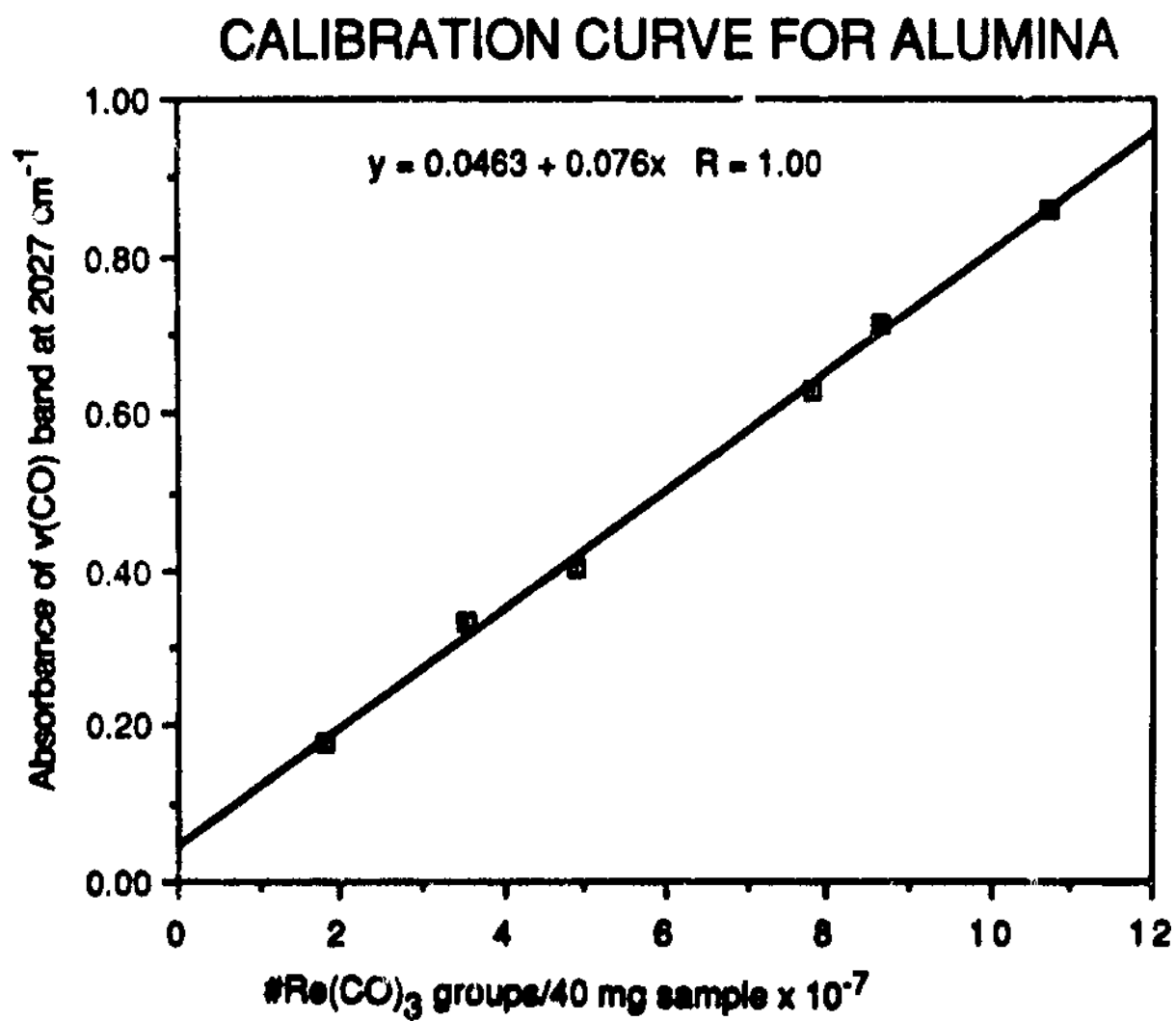


FIGURE 6. Calibration curve for $[\text{Re}(\text{CO})_3\text{OH}]_4/\text{Al}_2\text{O}_3$.

it was a sharp peak with no other overlapping bands (Figure 3). By plotting the absorbance of 2027 cm^{-1} band versus loading of the standard samples, a calibration curve was obtained (Figure 6). Because 40 mg samples were used for the IR measurements and since we are interested in the number of $\text{Re}(\text{CO})_3$ groups rather than $[\text{Re}(\text{CO})_3\text{OH}]_4$ molecules, the loadings were converted to $\text{Re}(\text{CO})_3$ groups/ 40 mg sample.

