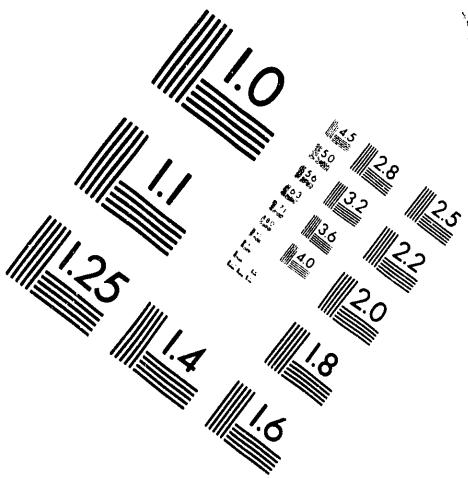




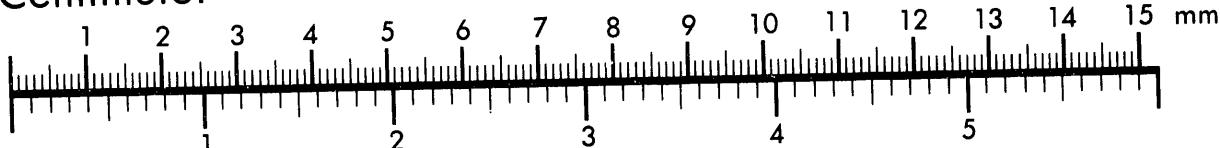
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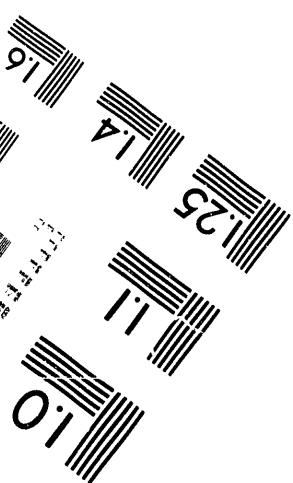
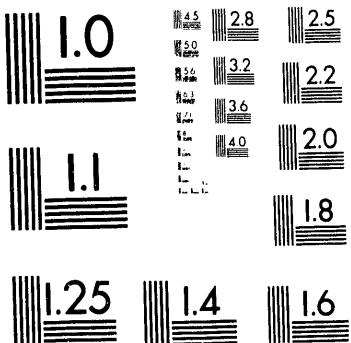
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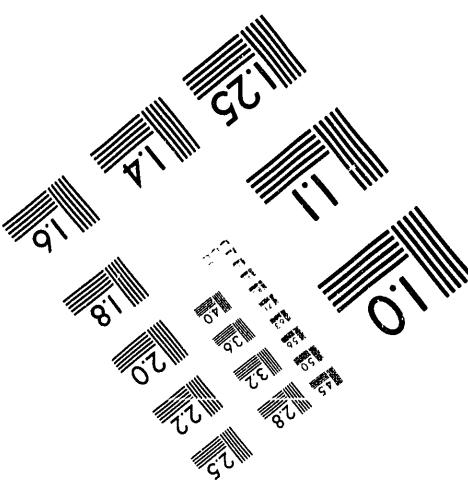
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**NOVEL APPROACHES TO THE PRODUCTION OF HIGHER
ALCOHOLS FROM SYNTHESIS GAS**

Quarterly Technical Progress Report No. 9

For The Period October 1, 1992 to December 31, 1992

Contractor

NORTH CAROLINA STATE UNIVERSITY
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April 28, 1993

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-90PC90043
Contract Period 25 September 1990 - 24 September 1993

MASTER

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
October 1, 1992 to December 31, 1992

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:

Several possible high-temperature reactor oils have been identified and are being evaluated. One candidate, Drakeol® 34 mineral oil, appeared to decompose rapidly during testing at 425°C in the stirred autoclave. However, a thermal stability test in laboratory glassware showed that Drakeol® 34 was stable at about 360°C, suggesting that the decomposition observed in the autoclave was not caused simply by high temperature. Another oil, Ethylflo® 180, also showed no signs of decomposition during thermal stability testing in the laboratory, also at a temperature of about 360°C.

The first of three methanol synthesis verification runs was conducted in the stirred autoclave, using the commercial BASF Cu/ZnO catalyst. Gas chromatograph failures and apparent catalyst deactivation prevented collection of any meaningful data during the run.

- Under Task 3:

The study of syngas conversion to oxygenates on Rh/Nb/Al₂O₃ catalysts was continued. Catalyst activity increased, but selectivity to oxygenates decreased, as the Nb content was increased from 0 to 6 wt.%. A concentration of 6 wt% Nb roughly corresponds to the theoretical amount required to cover an alumina

surface area of 100 m²/g with a monolayer of Nb₂O₅. A further increase in Nb content beyond 6 wt.% resulted in a decrease in syngas conversion, with no change in oxygenate selectivity.

