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**NOVEL APPROACHES TO THE PRODUCTION OF HIGHER  
ALCOHOLS FROM SYNTHESIS GAS**

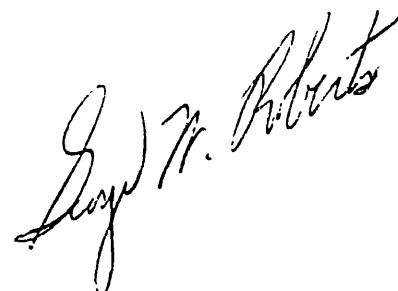
Quarterly Technical Progress Report No. 10

For The Period January 1, 1993 to March 31, 1993

Contractor

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# NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report  
January 1, 1993 to March 31, 1993

## CONTRACT OBJECTIVES

Task 1. Program Management.

Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.

Task 3. Novel Catalysts for Synthesis of Higher Alcohols.

Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis.

Task 5. Technology Evaluation.

## SUMMARY

- Under Task 2:

Catalyst analyses suggest that deactivation due to poisoning by iron and nickel carbonyls was probably responsible for poor methanol production during the first MeOH synthesis verification run in December, 1992.

- Under Task 3:

The promoting effect of rhenium (Re) on rhodium (Rh)/alumina ( $\text{Al}_2\text{O}_3$ ) higher oxygenate synthesis (HAS) catalysts was studied. All of these catalysts contained a nominal 1 wt. % Rh. Some of the Rh/Re/ $\text{Al}_2\text{O}_3$  catalysts were more selective for CO conversion to oxygenates than any of the catalysts previously studied. Both the syngas conversion and the oxygenate selectivity increased as the Re content was increased to 12 wt. %. This concentration roughly corresponds to the amount required to cover an alumina surface area of 170  $\text{m}^2/\text{g}$  with a monolayer of  $\text{Re}_2\text{O}_7$ . The 1wt.%Rh/12wt.%Re/ $\text{Al}_2\text{O}_3$  catalyst had a carbon efficiency to oxygenates of 58%. However, the CO conversion was less than 1%.

Extended X-ray Absorption Fine Structure (EXAFS) analysis showed that when  $[\text{Rh}_4(\text{CO})_{12}]$  is adsorbed onto Re/ $\text{Al}_2\text{O}_3$ , small Rh particles with a coordination number less than three are formed. These particles do not appear to grow to any significant extent upon heat treatment at 200°C. Major growth of Rh particles is observed with a "plain"  $\text{Al}_2\text{O}_3$  support. .

The use of a silica ( $\text{SiO}_2$ ) support was also investigated. Re oxide was unstable on  $\text{SiO}_2$  and Rh/Re/ $\text{SiO}_2$  catalysts did not give promising performance results compared to Rh/Nb/ $\text{Al}_2\text{O}_3$  catalysts.

## TECHNICAL PROGRESS

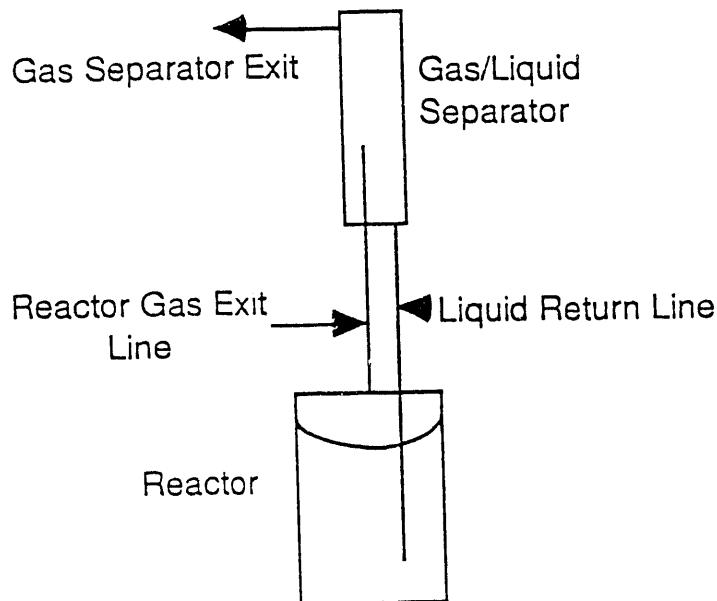
- Under Task 2:

### High Temperature Reactor Oil

A more plausible explanation has surfaced regarding the hypothesized decomposition of Drakeol® 34 mineral oil during high temperature testing in the stirred autoclave in October and November, 1992. Most of the mineral oil probably did not decompose, but instead was carried out due to a pressure difference between the reactor and gas/liquid separator. Referring to Figure 1, calculations showed that the pressure in the reactor was at least 4.4 psi greater than the pressure in the separator at the process conditions that existed during the high temperature run. This pressure drop is equivalent to a 141 inch head of oil, but the liquid return line was not nearly this long. Obviously, with this pressure difference, oil flowed out of the reactor into the separator, and then probably out the top of the separator. As partial verification of this hypothesis, an increase in oil level was observed in the wet test meter downstream of the separator during the run. This carry over of oil can account for about 170 ml of the total 250 ml originally placed in the reactor. About 8 ml of the remaining oil can be accounted for by simple vaporization. The balance could have been adsorbed by the carbon forming in the reactor.

The Boudouard reaction can account for the carbon formed; sufficient CO was fed to account for all 50 gr of carbon present in the reactor. Analysis of the reactor exit gas might have shown the  $\text{CO}_2$  formed by the Boudouard reaction, but the run ended before any detailed gas analyses could be made. Iron and nickel are known catalysts for CO disproportionation to C and  $\text{CO}_2$ . Inductive Coupled Plasma analysis of the carbon from the reactor showed 22,400 ppm Fe and 4,240 ppm Ni. The iron and nickel probably came from carbonyls generated in the gas feed lines. These carbonyls are not stable above about 300°C, so would likely decompose in the reactor. The only working carbonyl trap for this run was in the CO feed line, well upstream of the reactor.

FIGURE 1  
Existing Gas/Liquid Separator Configuration



To prevent these problems from reoccurring, the following steps have been taken:

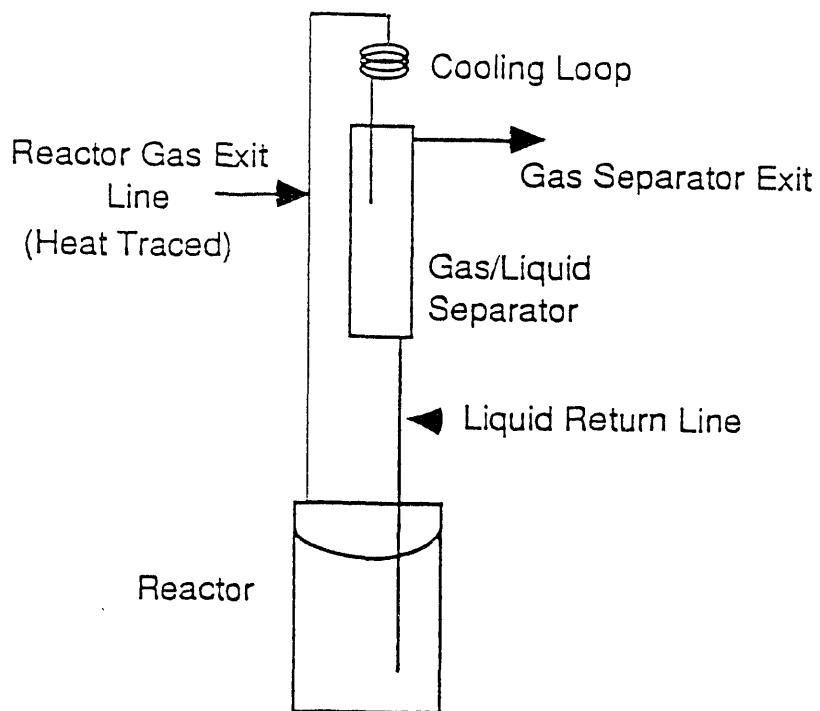
- The existing 1/8" diameter reactor exit tubing has been replaced with 1/4" tubing. Calculations show that this change decreases the pressure drop to only 0.07 psi, or 2.33 inches of mineral oil.
- A small cooling loop has been installed before the gas/liquid separator so the separator can act only as a separator, not a cooler/separator combined. As shown in Figure 2, the new configuration will have the reactor exit gas line heated to reactor temperature, ensuring no oil condensation. The tubing then turns downward into the cooling loop, allowing condensing liquid to drain into the separator. The separator temperature will be controlled based on the separator exit gas temperature.
- A carbonyl trap has been installed immediately before the reactor, and the tubing between the trap and the reactor is heated to ensure that no additional carbonyls are formed.