For $\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$, heated to 220°C or 320°C in flowing hydrogen an absorbance of 0.17 (Figure 4) was obtained at both temperatures, which from the calibration plot corresponds to 1.88×10^{-7} $\text{Re}(\text{CO})_3$ groups/ 40 mg of sample. This reflects a 17.6% conversion of the parent carbonyl to the $\text{Re}(\text{CO})_3$ surface species. Similarly for $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$ an absorbance of 0.016 (Figure 5) corresponds to 2.11×10^{-8} $\text{Re}(\text{CO})_3$ groups/ 40 mg of sample. This in turn reflects an 2% conversion of the parent carbonyl to $\text{Re}(\text{CO})_3$ surface species.

There are two possible explanations for such low conversion percentages in the case of $\text{Re}_2(\text{CO})_{10}$. First, the parent carbonyl can volatilize off the support surface and get carried in the hydrogen gas stream. A rhenium analysis, after the sample has been heated in

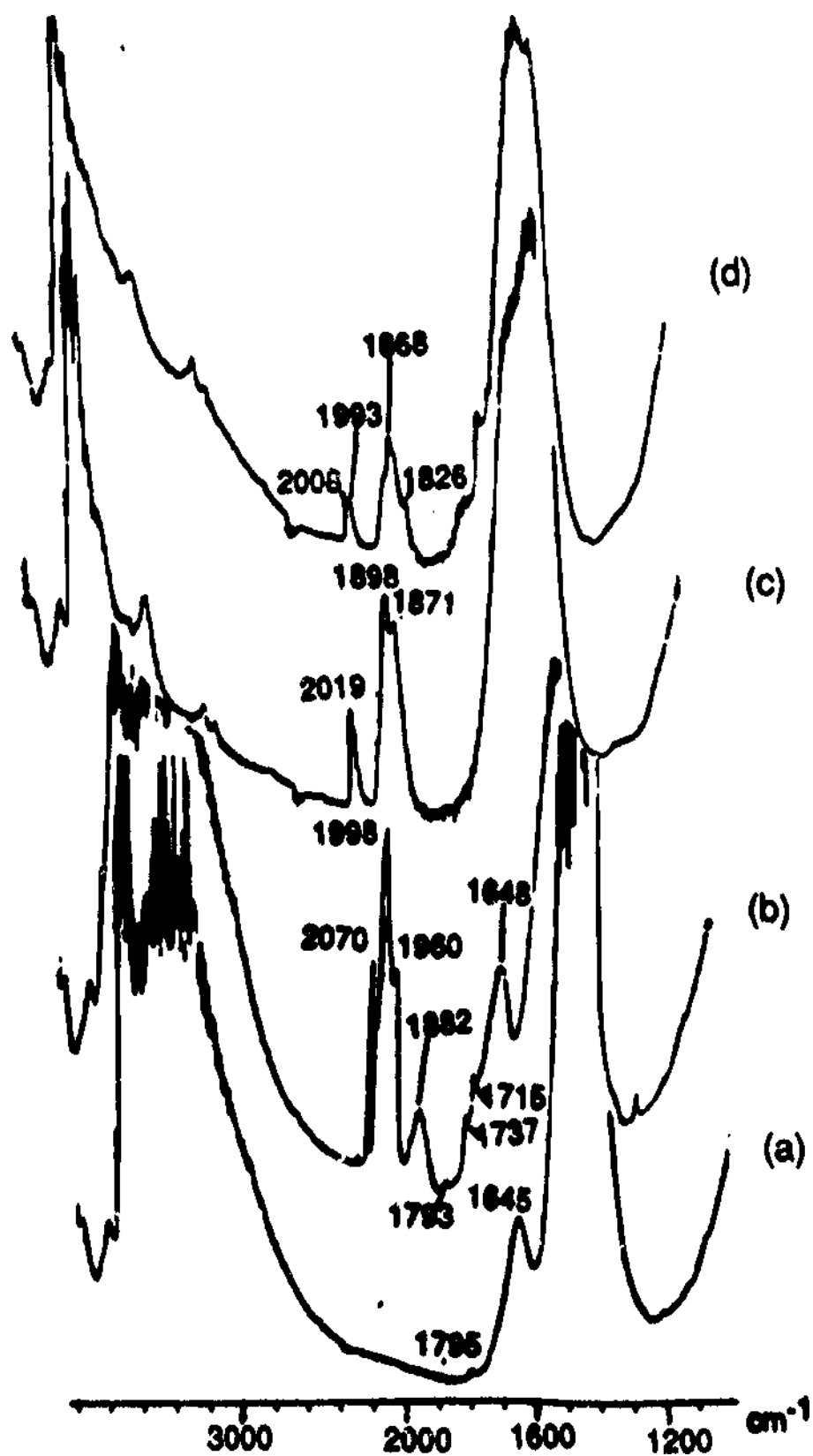


FIGURE 7. $\text{Re}_2(\text{CO})_{10}/\text{MgO}$ (a) MgO only; (b) after impregnation but before heating; (c) after heating to 220°C in flowing hydrogen; (d) after heating to 300°C in flowing hydrogen.

flowing hydrogen, is necessary to determine the rhenium content of the sample after decomposition. Another possibility is that the parent carbonyl converted to a species that is not observable by infrared spectroscopy. For example, the parent carbonyl could have possibly decomposed to elemental rhenium on the surface.

In the case of $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$ volatility is not expected; however, an "invisible" surface species may still be present. Again, a rhenium microanalysis is necessary to determine the rhenium content of the sample after decomposition.

B. Magnesia

When $\text{Re}_2(\text{CO})_{10}$ was deposited, by incipient wetness, on magnesia (0.5% Re) the structural integrity of $\text{Re}_2(\text{CO})_{10}$ was not maintained. This was evident by examining the IR bands of $\text{Re}_2(\text{CO})_{10}$ in acetone versus after deposition on magnesia (Figure 7b). The IR bands at 2070, 1998, and 1960 cm^{-1} for $\text{Re}_2(\text{CO})_{10}/\text{MgO}$ match closely with those of the molecular complex in solution. The bands at 1793, 1737, 1715, and 1648 cm^{-1} can be assigned to MgO. The band at 1882 cm^{-1} however, indicates the $\text{Re}_2(\text{CO})_{10}$ has reacted with magnesia at room temperature.

Upon heating $\text{Re}_2(\text{CO})_{10}/\text{MgO}$ to 220°C in flowing H_2 , bands at 2019, 1898, and 1871 cm^{-1} were observed in the carbonyl region