Severe reduction of Rh/6%Nb/Al₂O₃ catalyst prior to reaction resulted in a very high carbon monoxide conversion, 77% versus a normal value of about 16%. The methane selectivity of the severely-reduced catalyst was 99% and the oxygenate selectivity was 0, compared to a normal oxygenate selectivity of about 10%. This suggests that partially-reduced Rh, such as Rh¹, may be necessary for good oxygenate selectivity. Consistent with this hypothesis, a milder pretreatment of Mo/Rh/Al₂O₃ catalyst resulted in an increase in oxygenate carbon efficiency from 34 to 41%.

The preparation of silica-supported catalysts was begun. In the presence of Nb and Re promoters, the amount of Rh adsorbed from Rh₄(CO)₁₂ increased by an order of magnitude relative to unpromoted SiO₂ support. This increase may result from the formation of Rh-CO-Nb and Rh-CO-Re bonds on Rh/Nb/SiO₂ and Rh/Re/SiO₂ catalysts, respectively. The Fourier Transform Infrared (FTIR) spectrum for Rh/Re/SiO₂ suggested that Rh was uniformly highly dispersed on this catalyst.

TECHNICAL PROGRESS

- Task 2:

High Temperature Reactor Oils

Possible Candidates:

A search has begun for reactor oils that can survive temperatures up to 425°C at total pressures exceeding 1000 psig. This high temperature oil is required for the synthesis of methanol and higher alcohols using zinc-chromite-based catalysts in a slurry reactor, as outlined in the previous Quarterly Report.

General specifications for the oil are:

- low vapor pressure at 425°C
- specific gravity less than the bulk catalyst
- no thermal decomposition
- chemically inert with respect to the operating environment.

Based on experience at Air Products, the last specification requires a 100% saturated hydrocarbon, i.e., no alkenes, alkynes or aromatics.

A survey of the candidate oils, with their available technical information, is listed in Table 1. For comparison, Drakeol® 10 mineral oil, the oil currently used in liquid-phase methanol synthesis, is also listed. Note that most of the oils are simply longer-chain hydrocarbon mineral oil mixtures than Drakeol® 10, as reflected by their average molecular weights. Besides their higher boiling points, these oils generally have the same properties as the Drakeol® 10, making them excellent candidates for high-temperature reactor service.

The last two high temperature oils, Krytox® 16350 and Syltherm® 800, appear to be less desirable candidates. The Krytox® oil possesses extremely low vapor pressure and is the most chemically inert of all the oils. However, the thermal stability of Krytox® is questionable at the desired operating conditions. This is further aggravated by the high toxicity and corrosiveness of the Krytox® decomposition products. Also, catalyst dispersion could be adversely affected by the high specific gravity (1.86-1.91) of Krytox relative to that of the bulk zinc chromite catalyst (1.8). Syltherm® 800 has a good operating temperature range, but its vapor pressure is relatively large and its thermal expansion is very high, again possibly adversely affecting catalyst dispersion. Also, Syltherm® can decompose and form volatile products upon exposure to water, a potential product of higher alcohol synthesis.

High Temperature Oil Testing

A high temperature oil test in the stirred autoclave reactor with Drakeol® 34 mineral oil ended abruptly after about 18 hours due to formation of what appeared to be elemental carbon in the reactor. The test conditions were 1:1 H₂:CO feed ratio; reactor pressure of 1000 psig; maximum reactor temperature of 425°C, and; no catalyst present in the reactor. After the run was stopped, the reactor contained approximately 50 g. of "black" carbon powder. However, no mineral oil remained. The "carbon" could have formed from either mineral oil decomposition or from CO feed gas decomposition via the Boudouard reaction. Enough carbon was fed as CO over the course of the run to account for all of the "carbon" present in the reactor. Mineral oil decomposition would seem unlikely since decomposition to carbon is basically dehydrogenation, and the hydrogen

partial pressure was 500 psi in the feed gas. A previous high temperature oil test at 305°C reactor temperature with the Drakeol® 34 mineral oil did show some "carbon" formation on the surfaces of the reactor.

A simple thermal stability test, performed in laboratory glassware in an inert environment at atmospheric pressure, was conducted with the Drakeol® 34 mineral oil. After 31 hours of boiling at 360 to 370°C, the mineral oil had discolored to a clear yellow, but there were no signs of "carbon" formation. Another test with Drakeol® 10 mineral oil under the same conditions had similar results. Based on these findings, simple thermal instability is not a viable explanation for mineral oil decomposition in the stirred autoclave test.

Other decomposition mechanisms, such as catalytic dehydrogenation or carbon monoxide disproportionation caused by iron or nickel from Fe or Ni carbonyls, will be investigated. Compositional analyses will be made of the "carbon" material from the autoclave experiment.