## Methanol Synthesis Verification Run

### Gas Chromatograph Problems

During the methanol synthesis verification run conducted in December, 1992, a gas chromatograph (GC) failure limited the amount of analytical data that could be taken. More specifically, a gas sampling valve leaked and the sample did not flow into the thermal conductivity detector (TCD) which measures H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O. The flame ionization detector (FID), which measures alcohol and other organics, was not affected. The rotor of the gas sampling valve was replaced, and the gas chromatograph was placed into operation. However, upon close analysis of the resulting data, a "ghost" peak appeared in the TCD results. This peak, with the shortest retention time of any peak, was probably caused by sample bypassing the column, again attributed to malfunction of the gas sampling valve. Therefore, all data taken with the TCD during the run was not reliable, and no mass balances or true stream compositions could be calculated for this run.

FIGURE 2  
Modified Separator Configuration



### Catalyst Poisoning:

Despite the GC problems described above, the methanol composition measured by the FID appeared to be reliable. The data, which was taken only during the last 12 hours of the 200-hour run, showed only 1 volume % methanol in the reactor exit stream, well below the expected range of 5 to 15 volume %.

Two explanations could account for these low numbers:

1) insufficient heat tracing allowed methanol condensation somewhere downstream of the reactor exit, or; 2) catalyst deactivation caused poor conversion of CO. The first explanation is not likely since the vapor pressure of methanol at 25°C is 0.17 atm, which means that even if methanol were condensing, the gas stream would still contain about 17% methanol. Also, no problems with the heating tapes were experienced during the run.

Therefore, catalyst deactivation is the most plausible explanation for the low methanol production. Two types of deactivation are possible, thermal deactivation and chemical deactivation or poisoning. The reactor temperature was stable at about 250°C throughout the run; no periods of high temperature were observed, so serious thermal deactivation was not considered likely. In order to evaluate poisoning, bulk elemental analyses of fresh, unreduced catalyst and spent catalyst were conducted using Inductive Coupled Plasma (ICP). As shown in Table 1, there was over 1500 ppm of iron present in the bulk catalyst after the run, compared to less than 50 ppm in the fresh catalyst. Increased levels of nickel, chromium, and manganese were also observed.

TABLE 1  
ICP Elemental Analysis of Fresh and Spent Samples  
of BASF Cu/ZnO Catalyst from the 12/92 Methanol Synthesis Run

Component	Fresh Catalyst	Spent Catalyst
Iron	44 ppm	1552 ppm
Nickel	68 ppm	460 ppm
Chromium	3 ppm	102 ppm
Manganese	2 ppm	22 ppm
Copper	69%	70%
Zinc	26%	25%
Aluminum	4%	4%

Note that the copper, zinc, and aluminum levels did not change significantly. These levels also agree with the original BASF catalyst analysis.

These catalyst samples were also examined using scanning electron microscopy (SEM) coupled with x-ray elemental spectroscopy (EADS). Preliminary results indicate that certain spots of catalyst contain up to 7700 ppm iron, while most areas give no iron response. The SEM/EADS scans only a specific volume of catalyst particles, about 1 cubic micron. At present, no correlation has been found between the iron concentration and either the copper, zinc or alumina concentrations. However, additional analysis are being carried out.

- Under Task 3:

Rhenium-promoted (1%Rh/Re/Al<sub>2</sub>O<sub>3</sub>) catalysts containing variable amounts of Re were tested for syngas conversion to oxygenates. The nature of these catalysts was investigated using Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy of Re and Rh edges and Fourier Transform Infrared (FTIR) spectroscopy. Silica-supported catalysts, 1%Rh/12%Re/SiO<sub>2</sub> and 1%Rh/6%Nb/SiO<sub>2</sub>, were also studied.

The literature provides a rationale for studying Re as a promoter in supported Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, with the goal of increased CO hydrogenation selectivity to higher oxygenates. First, rhenium (Re) follows the best-known promoters, such as V and Mo, in the periodic table. Second, Iizuka<sup>1</sup> has reported that supported rhenium catalysts, without Rh, produced oxygenates from CO + H<sub>2</sub> with a carbon efficiency (CE) of 75%. In our work, the desired Rh/Re/Al<sub>2</sub>O<sub>3</sub> catalyst structure was highly-dispersed Rh clusters among ReO<sub>x</sub> patches supported on a high-surface-area alumina. These catalysts were prepared by impregnation of ammonium perrhenate (NH<sub>4</sub>ReO<sub>4</sub>) onto 170 m<sup>2</sup>/g gamma-alumina (Al<sub>2</sub>O<sub>3</sub>) support, followed by adsorption of rhodium (IV) carbonyl [Rh<sub>4</sub>(CO)<sub>12</sub>].

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<sup>1</sup>Iizuka T., 8th Inter. Cong. Cat. Proceedings, Vol. 2, pp. 221-232, 1984.

## EXPERIMENTAL

### Catalyst Preparation

Catalyst preparation procedures are given in Appendix A. The target compositions of the catalysts synthesized were: 1%Rh/1.5%Re/Al<sub>2</sub>O<sub>3</sub>, 1%Rh/6%Re/Al<sub>2</sub>O<sub>3</sub>, 1%Rh/12%Re/Al<sub>2</sub>O<sub>3</sub>, 1%Rh/24%Re/Al<sub>2</sub>O<sub>3</sub>, 1%Rh/12%Re/SiO<sub>2</sub>, and 1%Rh/6%Nb/SiO<sub>2</sub>.

The literature suggests that 12 wt. % Re gives monolayer coverage of a 170 m<sup>2</sup>/g surface area support<sup>2,3,4</sup>. Therefore, 12% Re was impregnated on SiO<sub>2</sub> (200 m<sup>2</sup>/g) and Al<sub>2</sub>O<sub>3</sub> (170 m<sup>2</sup>/g) supports using NH<sub>4</sub>ReO<sub>4</sub> and the incipient wetness technique. The impregnated supports were then calcined at 400°C in O<sub>2</sub> for 4 hrs and evacuated at 400°C for 1 hr. Re oxides have low boiling temperatures. With the SiO<sub>2</sub> support, almost the entire amount of Re was lost as ReO<sub>3</sub> (red-blue color, 100°C bp) during this pretreatment. Except as noted below, very little loss of Re from the Al<sub>2</sub>O<sub>3</sub> support was observed, presumably due to stronger adsorption of Re oxides by Al<sub>2</sub>O<sub>3</sub>.