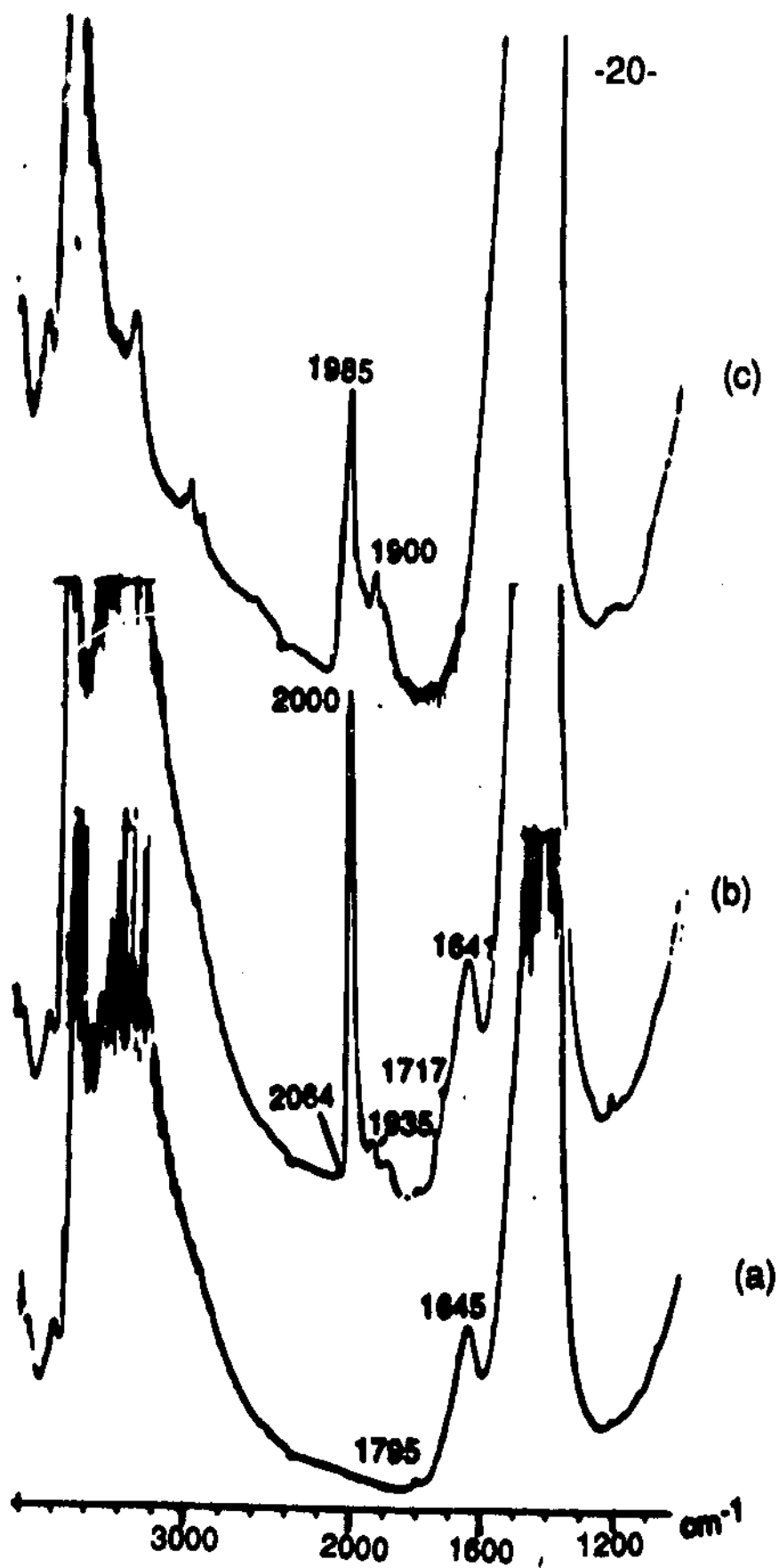


FIGURE 8. [NEt₄]₂[Re₈C(CO)₂₄]/MgO (a) MgO only; (b) after impregnation but before heating; (c) after heating 300°C in flowing hydrogen.

(Figure 7c). The bands at 1898 and 1871 cm^{-1} can possibly be assigned to $[\text{Re}(\text{CO})_5]^-$. The anion has bands at 1910 and 1864 cm^{-1} (Table 2). Upon further heating to 300°C in flowing hydrogen, dehydration is evident since, as evident, there is a decrease in intensity of the peak at 3000 cm^{-1} .