Ethylflo® 180, a hydrogenated poly- α -olefin mixture, remained thermally stable during testing in the same laboratory apparatus. The liquid started boiling at 385°C, but the boiling point decreased to 355°C over 6 hours. No "carbon" formation was observed, just slight discoloration of the fluid. This behavior is consistent with the previously tested Drakeol® 10 and 34 mineral oils. The liquid was tested under a nitrogen atmosphere at 1 atm pressure.

Methanol Synthesis Verification Run

The first of three planned methanol synthesis verification runs was conducted, but analytical problems plagued the entire run and no useful data were obtained. The autoclave reactor was loaded with 225 ml. of 20 wt.% BASF commercial Cu/ZnO methanol synthesis catalyst with Penreco Drakeol® 10 mineral oil. The catalyst was reduced in-situ per the procedure of Air Products' Patent # 4,801,574. During the reduction procedure, reactor slurry somehow plugged the carbonyl trap located immediately upstream of the reactor. Fortunately, a bypass line around the trap allowed the reduction to continue, but this carbonyl trap remained inactive for the rest of the run. Another carbonyl trap located in the CO feed line operated during the entire run.

After the catalyst reduction was complete, methanol synthesis was started using a Texaco feed gas composition; 35% H₂, 51% CO, 13% CO₂, and 1% N₂.

After an hour of operation, the N₂ mass flow controller failed, so N₂ was excluded from the feed for the remainder of the run. The synthesis run lasted about 200 hours with no process interruptions. However, a gas sampling valve failure in the gas chromatograph prevented analytical data collection until the last 24 hours of the run. At that time, less than 1 volume % methanol was detected in the reactor exit stream. After the run, the CO, H₂ and CO₂ measurements were found to be meaningless due to a leak in the gas sampling valve, which allowed a portion of the gas sample to bypass the column and travel directly to the detector.

Based on the few results obtained, the run will have to be repeated. However, catalyst deactivation was apparent since the methanol concentration in the reactor effluent was only about 1 vol. %. The spent catalyst from this run has been sent for elemental analysis to determine whether catalyst poisoning due to metal carbonyls occurred.

- Task 3:

Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) data for Rh/Al₂O₃ and Rh/Nb/Al₂O₃ catalysts were presented in the September, 1992 Monthly Report. The EXAFS results showed that only Rh-Rh, Rh-O (or Rh-C) and Nb-O bonds were formed on the Rh/Nb/Al₂O₃ catalysts; Rh-Nb and Nb-Nb bonds were not observed. Based on these observations, a model for the Rh/Nb/Al₂O₃ catalyst system is proposed in which the high-surface-area alumina is covered by "patches" of NbO_x with a thickness close to one monolayer. Rh particles are attached to the NbO_x "patches".

Higher Alcohol Synthesis (HAS) Reaction Results

Several Rh/Al₂O₃, Rh/Nb/Al₂O₃, and Rh/Mo/Al₂O₃ catalysts were tested for syngas conversion to oxygenates. The data, along with the testing conditions and catalyst descriptions, are shown in Table 2.

The activity for carbon monoxide conversion and the oxygenate selectivity (carbon efficiency for oxygenates) for a series of Rh/Nb/Al₂O₃ catalysts are shown as a function of niobium content in Figure 1. With an increase in Nb content, the catalyst activity increased sharply until about 6 wt.% Nb was reached. However, the selectivity for oxygenates decreased gradually with increasing Nb content. According to calculations based on the assumption that Nb is present on the catalyst as Nb₂O₅, about 7 wt.% Nb gives monolayer

coverage on a 100 m²/g surface area alumina. This calculation is confirmed by the experimental results of Wachs¹ and Iwasawa².

The maximum CO conversion of 16% was given by 1%Rh/6%Nb/Al₂O₃. This catalyst was prepared by two sequential impregnations of 3% Nb on 100 m²/g. surface area alumina to get close to a theoretical monolayer coverage. A further increase in Nb content beyond 6 wt.% resulted in a decrease in syngas conversion activity, with unchanged oxygenate carbon efficiency.

These data appear to show the transition from Rh on a pure Al₂O₃ surface to Rh on a niobia surface. Rh/Al₂O₃ appears to have a higher oxygenate selectivity and a lower activity than Rh/NbO_x. The high activity at 6% Nb is anomalous; this experiment is being repeated.

Several catalysts were prepared and tested in order to evaluate the effect of the surface area of the Al₂O₃ support. Catalysts consisting of 1% Rh on either 100 m²/g or 170 m²/g surface area alumina (1%Rh/Al₂O₃) gave similar activity and selectivity. The catalysts 1%Rh/3%Nb/Al₂O₃ (surface area=100m²/g) and 1%Rh/5.1%Nb/Al₂O₃ (surface area=170m²/g) were also compared. These loadings of Nb were chosen to obtain the same theoretical Nb coverage per unit surface area on both catalysts. As the alumina surface area increased from 100 to 170 m²/g, an increase in activity and decrease in oxygenate selectivity was observed. It is possible that on the high-surface-area 1%Rh/5.1%Nb/Al₂O₃ catalyst, Rh catalytic centers were able to interact with more Nb promoters than on the low-surface-area 1%Rh/3%Nb/Al₂O₃ catalyst.