In the 1%Rh/Re/Al<sub>2</sub>O<sub>3</sub> preparations at 6 and 12 wt. % Re, the alumina was first heated at 400°C for 4 hr in oxygen and then for 1 hr in vacuum. Re was then added using the incipient wetness impregnation technique based on about 3 gr. of Al<sub>2</sub>O<sub>3</sub> and 10 gr. of distilled H<sub>2</sub>O. The amount of NH<sub>4</sub>ReO<sub>4</sub> that was dissolved in the distilled water was chosen to give the desired final Re loading. The highest Re loading (24%Re) was attempted by two attachments of 12% Re. After each Re impregnation, the catalyst was heated to 400°C in O<sub>2</sub> for 4 hr and then in 10<sup>-4</sup> torr vacuum for 1 hr. However, a large quantity of Re was lost from the 24%Re/Al<sub>2</sub>O<sub>3</sub> preparation as red-blue ReO<sub>3</sub> during the second calcination.

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<sup>2</sup>Wachs I., E., Jehng J. M., Hardcastle F. D., Solid State Ionics, Vol. 32-33, pp. 904-910, 1989.

<sup>3</sup>Turek A. M., Wachs, I. E., DeCanio, E., J. Phys. Chem., Vol. 96, pp. 5000-5007, 1992.

<sup>4</sup>Vuurman, M. A., Wachs, I. E., J. Phys. Chem., Vol. 96, pp. 5008-5016, 1992.

An alternative catalyst preparation was made in which Re was attached using  $\text{Re}_2(\text{CO})_{10}$  in dry hexane. A solution of hexane was dried by distilling in a sodium-benzophenone mixture. Starting with 0.335g  $\text{Re}_2(\text{CO})_{12}$  in 67 cc dry hexane, which is equivalent to 6 wt. % Re on 3 g  $\text{Al}_2\text{O}_3$ , only 1.5 wt. % Re was present on the final catalyst as measured by the intensity of CO bands in the parent and "spent" hexane solutions.

Rh was adsorbed at room temperature on  $\text{Al}_2\text{O}_3$  or  $\text{Re}/\text{Al}_2\text{O}_3$  using  $[\text{Rh}_4(\text{CO})_{12}]$  dissolved in dry hexane. In a typical procedure, 1%Rh was attached by stirring 0.063g  $\text{Rh}_4(\text{CO})_{12}$  dissolved in 63 cc dry hexane with 12%Re/ $\text{Al}_2\text{O}_3$  for 12 hr. The mixture was then filtered and the catalyst was washed with fresh dry hexane solution, dried under flowing nitrogen for 15 minutes, and stored under nitrogen. The Rh loading was determined using FTIR spectroscopy to measure the concentration of  $[\text{Rh}_4(\text{CO})_{12}]$  in the hexane solution before and after adsorption on the support.

#### FTIR Spectroscopy

The in-situ quartz IR cell was fitted with  $\text{CaF}_2$  windows. The self-supporting wafer density was 45 mg/cm<sup>2</sup>. Infrared spectra were recorded on a RFX-65 FTIR spectrometer from Laser Precision Analytical. The resolution was 4 cm<sup>-1</sup> at 4000 cm<sup>-1</sup> wave number.

#### EXAFS Study

The EXAFS experiments were performed on X-ray beam line X11-A at the National Synchrotron Light Source in Brookhaven Laboratory. Self-supporting wafers of 100-400 mg were mounted in the sample holders. The ring energies of 3 GeV and ring currents of 40-80 mA were used. EXAFS samples were held at liquid nitrogen temperature. Parent samples were observed under  $10^{-5}$  torr vacuum. The samples were then heated in 50 cc/min helium at 200°C for 1 hr, cooled to room temperature, and the EXAFS spectra were recorded.

### HAS Reaction

Catalyst preparation and charging of the CO hydrogenation reactor were carried out in a dry, oxygen-free environment. Catalysts were activated in 50 cc/min helium (Linde, 99.999%) at 200°C for 1 hr, which removed all CO ligands and formed naked Rh clusters, as evidenced by IR and EXAFS spectroscopies.

Research grade hydrogen (Linde, 99.9995%) and ultra-high-purity grade carbon monoxide (Linde, 99.999%) from an aluminum cylinder were used as a feed. The gases were passed through 5A molecular sieve traps and oxytraps. In addition, CO was also passed over alpha-alumina at 300°C to decompose carbonyls. The reactor was lined with copper. With the exceptions noted in Table 2, the reaction conditions were: 30 atm, 200°C, 9000 l/kg/hr GHSV, and H<sub>2</sub>:CO ratio of 2. Pre- and post-reactor zones were maintained at 200°C. Exit gases were analyzed using a FID in a Varian model 3700 gas chromatograph. The products were separated using a Porapak Q column from Supelco.

### **RESULTS & DISCUSSION**

Table 2 shows the catalyst compositions that were synthesized and the results of testing these catalysts for higher-alcohol synthesis (HAS) activity. This table also contains some information concerning the catalyst preparation techniques and the testing conditions. The catalysts were characterized by Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy and by Infrared (IR) Spectroscopy of adsorbed CO. Table 3 contains EXAFS results on Rh/Al<sub>2</sub>O<sub>3</sub> and Rh/Re/Al<sub>2</sub>O<sub>3</sub> catalysts.

### Catalyst Characterization

EXAFS analysis of 1%Rh/12%Re/Al<sub>2</sub>O<sub>3</sub> catalyst revealed that Rh-Re, Re-Re, and Re-O-Re bonds were not formed. Only Rh-Rh, Rh-O and Re-O bonds were present. These observations are in agreement with the model proposed by Wachs and co-workers (1,2,3) for the Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> system, i.e., isolated ReO<sub>4</sub><sup>-</sup> units, comprised of three equivalent Re = O bonds and one Re-O-Al bond, on the Al<sub>2</sub>O<sub>3</sub> surface.

Rh clusters formed by adsorbing [Rh<sub>4</sub>(CO)<sub>12</sub>] on 12%Re/Al<sub>2</sub>O<sub>3</sub> had a Rh-Rh coordination number of 2.2, as shown in Table 3. Upon heating this catalyst to 200°C in 50 cc/min He for 1 hr, the Rh-Rh coordination number increased marginally to 2.6, indicative of very small Rh crystallites. On a bare alumina surface, the Rh-Rh coordination number of the adsorbed complex was 2.7. However, this coordination number increased to 4.3 upon heating the catalyst to

However, this coordination number increased to 4.3 upon heating the catalyst to 200°C in He. From this data, it appears that the isolated patches of rhenium oxide on  $\text{Al}_2\text{O}_3$  may have prevented agglomeration of Rh clusters.

The FTIR spectra of as-synthesized 1%Rh/12%Re/ $\text{Al}_2\text{O}_3$  catalyst is shown in Figure 3. Similar to 1%Rh/ $\text{Al}_2\text{O}_3$ , it consisted of four CO bands at 2109, 2086, 2041 and 1839  $\text{cm}^{-1}$ . The bands at 1839  $\text{cm}^{-1}$  and 2086  $\text{cm}^{-1}$  are attributed to adsorbed  $\text{Rh}_6(\text{CO})_{16}$ <sup>5</sup> and the bands at 2109 and 2041  $\text{cm}^{-1}$  are attributed to CO that is adsorbed on Rh in a gem-dicarbonyl configuration. The absence of a band at about 1885  $\text{cm}^{-1}$  wavenumber<sup>6</sup>, corresponding to the bridge carbonyl in  $\text{Rh}_4(\text{CO})_{12}$ , suggests that this compound per se is not present on the catalyst surface. This spectrum indicates that  $\text{Rh}_4(\text{CO})_{12}$  is partially decomposed<sup>7</sup> as it adsorbs onto Re/ $\text{Al}_2\text{O}_3$ . As shown in the Quarterly Report for October 1 to December 31, 1992, partial decomposition was also observed when  $\text{Rh}_4(\text{CO})_{12}$  was adsorbed onto plain  $\text{Al}_2\text{O}_3$  and Nb/ $\text{Al}_2\text{O}_3$ . However, Figure 1 suggests that decomposition is more extensive with the Re/ $\text{Al}_2\text{O}_3$  support.