The structural integrity of $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$, was maintained upon deposition on MgO. $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]$, unlike $\text{Re}_2(\text{CO})_{10}$, did not react with MgO at room temperature. This is evident because the IR bands at 2000, 1935, and 1890 cm^{-1} (Figure 8b) correspond to the bands present in the molecular complex as well. Upon heating of $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{MgO}$ in flowing hydrogen peaks at 1985 and 1900 cm^{-1} were observed (Figure 8c). These bands could possibly be assigned to $\text{Re}(\text{CO})_3$ surface species but the frequencies are different from those apparently obtained for $[\text{Re}(\text{CO})_3\text{OH}]_4$.

A similar approach was used to obtain a calibration curve for the tetramer, $[\text{Re}(\text{CO})_3\text{OH}]_4$, on magnesia, as opposed to an alumina support. A calibration curve was however not obtainable since $[\text{Re}(\text{CO})_3\text{OH}]_4$ reacted with MgO at room temperature. This resulted in overlapped bands in the carbonyl region, preventing an accurate value for the absorbance to be measured. The bands at 2022 and 2015 cm^{-1}

overlapped (Figure 9) unlike the sharp band that was obtained at 2027 cm^{-1} for $[\text{Re}(\text{CO})_3\text{OH}]_4/\text{Al}_2\text{O}_3$ (Figure 3). It was also observed that the bands at 2022 and 2015 cm^{-1} varied in relative intensity over time, thus further preventing reproducible values for the intensity of the absorbance. Hence a "quantitative" calibration curve was not possible.