Following the usual catalyst pretreatment for cluster-derived catalysts, i.e. decomposing Rh clusters at 200°C for 1 hr in flowing He, a sample of the 1%Rh/6%Nb/Al₂O₃ catalyst was severely reduced in hydrogen at 400°C for 4 hr. The CO conversion increased from 16% to 77%. However, methane and water were the only major products observed. The carbon efficiency for methane was

¹Wachs I.E., Jehng J.M., Hardcastle F.D., Solid State Ionics, Vol. 32-33, pp. 904-910, 1989.

²Asakura K., Iwasawa Y., J. Phys. Chem., Vol. 95, pp. 1711-1716, 1991.

99%. Clearly, the oxygenate selectivity decreased dramatically on the severely-reduced Rh particles, which were possibly in the Rh^0 state. This result suggests that partially-reduced Rh, such as Rh^1 , may be necessary for good oxygenate selectivity.

A mechanical mixture of 1%Rh/ Al_2O_3 and 5.1%Nb/ Al_2O_3 was tested to study the reaction mechanism. With the mechanical mixture, conversion decreased, carbon efficiency for C_1 oxygenates and C_2^+ hydrocarbons increased, and carbon efficiency for methane and higher oxygenates decreased relative to the Rh/5.1% Nb/ Al_2O_3 catalyst.

Several Rh/Mo/ Al_2O_3 catalysts were also tested. With the normal pretreatment in flowing H_2 for 1 hr at 400°C, the CO conversion was 3.7% and the oxygenate selectivity was about 34%. Another sample of the same catalyst was activated at 200°C in He for 1 hr. Under these mild pretreatment conditions, the syngas conversion increased from 3.7% to 7.8% and the oxygenate carbon efficiency increased simultaneously from 34 to 41%. The milder pretreatment may have resulted in partially-reduced Rh or Mo. If so, the increase in oxygenate selectivity is consistent with the increase observed on partially-reduced Rh on Al_2O_3 .

Infrared Studies on Rh/Nb/ Al_2O_3 Catalysts

Fourier Transform InfraRed (FTIR) studies were run on Rh/Nb/ Al_2O_3 , Rh/ Al_2O_3 , and Nb/ Al_2O_3 samples to examine the effect of Nb on the adsorption of $[\text{Rh}_4(\text{CO})_{12}]$. Figure 2 shows the spectra for various samples produced by adsorbing $[\text{Rh}_4(\text{CO})_{12}]$ onto supports containing differing amounts of Nb.

The peaks at about 2095 and 2020 cm^{-1} are attributable to the gem-dicarbonyl form of CO. The peak at about 2060 cm^{-1} corresponds to linearly-adsorbed CO and the peak at about 1840 cm^{-1} shows the bridged form of CO. This peak is shifted from the "normal" position of about 1890 cm^{-1} for the bridged carbonyl in dissolved $\text{Rh}_4(\text{CO})_{12}$ to a position that more nearly corresponds to the bridged carbonyl in dissolved $\text{Rh}_6(\text{CO})_{16}$. There is a distinct, low-frequency shoulder on this peak for the Nb-containing supports, the intensity of which increases as the

Nb content increases from 3 to 9 weight percent. This shoulder may indicate an electrostatic interaction between CO and Nb, which increases as the Nb content increases.

In order to better understand the effect of the support on the deposition of Rh from $\text{Rh}_4(\text{CO})_{12}$, 1% Rh as $\text{Rh}_4(\text{CO})_{12}$ was adsorbed onto Al_2O_3 and 9 wt.% Nb on Al_2O_3 . These two materials were then heated in 30 cc/min He from 25 to 275°C at a heating rate of 5°C/min. After each 25°C increment of heating, the catalyst was held at a constant temperature for 10 min. The Fourier Transform Infrared (FTIR) spectra were recorded at each constant temperature. These spectra are shown in Figures 3 and 4 for 1%Rh/ Al_2O_3 and 1%Rh/9%Nb/ Al_2O_3 , respectively. On both catalysts at 25°C, the FTIR spectra was comprised of a Rh bridged carbonyl band near 1840 cm^{-1} , a linear Rh carbonyl band near 2060 cm^{-1} , and Rh-geminal dicarbonyl bands near 2090 and 2040 cm^{-1} , consistent with the results shown in Figure 2.