Upon heating Rh/Re/ $\text{Al}_2\text{O}_3$  in 50 cc/min He at 5°C/min, the original Rh clusters decomposed at about 100°C, leaving only Rh-gem-dicarbonyl bands at 2109 and 2041  $\text{cm}^{-1}$ . CO bands disappeared completely at about 275°C. On Rh/ $\text{Al}_2\text{O}_3$  catalysts, the as-synthesized clusters lost CO completely at 200°C.

After cooling to 25°C, CO at 100 torr was adsorbed on the Rh/Re/ $\text{Al}_2\text{O}_3$  catalyst. The FTIR spectra are shown in Figure 4. Similar to Rh/ $\text{Al}_2\text{O}_3$ , Rh-gem-dicarbonyl species were formed, as indicated by CO bands at 2109 and 2041  $\text{cm}^{-1}$ . After heating in 50 cc/min He at 5°C/min, the CO desorbed completely at about 200°C. The same observation was made on Rh/ $\text{Al}_2\text{O}_3$  catalyst.

FTIR results on as-synthesized 1%Rh/6%Re/ $\text{Al}_2\text{O}_3$ , 1%Rh/1.5%Re(from  $\text{Re}_2(\text{CO})_{10}$ )/ $\text{Al}_2\text{O}_3$  (at 100°C), 0.6%Rh/12%Re/ $\text{SiO}_2$  and 0.6%Rh/6%Nb/ $\text{SiO}_2$  catalysts are shown in Figures 5 to 8, respectively. The spectra for 1%Rh/6%Re/ $\text{Al}_2\text{O}_3$  (Figure 5), and 0.57%Rh/6%Nb/ $\text{SiO}_2$  (Figure 8) showed predominantly linearly-adsorbed CO, with some contribution from Rh-gem-dicarbonyl species. The spectrum for 0.6%Rh/12%Re/ $\text{SiO}_2$  (Figure 7) showed

<sup>5</sup>Chini P., Chem. Commun., p. 440, 1967.

<sup>6</sup>Beck W., Lottes K., Chem. Ber., Vol. 94, p. 2578, 1961.

<sup>7</sup>Evans J., McNulty G.S., J. Chem. Soc. Dalton Trans., pp. 587-594, 1984.

only Rh-geminal dicarbonyl species, indicative of finely-dispersed Rh.

With 1%Rh/6%Re/Al<sub>2</sub>O<sub>3</sub>, 0.08%Rh/SiO<sub>2</sub>, 0.6%Rh/12%Re/SiO<sub>2</sub> and 0.57%Rh/6%Nb/SiO<sub>2</sub>, CO from the original Rh cluster compound always desorbed at 200°C. However, when the promoter amount was close to, or more than, the amount corresponding to monolayer coverage, as with 1%Rh/12%Re/Al<sub>2</sub>O<sub>3</sub> and 1%Rh/9%Nb/Al<sub>2</sub>O<sub>3</sub>, CO from the original cluster desorbed at a temperature higher than 200°C. Adsorbed CO always desorbed from all these catalysts at 200°C.

In addition to Rh-gem-dicarbonyl bands, the 1%Rh/1.5%Re/Al<sub>2</sub>O<sub>3</sub> catalyst (Figure 7) also showed bands from CO attached to Re. These Re-CO bands were present at 2097, 2025, and 1926 cm<sup>-1</sup> and did not disappear even at 275°C.

### Reaction Results

To study the catalytic effect of Re, 1%Rh/Re/Al<sub>2</sub>O<sub>3</sub> catalysts containing 1.5%, 6%, and 12% Re and 0.6%Rh/12%Re/SiO<sub>2</sub> were tested for syngas conversion to oxygenates. The results are summarized in Table 2. On 0.6%Rh/12%Re/SiO<sub>2</sub>, both CO conversion (0.28%) and oxygenate selectivity (5%) were very low. This poor performance might be due to the loss of most of the Re during pretreatment. Therefore, it was decided that SiO<sub>2</sub> was not a suitable support for Re promoted catalysts.

At standard operating conditions, the 1% Rh/12%Re/Al<sub>2</sub>O<sub>3</sub> catalyst gave a low CO conversion (0.60%), and a high oxygenate carbon efficiency (53%). The oxygenate carbon efficiency was 35% for C<sub>1</sub>, and 18% for C<sub>2</sub><sup>+</sup>. At slightly different conditions (higher pressure, lower H<sub>2</sub>/CO ratio), the oxygenate selectivity was as high as 58%. This Re-promoted catalyst gave higher oxygenate selectivity than all other catalysts investigated to date, including the Mo-promoted catalysts. Oxygenates were mainly C<sub>1</sub>-C<sub>4</sub> alcohols with small quantities of aldehydes. The alcohol to aldehyde ratio was 2.1, which is higher than that obtained with Mo, Nb, and W promoters.

As the Re content of the catalyst was increased from 1.5% to 12%, the CO conversion increased from 0.25 to 0.60%. Oxygenate selectivity also increased with increasing Re content. However, on the catalyst with a target composition of

1%Rh/24%Re/Al<sub>2</sub>O<sub>3</sub>, both the syngas conversion and the oxygenate carbon efficiency were lower than any other Rh/Re/Al<sub>2</sub>O<sub>3</sub> catalyst.

The 1%Rh/12%Re/Al<sub>2</sub>O<sub>3</sub> catalyst was tested by varying one operating variable at a time. When H<sub>2</sub>:CO ratio was decreased from 2 to 1, the oxygenate carbon efficiency increased from 52 to 58%; C<sub>1</sub> oxygenate carbon efficiency was 32% and C<sub>2</sub><sup>+</sup> oxygenate carbon efficiency was 26%. When the pressure was increased from 30 atm to 50 atm, the CO conversion increased to 0.75% and the oxygenate selectivity improved to 56%. An increase in temperature from 200°C to 250°C and a decrease in pressure from 30 atm to 1 atm had detrimental effects on oxygenate selectivity.

The alcohol-to-aldehyde ratio was about 1.9 to 2.1 on Rh/Re/Al<sub>2</sub>O<sub>3</sub> catalysts. This is higher than the alcohol-to-aldehyde ratio of about 1 for 1%Rh/Al<sub>2</sub>O<sub>3</sub> catalyst. The rate of formation of methane on 1%Rh/Re/Al<sub>2</sub>O<sub>3</sub> catalysts was independent of their Re content. However, it was much higher on the 1%Rh/Al<sub>2</sub>O<sub>3</sub> catalyst. As the conversion increased with an increase in Re content, the methane carbon efficiency decreased concurrently.

The 0.57%Rh/6%Nb/SiO<sub>2</sub> catalyst was less active for syngas conversion, but more selective for oxygenate synthesis than 1%Rh/6%Nb/Al<sub>2</sub>O<sub>3</sub>.