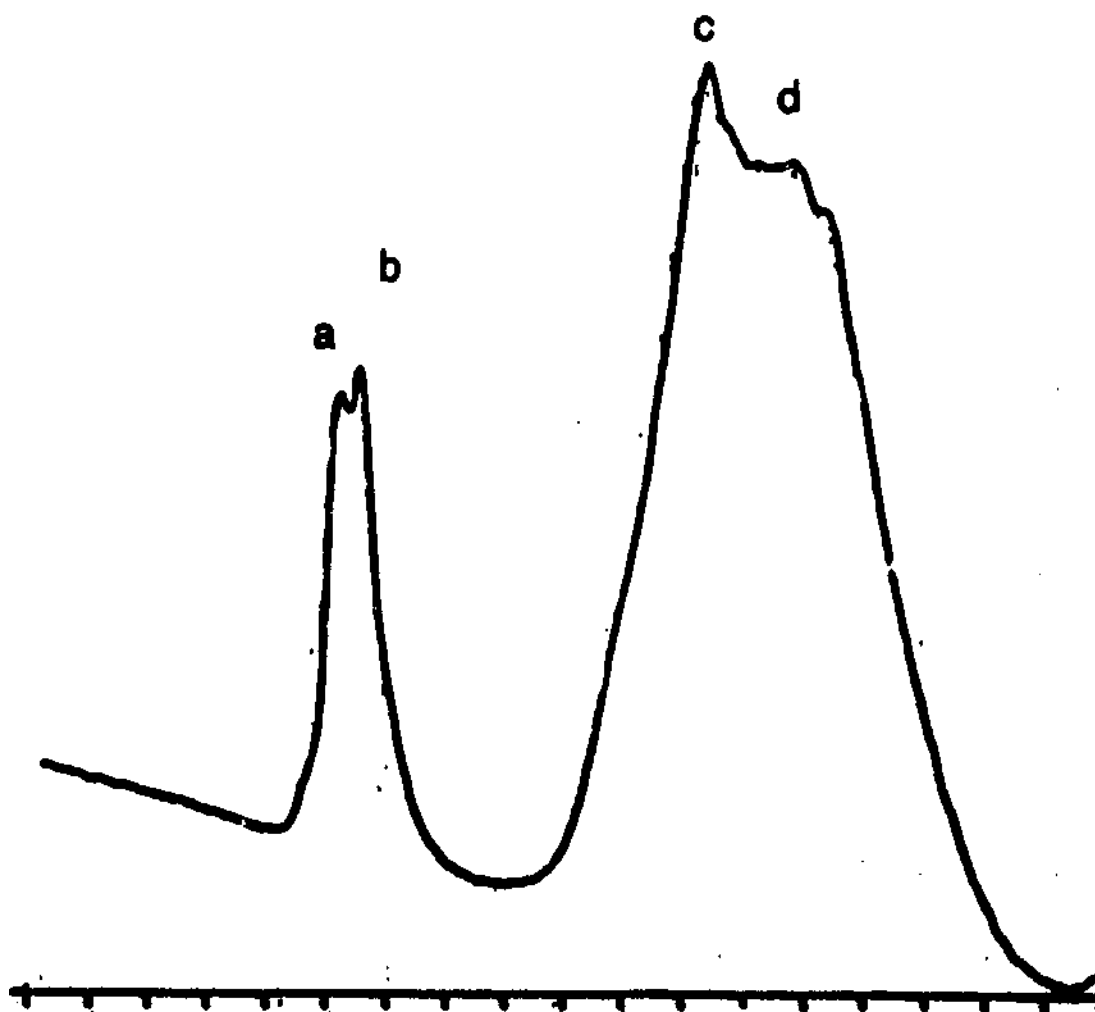


FIGURE 9. Overlapping of bands for $[\text{Re}(\text{CO})_3\text{OH}]_4/\text{MgO}$ (0.5% Re).
a = 2022 cm^{-1} ; b = 2015 cm^{-1} ; c = 1905 cm^{-1} ; d = 1182 cm^{-1} .

IV. DISCUSSION

Previous work in identifying and characterizing $\text{Re}(\text{CO})_3$ surface species involved catalysts that were prepared to incorporate ensembles consisting of three rhenium centers by reaction of the metal cluster $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$ with MgO . Catalysts designed to incorporate single, isolated rhenium centers were made by the reaction of $[\text{HRe}(\text{CO})_5]$ with MgO . The rhenium complexes interacted with the basic MgO surface, which resulted in deprotonation (dissociative chemisorption) to form the adsorbed anions, $[\text{H}_2\text{Re}_3(\text{CO})_{12}]^-$ or $[\text{Re}(\text{CO})_5]^-$. These anions were characterized as surface-bound intermediates, which upon heating are oxidized by surface $-\text{OH}$ groups of the MgO to form groupings which have been inferred to consist of three rhenium complexes (ensembles) or isolated rhenium complexes.¹

These surface-bound rhenium subcarbonyls were characterized spectroscopically and inferred to have the composition $[\text{Re}(\text{CO})_3\{\text{O-Mg}\}\{\text{HO-Mg}\}_2]$ and $[\text{Re}(\text{CO})_3\{\text{O-Al}\}\{\text{HO-Al}\}_2]$ (Figure 1) where the curly brackets enclose groups terminating the metal-oxide surfaces), formed by the fragmentation of $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$ on the MgO and Al_2O_3 surfaces. These reactions were carried out either by heating the supported rhenium cluster to 200°C in H_2 or by exposing the bound cluster to air at 25°C .³