Figure 3 shows that: 1) both the linear and the bridged carbonyl peaks disappear between 75°C and 100°C, indicating decomposition of the cluster; 2) CO was completely desorbed from 1%Rh/ Al_2O_3 at 200°C. Figure 4 shows that, with 1%Rh/9%Nb/ Al_2O_3 , the cluster did not completely decompose until the temperature was between 150°C and 200°C, and that the gem-dicarbonyl form of CO was present on the catalyst even at 275°C. These data indicate that the cluster was stabilized by adsorption on the Nb/ Al_2O_3 catalyst, relative to adsorption on Al_2O_3 alone, and that CO is more strongly adsorbed on Rh/9%Nb/ Al_2O_3 after the cluster decomposes than it is on Al_2O_3 alone. This further supports the hypothesis, outlined earlier, of Rh-CO-Nb bond formation.

After heating to a temperature sufficient to decompose the Rh complex, these catalysts were cooled to 25°C and CO was adsorbed at 100 torr. As shown in Figure 5, only the Rh-gem-dicarbonyl species was formed on Al_2O_3 . The catalyst was then taken through the same temperature program described above. The FTIR spectra were recorded at each constant temperature. CO was desorbed completely from 1%Rh/ Al_2O_3 at about 200°C.

Figure 6 shows the results of the same experiment for Rh/9%Nb/Al₂O₃ catalyst. Once again, only the gem-dicarbonyl species was observed. However, adsorbed CO was present on this sample even at 250 to 275°C. No CO adsorption was observed on Nb/Al₂O₃, without Rh.

Based on the spectra for Rh₄(CO)₁₂ adsorbed on Al₂O₃ and on Nb/Al₂O₃, it appears that Rh₄(CO)₁₂ converts to Rh₆(CO)₁₆ as it is adsorbed at room temperature. On heating, the CO is driven off leaving a crystallite containing 6 Rh atoms remaining on the surface of the support. At all of the temperatures studied, the only form of CO adsorption on catalysts prepared by decomposing Rh₄(CO)₁₂ is the gem-dicarbonyl configuration. This is consistent with very small crystallites, of the order of 6 atoms.

Synthesis of Silica Supported Catalysts

Literature data³ suggests that when silica is used instead of alumina as a support for Rh, the syngas conversion decreases and the oxygenate selectivity increases. Therefore, in an attempt to increase oxygenate selectivity, the preparation of Rh/6%Nb/SiO₂ and Rh/12%Re/SiO₂ catalysts was attempted. The promoters Nb and Re were impregnated using the incipient wetness technique and Nb(HC₂O₄)₇ and NH₄ReO₄ precursors, respectively.

For the 6%Nb/SiO₂ catalyst, the target Nb loading was half the theoretical amount required for monolayer coverage on 200 m²/g SiO₂ support. The SiO₂ and 6%Nb/SiO₂ supports were exposed to 1%Rh using Rh₄(CO)₁₂ precursor. Although silica could adsorb only .08% Rh, the Rh loading increased to about 0.6% on 6%Nb/SiO₂ catalyst. Similar to Rh/Nb/Al₂O₃ catalysts, Rh-CO-Nb bonds may have been formed on Rh/Nb/SiO₂ catalysts. This may explain the increase in Rh loading in the presence of Nb on silica supports.

The desired structure of Rh/Re/SiO₂ catalyst was monolayer coverage of the silica surface by Re₂O₇, on which Rh crystallites reside. The theoretical monolayer coverage of Re₂O₇ on 200 m²/g SiO₂ catalyst was calculated to be 24% Re. However, using Raman measurements, Wachs et al.^{4,5}

³Sachtler W.H.M., Ichikawa M., J. Phys. Chem., Vol. 90, p. 4752, 1986.

⁴Turek A. M., Wachs, I.E., DeCanio, E., J. Phys. Chem., Vol. 96, pp. 5000-5007, 1992.

⁵Vuurman, M.A., Wachs, I.E., J. Phys. Chem., Vol. 96, pp. 5008-5016, 1992.

determined that 11% Re gave a monolayer coverage on 180m²/g Al₂O₃. The source of this large discrepancy is not clear. The experimental result was presumed to be accurate and, to obtain monolayer coverage of Re, a 12%Re/SiO₂ catalyst preparation was attempted by impregnating NH₄ReO₄ on 200 m²/g SiO₂ using the incipient wetness technique. This support was calcined at 400°C for 4 hr in O₂ followed by evacuation for 1 hr. During this treatment, about half of the impregnated Re was lost from the support. Rh was adsorbed on this support using Rh₄(CO)₁₂ dissolved in hexane. If all of the Rh in solution had adsorbed on the support, the loading would have been 1 wt.% Rh. The actual loading was only about 0.6%. The presence of the Re increased the amount of Rh.

FTIR spectra for the 0.6%Nb/SiO₂ and 0.6%Rh/12%Re/SiO₂ catalysts are shown in Figures 7 and 8, respectively. The spectra for 0.08%Rh/SiO₂ (not shown) and 0.6%Rh/6%Nb/SiO₂ show mainly linearly-adsorbed CO, whereas the spectrum for 0.6%Rh/6%Re/SiO₂ showed only Rh-geminal dicarbonyl species, indicative of finely dispersed Rh. This is in contrast to Rh/Nb/Al₂O₃ catalysts, which showed contributions from Rh-geminal dicarbonyl, linear and bridged CO, and Rh/Nb/SiO₂ catalyst that predominantly showed linear CO.