Table 2  
Syngas Conversion to Oxygenates Reaction Results

Catalyst	No. Composition	Yield (based on carbon efficiency)				Alcohol to Aldehyde Ratio	
		Conversion %CO	Hydrocarbons C <sub>1</sub>	Oxygenates C <sub>2</sub> <sup>+</sup>	C <sub>1</sub>		
$\text{Rh}_4(\text{CO})_{12}$ , $\text{NH}_4\text{ReO}_4$ , $\text{Al}_2\text{O}_3$ with surface area 170 $\text{m}^2/\text{g}$							
1	1%Rh/ $\text{Al}_2\text{O}_3$ at 250°C	2.5	60	15	8	17	0.86
2	1%Rh/12%Re/ $\text{Al}_2\text{O}_3$	0.6	23	25	35	18	2.1
Catalyst No. 2 after $\text{H}_2:\text{CO}=1$ by $\text{H}_2$ flow reduced from 50 cc/min to 25 cc/min							
		0.35	15	28	32	26	1.4
Catalyst No 2, 750 psi							
		0.75	23	21	39	17	1.9
Catalyst No 2, Reaction at 250°C							
		4.2	48	37	4	11	1.0
Catalyst No 2, Reaction at 1 atm							
		0.1	39	50	11	0	--
3	12%Re/ $\text{Al}_2\text{O}_3$	0.05	36	49	15	0	--
4	1%Rh/6%Re/ $\text{Al}_2\text{O}_3$	0.38	35	12	35	18	2.1
5	1%Rh/24%Re/ $\text{Al}_2\text{O}_3$	0.21	67	22	9	2	--
6	1%Rh/1.5%Re (from 6%Re in $\text{Re}_2(\text{CO})_{10}$ )/ $\text{Al}_2\text{O}_3$	0.25	49	13	26	12	2.1
$\text{Rh}_4(\text{CO})_{12}$ , $\text{NH}_4\text{ReO}_4$ , $\text{SiO}_2$ with surface area 200 $\text{m}^2/\text{g}$ , 200°C reaction temp							
7	0.60%Rh/12%Re/ $\text{SiO}_2$	0.28	62	33	2	3	0
Catalyst No. 18 after 200°C 1hr He, 3 hr $\text{H}_2$ pretreatment							
		0.34	52	44	2	3	0
Catalyst No 18 after 200°C 1 hr He, 3 hr $\text{H}_2$ pretreatment and reaction at 250°C							
		2.4	62	34	1	3	0
$\text{Rh}_4(\text{CO})_{12}$ , $\text{Nb}(\text{HC}_2\text{O}_4)_7$ , $\text{SiO}_2$ with surface area 200 $\text{m}^2/\text{g}$ , 200°C reaction temp							
8	0.57%Rh/6%Nb/ $\text{SiO}_2$	0.9	40	39	5	16	0.18

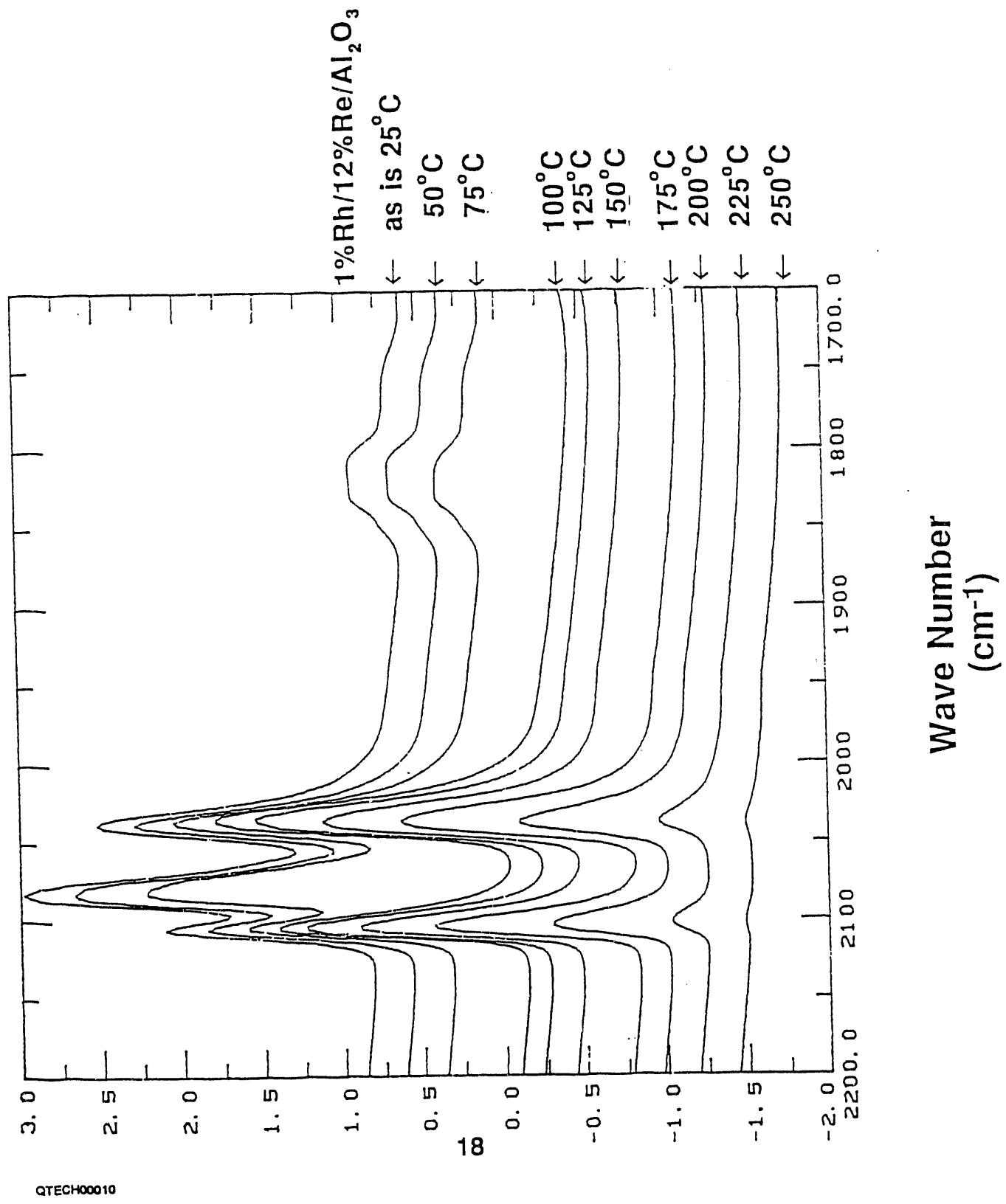
Table 3

Cluster Configuration and Geometry by EXAFS Spectroscopy  
on Re Promoted Rh/Al<sub>2</sub>O<sub>3</sub> Catalysts