Examining the infrared spectra in the carbonyl region of the rhenium subcarbonyls by Gates and co-workers showed that the two low-energy bands in the carbonyl stretching region of the Re complex supported on MgO (1905, 1862 cm^{-1}) are shifted to lower energies relative to the spectrum of the analogous complex on Al_2O_3 (1915, 1887 cm^{-1}). The shift indicated a greater amount of π backbonding in the MgO supported sample. The enhancement in π backbonding was consistent with a slightly higher electron density on the rhenium center on the MgO surface. The high-energy band (the symmetric stretch) is less strongly dependent on the support, as expected, appearing at 2028 cm^{-1} for both the MgO and Al_2O_3 supported samples.³

The catalytic properties of isolated rhenium complexes and the conventional form of an oxide-supported rhenium catalyst, namely as small nonuniform crystallites of rhenium metal on the MgO surface have been investigated.^{1,2} The catalytic properties were investigated for a structure sensitive conversion, the isomerization/hydrogenolysis of cyclopropane. It was found that the close agreement between the apparent activation energies for propene hydrogenation on the catalysts derived from $[\text{HRe}(\text{CO})_5]$ and $[\text{H}_3\text{Re}_3(\text{CO})_{12}]$ was consistent with the observation that the rhenium complex shown in Figure 1 was present on the surface of each

catalyst, as determined by infrared spectra of the functioning catalysts. These complexes are catalyst precursors, while the precise structures of the catalytic intermediates are unknown.¹