Table 1

High Temperature Oils

Name	Manufacturer	Composition	Boiling Point/ Distillation ¹	Vapor Pressure ²	Specific Gravity ²	Average Mol. Wt.	Comments
Drakeol® 10	Penreco	Mineral Oil- 65 % Paraffinic 35 % Naphthenic	283°C IBP 407°C 50% 481°C 90%	< 1 mm Hg	0.838 - 0.864	366	Currently used for <300°C operation
Drakeol® 34	Penreco	Mineral Oil - 68% Paraffinic 32% Naphthenic	437°C IBP 489°C 50% 529°C 90%	< 1 mm Hg	0.858 - 0.872	492	Mixture of longer hydrocarbon chains than the Drakeol 10
Drakeol® 500	Penreco	Mineral Oil - 68% Paraffinic 32% Naphthenic	419°C IBP 511°C 50% 541°C 80%	< 1 mm Hg	0.859 - 0.878	533	Mixture of longer hydrocarbon chains than either Drakeol 10 or 34
Ethyflo® 170	Ethyl	Hydrogenated homopolymer of 1-decene	424°C IBP 492°C 50% 537°C 90%	< 1 mm Hg	0.845 - 0.855	632	Mixture of C ₁₀ , C ₂₀ , C ₃₀ and C ₄₀ paraffins, contains some branched products
Ethyflo® 180	Ethyl	Hydrogenated homopolymer of 1-decene	Not available	< 1 mm Hg	0.845 - 0.855	2000	Mixture of C ₄₀ , C ₅₀ , C ₆₀ and C ₇₀ paraffins, contains some branched products
Krytox® 16350	DuPont	Perfluoroalkyl- polyether	Decomposes >290°C and 1 atm	10 ⁻¹⁵ torr @ 20°C 10 ⁻¹⁰ torr @ 100°C 1 atm	1.86 - 1.91	Not available	Decomposes to Perfluoro acetyl and carbonyl fluoride (on to CO ₂ and HF in the presence of water)
Syltherm® 800 Heat Transfer Liquid	Dow-Coming	Modified di- methylsiloxane polymer	Crosslinks/ volatilizes >400°C	<1 mm Hg @ 20°C 10,200 mm Hg @ 400°C	0.936	Not available	High thermal expansivity - about 70% from 15°C to 400°C Sensitive to water contamination

¹ Per ASTM D 1160 Distillation @ 760 mm Hg² At 20°C unless otherwise specified

Table 2

Syngas Conversion to Oxygenates on Nb or Mo Promoted Rh/Al₂O₃ Catalysts

Catalyst No. Composition	Conversion %CO	Yield (based on carbon efficiency)		Alcohol to Aldehyde Ratio		
		Hydrocarbons C ₁	Oxygenates ⁶ C ₁ C ₂ ⁺	C ₁	C ₂ ⁺	
IMPREGNATED CATALYSTS						
Rh(No ₃) ₃ , Mo(CO) ₆ , Al ₂ O ₃ with surface area 100 m ² /g						
1 1%Rh/Al ₂ O ₃	2.0	62	27	6	5	
2 ⁵ 0.06%Mo/1%Rh/Al ₂ O ₃	3.6	53	14	14	19	
					0.88	
					0.63	
CLUSTER-DERIVED CATALYSTS						
Rh ₄ (CO) ₁₂ , Nb(HC ₂ O ₄) ₇ , Al ₂ O ₃ with surface area 100 m ² /g						
3 1%Rh/Al ₂ O ₃	2.2	62	13	8	17	
4 1%Rh/3%Nb/Al ₂ O ₃	4.2	61	21	1	17	
5 1%Rh/6%Nb/Al ₂ O ₃	16	65	25	0	10	
6 1%Rh/9%Nb/Al ₂ O ₃	6.1	64	25	0	11	
7 1%Rh/10%Nb/Al ₂ O ₃	2.0	57	32	1	11	
8 1%Rh/6%Nb/Al ₂ O ₃ catalyst No. 3 reduced at 400°C in H ₂ for 4 hr						
	77	99	1	0	0	
					--	
Rh ₄ (CO) ₁₂ , Nb(HC ₂ O ₄) ₇ , Al ₂ O ₃ with surface area 170 m ² /g						
9 1%Rh/Al ₂ O ₃	2.5	60	15	8	17	
10 1%Rh/5.1%Nb/Al ₂ O ₃	6.8	58	30	1	11	
11 1%Rh/Al ₂ O ₃ and 5.1%Nb/Al ₂ O ₃ mechanical mixture						
	1.7	53	25	11	11	
					0.84	
Rh ₄ (CO) ₁₂ , Mo(CO) ₆ , Al ₂ O ₃ with surface area 170 m ² /g						
12 ⁵ 1%Rh/0.06%Mo/Al ₂ O ₃	3.7	50	16	15	19	
13 1%Rh/0.06%Mo/Al ₂ O ₃	7.8	42	16	25	16	
					0.62	
					0.92	