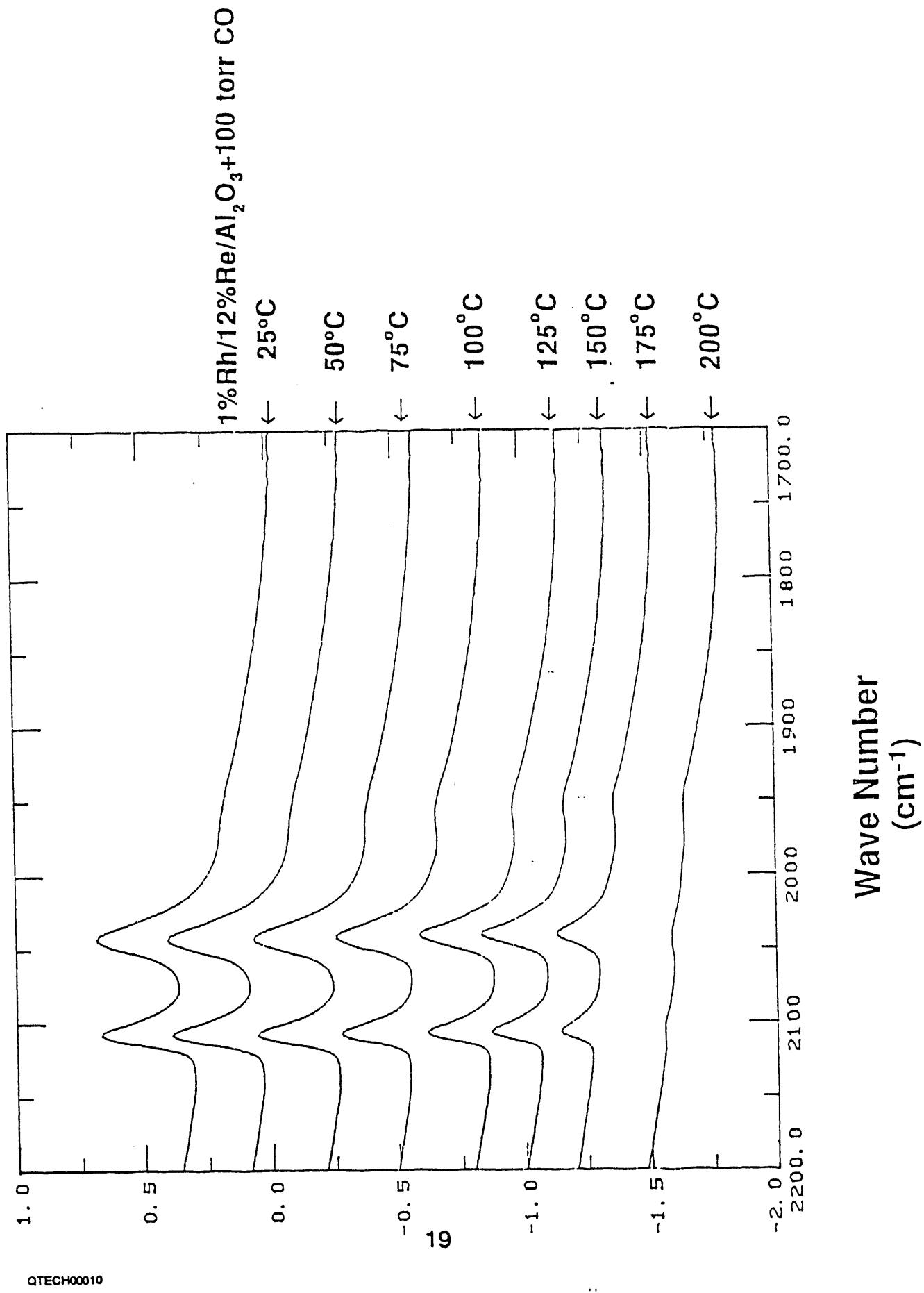
Catalyst	<u>Rh-Rh</u>		<u>Rh-C/O</u>	
	N*	R*	N*	R*
1%Rh/Al <sub>2</sub> O <sub>3</sub> (as prepared)	2.7	2.74	..	--
200°C, He, 1 hr	4.3	2.67	1.16	1.94
250°C, 1:1H <sub>2</sub> :CO, 1 hr	5.6	2.71	0.87	1.90
1%Rh/12%Re/Al <sub>2</sub> O <sub>3</sub> (as prepared)	2.2	2.77	--	--
200°C, He, 1 hr	2.6	2.67	1.19	1.94

\*N: coordination no; R: bond distance (angstroms)