Previous work has reported that on the basis of the consistency of the infrared, UV-vis, and tunneling spectra, the formation of $[\text{Re}(\text{CO})_3\{\text{O-X}\}\{\text{HO-X}\}_2]$ has been inferred to take place on two different metal oxide surfaces ($X = \text{Al, Mg}$).² It has been reported that $[\text{Re}(\text{CO})_3\{\text{O-Mg}\}\{\text{HO-Mg}\}_2]$ was present on the surface of each catalyst, i.e. these complexes are catalyst precursors.

The work described in this thesis has shown that conversion to $\text{Re}(\text{CO})_3$ surface species for $\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$ and $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$ occur at lower percentages than anticipated. From the obtained calibration curve, we found that there is a 17.6% conversion for the $\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$, and a 2% conversion for the $[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$.

A similar treatment to obtain a calibration curve for $[\text{Re}(\text{CO})_3\text{OH}]_4/\text{MgO}$ was not possible since the tetramer reacted with MgO indicating that there are other carbonyl species present.

The alumina supported catalysts appear to be well defined by infrared spectroscopy. For $\text{Re}_2(\text{CO})_{10}/\text{Al}_2\text{O}_3$ and

$[\text{NEt}_4]_2[\text{Re}_9\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$ however, much of the Re is unaccounted for. Possible explanations are that the parent carbonyl can volatilize off the support surface and get carried off into the hydrogen stream. The parent carbonyl could also have converted to a surface species that was not observable by infrared spectroscopy. However, the magnesia supported samples do not appear well defined, since both $[\text{Re}(\text{CO})_3\text{OH}]_4$ and $\text{Re}_2(\text{CO})_{10}$ reacted at room temperature with MgO which prevented us in obtaining an calibration curve.

$[\text{NEt}_4]_2[\text{Re}_8\text{C}(\text{CO})_{24}]/\text{Al}_2\text{O}_3$ however, much of the Re is unaccounted for. Possible explanations are that the parent carbonyl can volatilize off the support surface and get carried off into the hydrogen stream. The parent carbonyl could also have converted to a surface species that was not observable by infrared spectroscopy. However, the magnesia supported samples do not appear well defined, since both $[\text{Re}(\text{CO})_3\text{OH}]_4$ and $\text{Re}_2(\text{CO})_{10}$ reacted at room temperature with MgO which prevented us in obtaining an calibration curve.

V. REFERENCES

- (1) Kirilin, P.S.; Gates, B.C. Nature 1987, 325, 38-40.
- (2) Kirilin, P.S.; DeThomas, F.A.; Bailey, J.W.; Gold, H.S.; Dybowski, C.; Gates, B.C. J. Phys. Chem. 1986, 90, 4882-4887.
- (3) Kirilin, P.S.; DeThomas, F.A.; Bailey, J.W.; Moller, K.; Gold, H.S.; Dybowski, C.; Gates, B.C. Surf. Sci. 1986, 175, L707-L713.
- (4) Hayward, C.M.T.; Shapley, J.R. Organometallics 1988, Z, 448-452.
- (5) Herberhold, M.; Suss, G. Angew. Chem. Int. Ed. Engl. 1975, 14, 700.
- (6) Hileman, J.C.; Huggins, D.K.; Kaesz, H.D. Inorg. Chem., 1962, 1, 933.
- (7) Allen, D.M.; Cox, A.; Kemp, T.J.; Qaisar, S.; Pitts, R.B. J. Chem. Soc., Dalton Trans. 1976, 1189-1193.
- (8) Cotton, F.A.; Wing, R.M. Inorg. Chem. 1965, 1328-1334.