(continued)

Notes:

- 1 Catalyst Nos. 1 & 2 preparation conditions: On alumina, Rh was first attached using $\text{Rh}(\text{NO}_3)_3$ and the incipient wetness impregnation technique. Catalyst was dried overnight at 100°C, calcined at 500°C in O_2 for 4 hr and evacuated at 500°C for 1 hr. Then for catalyst No. 2, Mo was adsorbed from $\text{Mo}(\text{CO})_{12}$ at 50°C.
- 2 Catalyst Nos. 3 to 11 preparation conditions: On alumina, Nb was first attached using neat $\text{Nb}(\text{HC}_2\text{O}_4)_7$ and the incipient wetness impregnation technique. The catalyst was dried overnight at 100°C, calcined at 500°C in O_2 for 4 hr and evacuated at 500°C for 1 hr. Then Rh was attached from $\text{Rh}_4(\text{CO})_{12}$ using hexanes solution.
- 3 Catalyst Nos. 12 and 13 preparation conditions: On alumina, Rh was first attached using $\text{Rh}_4(\text{CO})_{12}$ in hexanes. Catalyst was evacuated at 200°C for 1 hr. Then Mo was adsorbed from $\text{Mo}(\text{CO})_{12}$ at 50°C.
- 4 Pretreatment conditions: Heating rate 5°C/min, 200°C 50 cc/min He 1 hr, pressurize and heat to reaction temperature under reaction gases.
- 5 Catalyst Nos. 2 and 12 pretreatment conditions: 200°C He 1 hr, 400°C H_2 1 hr.
- 6 Testing conditions: 30 atm, 250°C, 9000 1/kg/hr GHSV, $\text{H}_2:\text{CO}=2$, 0.5 g.