**Figure 3**  
**FTIR Spectra of As-Synthesized 1%Rh/12%Re/Al<sub>2</sub>O<sub>3</sub>**

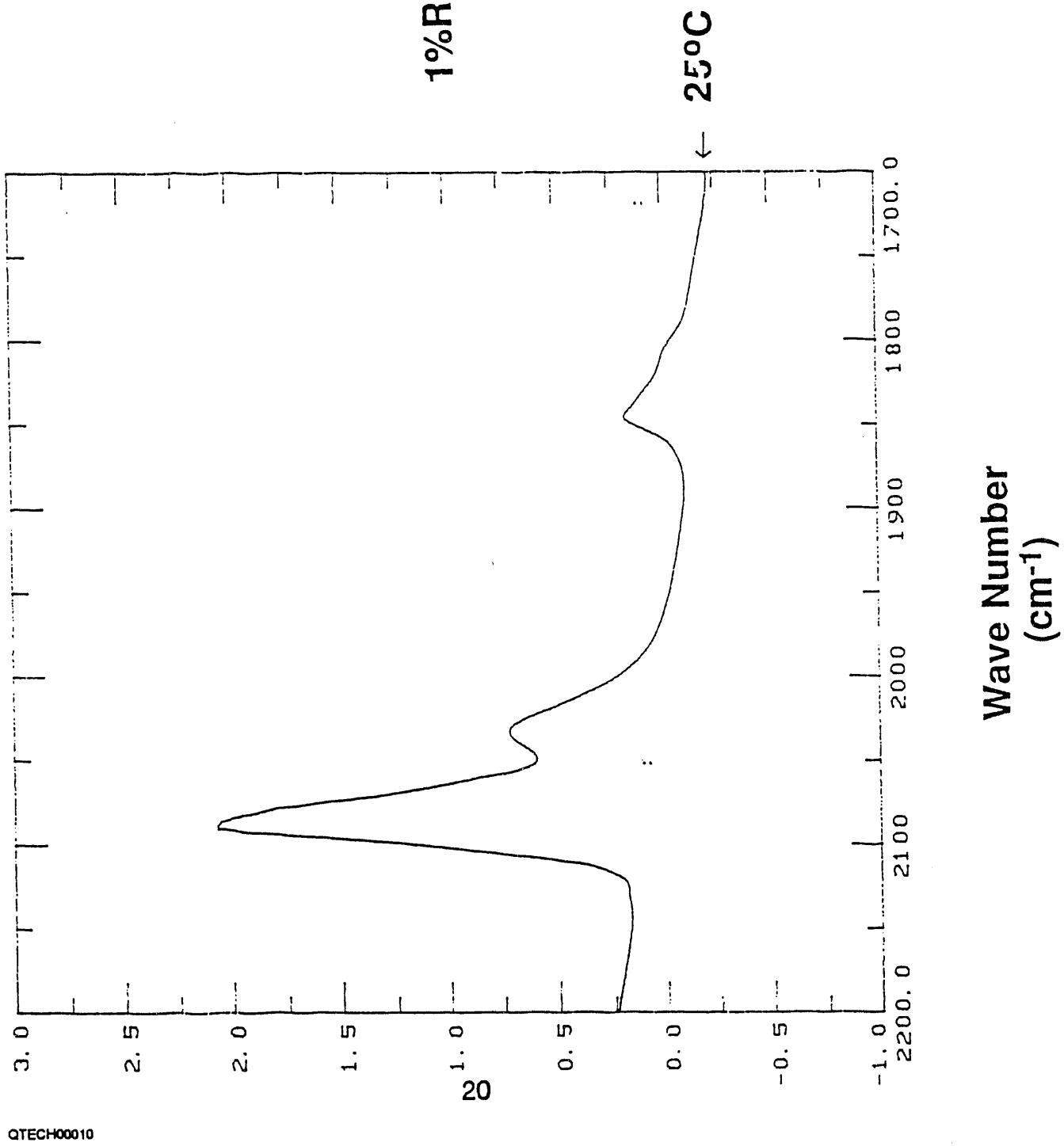


**Figure 4**  
**FTIR Spectra of CO Adsorbed on 1%Rh/12%Re/Al<sub>2</sub>O<sub>3</sub>**

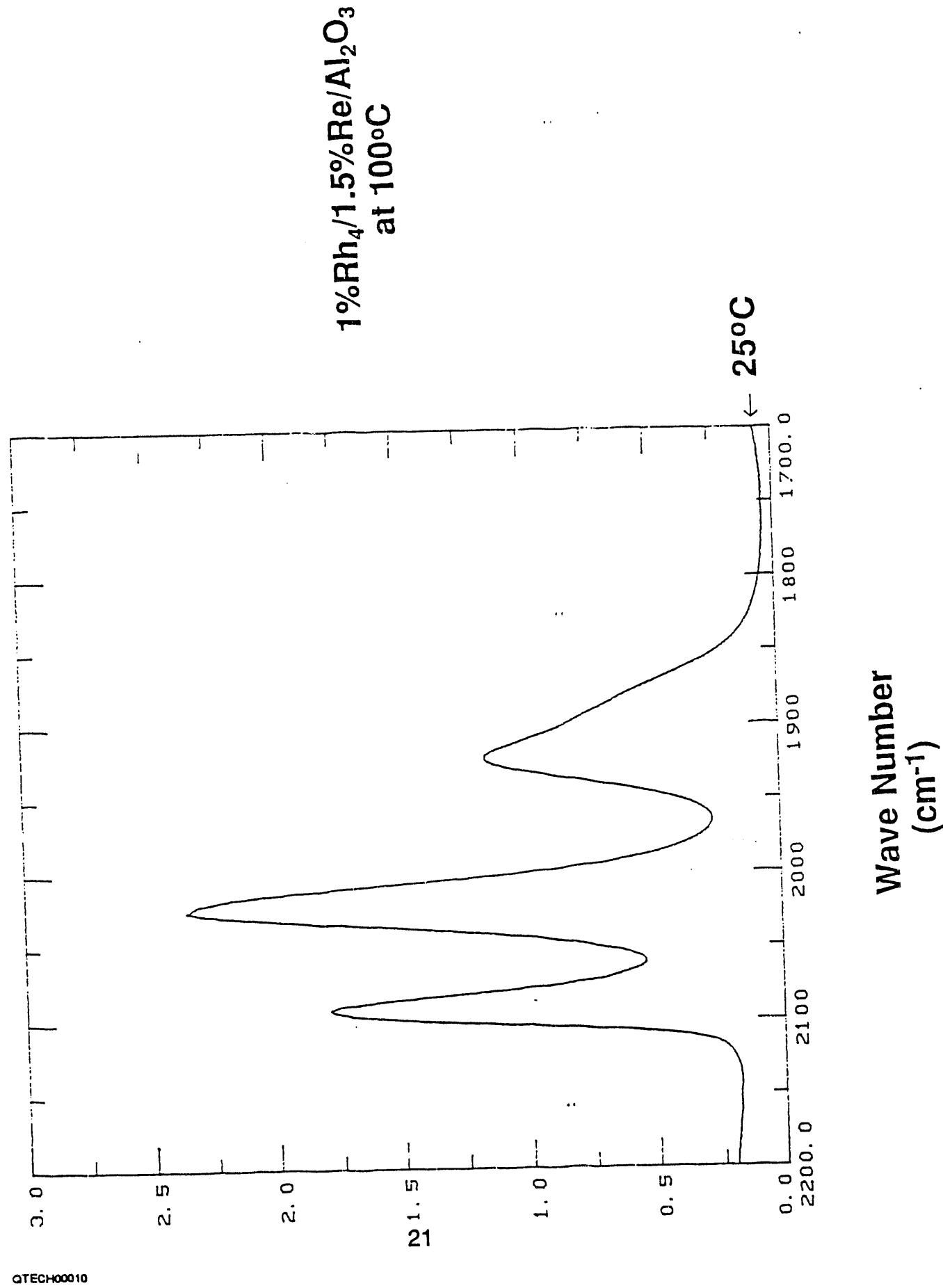


QTECH00010

Figure 5  
FTIR Spectrum for  $[\text{Rh}_4(\text{CO})_{12}]$  Adsorbed on  
6%Re/Al<sub>2</sub>O<sub>3</sub>



**Figure 6**  
**IR Spectrum of 1%Rh<sub>4</sub>/1.5%Re<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> at 100°C**  
**(Rh<sub>4</sub>(CO)<sub>12</sub> and Re<sub>2</sub>(CO)<sub>10</sub> Adsorbed on Al<sub>2</sub>O<sub>3</sub>)**



**Figure 7**  
**IR Spectrum for  $[\text{Rh}_4(\text{CO})_{12}]$  Adsorbed on**  
**12%Re/SiO<sub>2</sub>**

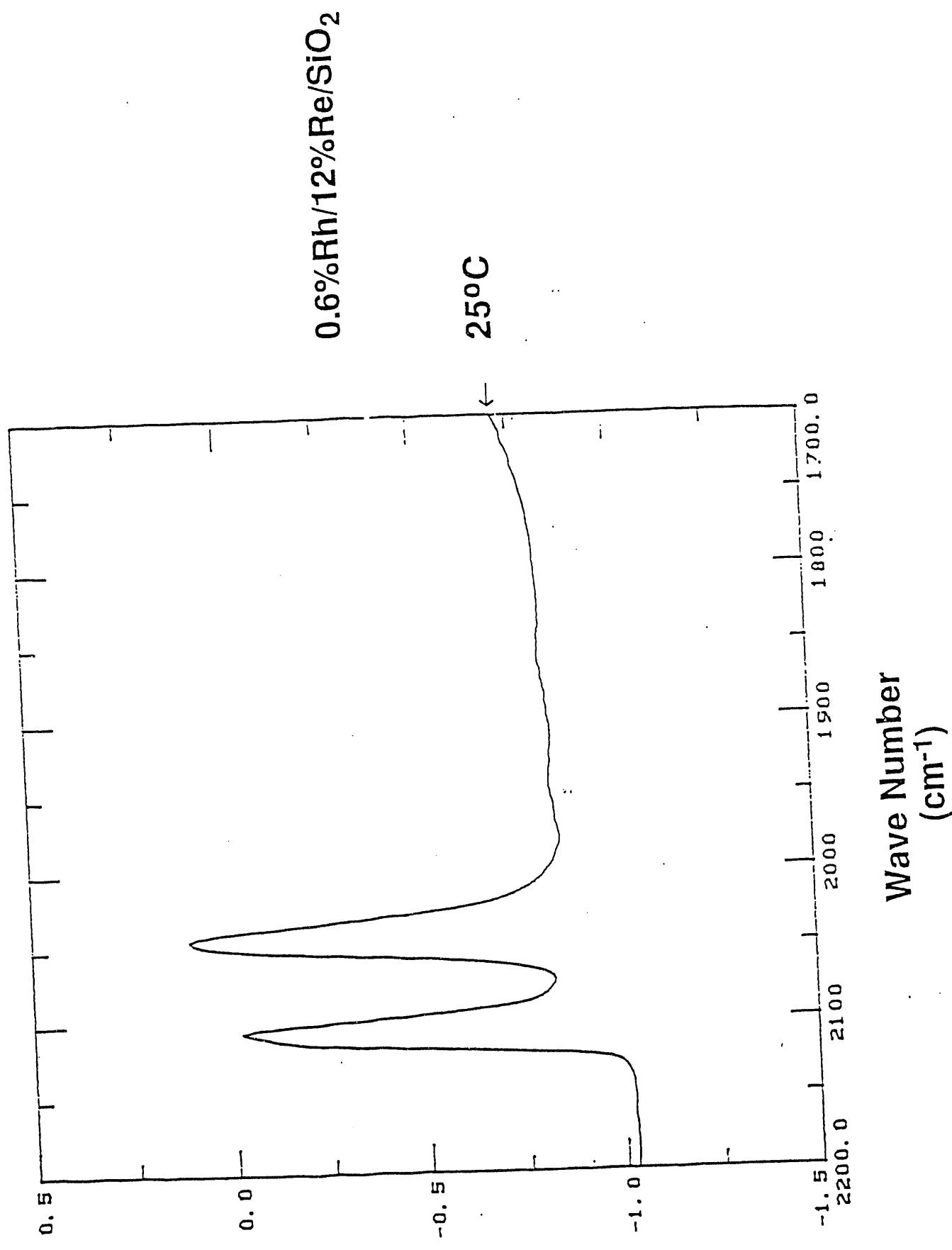
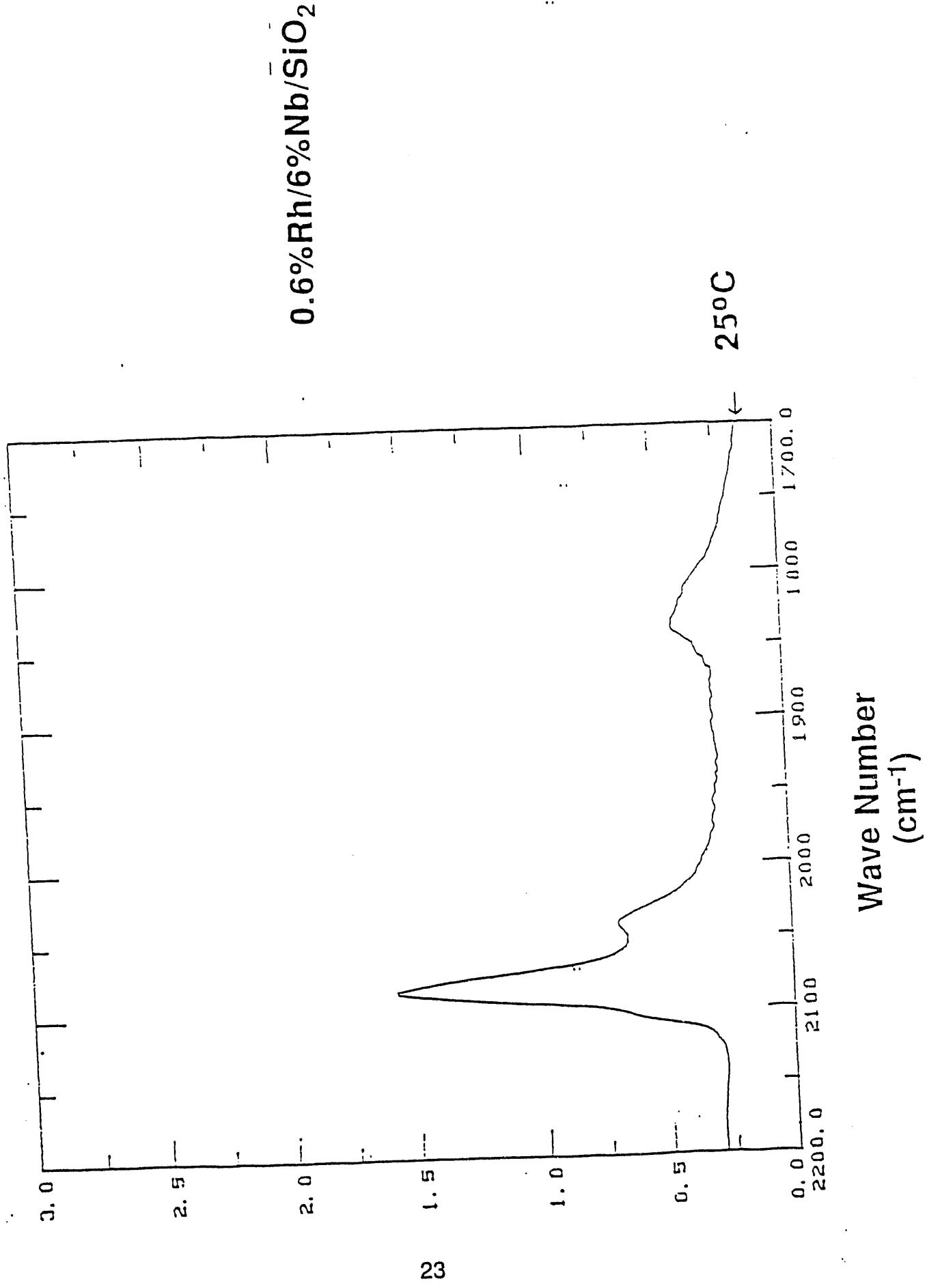


Figure 8  
IR Spectrum for  $[\text{Rh}_4(\text{CO})_{12}]$  Adsorbed on  
 $\text{Nb}/\text{SiO}_2$



## APPENDIX A

- 1 Catalyst No. 2 to 4 preparation conditions: Alumina obtained from Grace (MI-307, 170 m<sup>2</sup>/g surface area) was used as a catalyst support. It was calcined at 400°C for 4 hr and evacuated for 1 hr. Re was impregnated using NH<sub>4</sub>ReO<sub>4</sub> and the incipient wetness technique. The desired loading of Re was attached and the catalyst was calcined at 400°C for 4 hr and evacuated for 1 hr. During calcination, violet deposits of ReO<sub>3</sub> or yellow deposits of Re<sub>2</sub>O<sub>7</sub> were not observed. 1%Rh was attached using Rh<sub>4</sub>(CO)<sub>12</sub> in dry hexane. All Rh was adsorbed from solution by the catalyst, as confirmed by CO band intensity in FTIR spectra of hexane solutions. The catalyst was stored in a dry, oxygen-free environment for further testing.
- 2 Catalyst No. 5 preparation conditions: The preparative technique was the same as above for 1%Rh/Re/Al<sub>2</sub>O<sub>3</sub> Catalyst Nos. 2 to 4. However, 24%Re was loaded using two 12%Re impregnations. After each loading, the catalyst was heated to 400°C in O<sub>2</sub> for 4 hr and evacuated to 10<sup>-5</sup> torr for 1 hr. After the second calcination, violet deposits of ReO<sub>3</sub> were observed in the calcination tube.
- 3 Catalyst No. 6 preparation conditions: Alumina obtained from Grace (MI-307, 170 m<sup>2</sup>/g surface area) was used as a catalyst support. It was calcined at 400°C for 4 hr and evacuated for 1 hr. An attempt was made to attach 6% Re using Re<sub>2</sub>(CO)<sub>10</sub> in dry hexane. 1% Rh was attached using Rh<sub>4</sub>(CO)<sub>12</sub> in dry hexane. 1.5% Re and 1% Rh were present on the final catalyst as measured by the intensity of CO bands in the parent and "spent" hexane solutions. The catalyst was stored in a dry, oxygen-free environment for further analysis.
- 4 Catalyst No. 7 preparation conditions: Silica (200m<sup>2</sup>/g) was slurried in distilled water and dried at 100°C overnight. It was calcined at 400°C for 4 hr and evacuated for 1 hr. Re was impregnated using the incipient wetness technique and NH<sub>4</sub>ReO<sub>4</sub> precursor; the NH<sub>4</sub>ReO<sub>4</sub> solution contained enough Re to deposit 12 wt. % on the catalyst. The catalyst was calcined at 400°C for 4 hr and evacuated for 1 hr. Violet deposits of ReO<sub>3</sub> were observed in the calcination tube. Rh was attached using Rh<sub>4</sub>(CO)<sub>12</sub> in dry hexane.
- 5 Catalyst No. 8 preparation conditions: Silica (200m<sup>2</sup>/g) was slurried in distilled water and dried at 100°C overnight. It was calcined at 500°C for 4 hr and evacuated for 1 hr. Nb was impregnated using the incipient wetness technique and Nb(HC<sub>2</sub>O<sub>4</sub>)<sub>7</sub> precursor. 6% Nb was attached using two 3% Nb loadings; each time the catalyst was calcined at 500°C for 4 hr and evacuated for 1 hr. Rh was attached using Rh<sub>4</sub>(CO)<sub>12</sub> in dry hexane.

- 6 Pretreatment conditions: Heating rate 5°C/min, 200°C, 50 cc/min He 1 hr, pressurize and heat to reaction temperature under reaction gases.
- 7 Testing conditions: 30 atm, 200°C, 9000 1/kg/hr GHSV, H<sub>2</sub>:CO=2, 0.5 g. of catalyst.

**DATE  
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**10/19/93**

**END**