Figure 1
Catalyst Activity and Oxygenate Selectivity
on 1%Rh/Nb/Al₂O₃ Catalysts

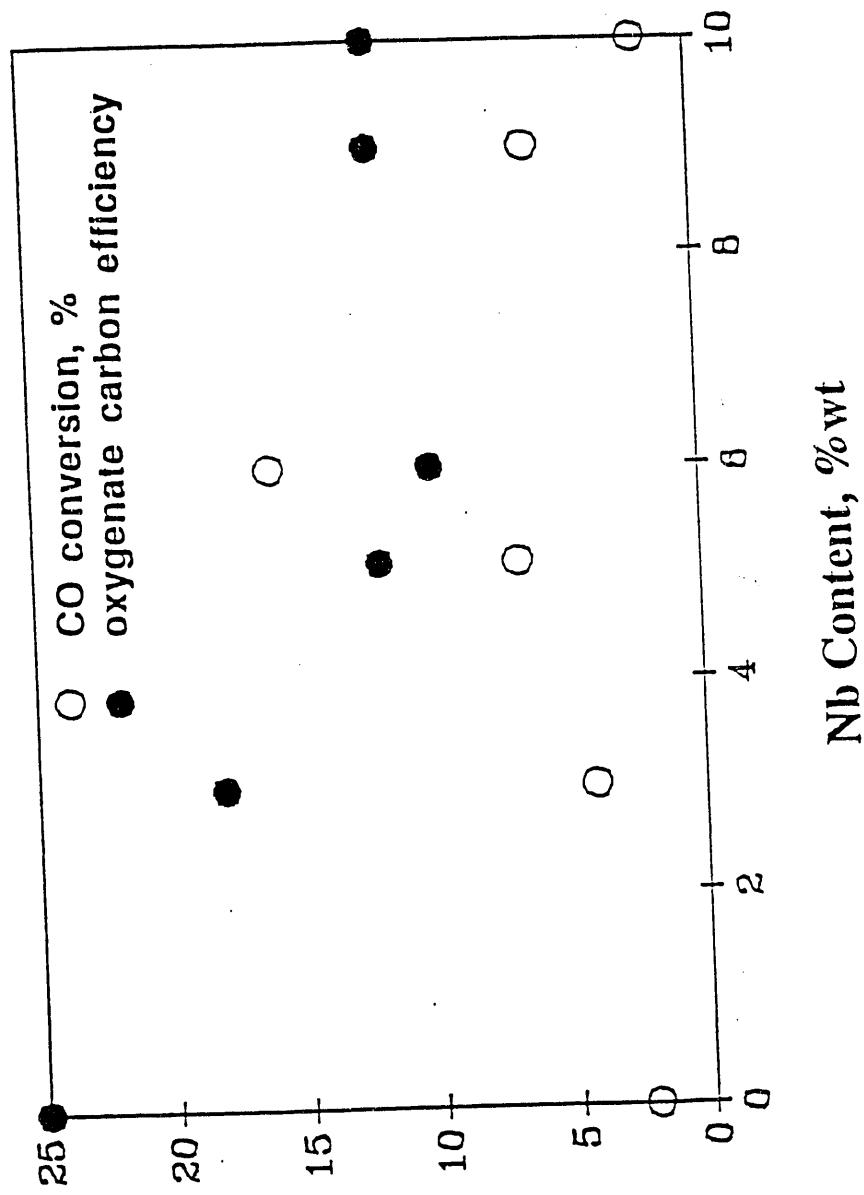


Figure 2
FTIR Spectra for $[\text{Rh}_4(\text{CO})_{12}]$ on $\text{Nb}/\text{Al}_2\text{O}_3$
(25°C)

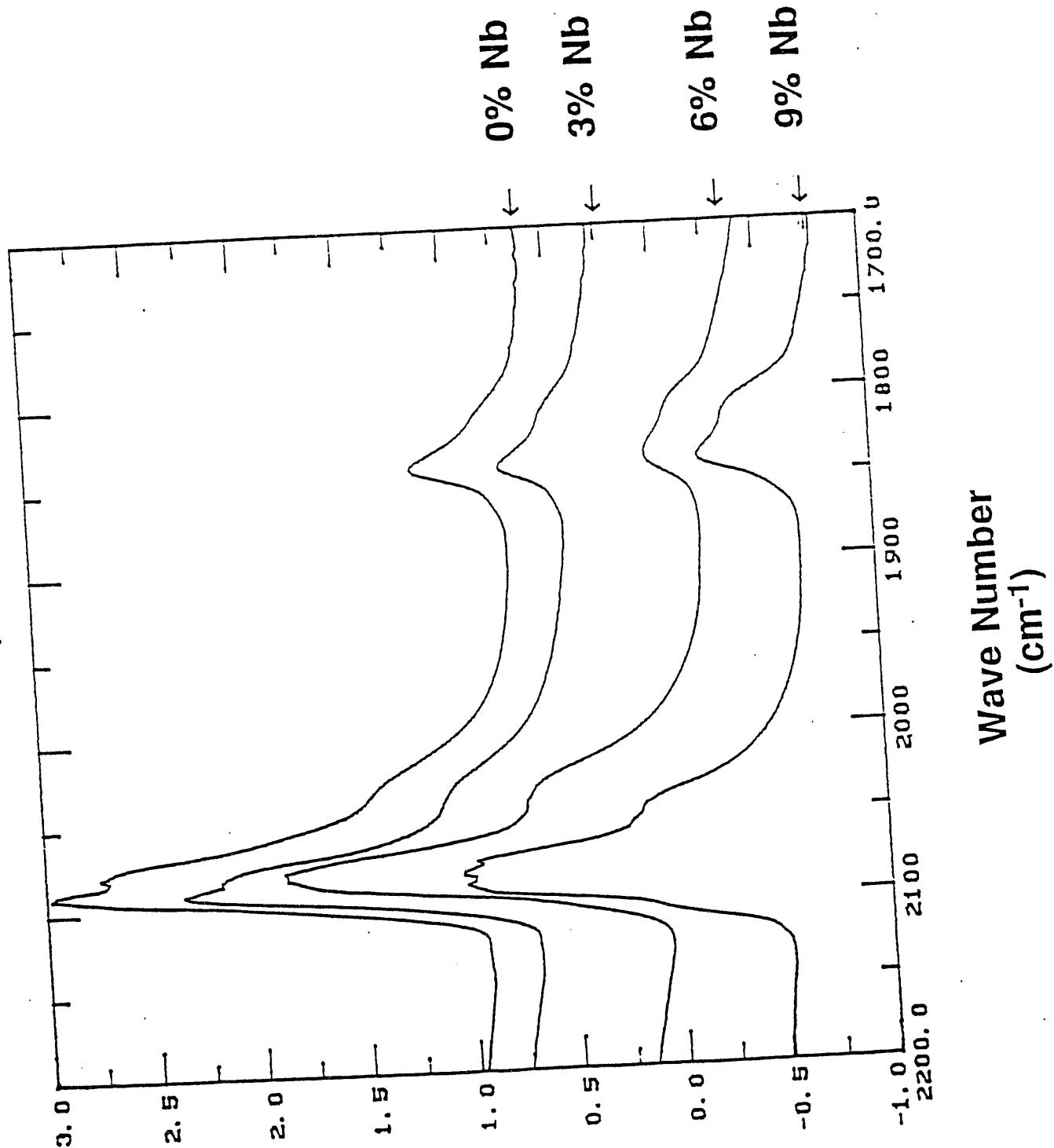


Figure 3
Spectra for $[\text{Rh}_4(\text{CO})_{12}]$ Adsorbed on Al_2O_3

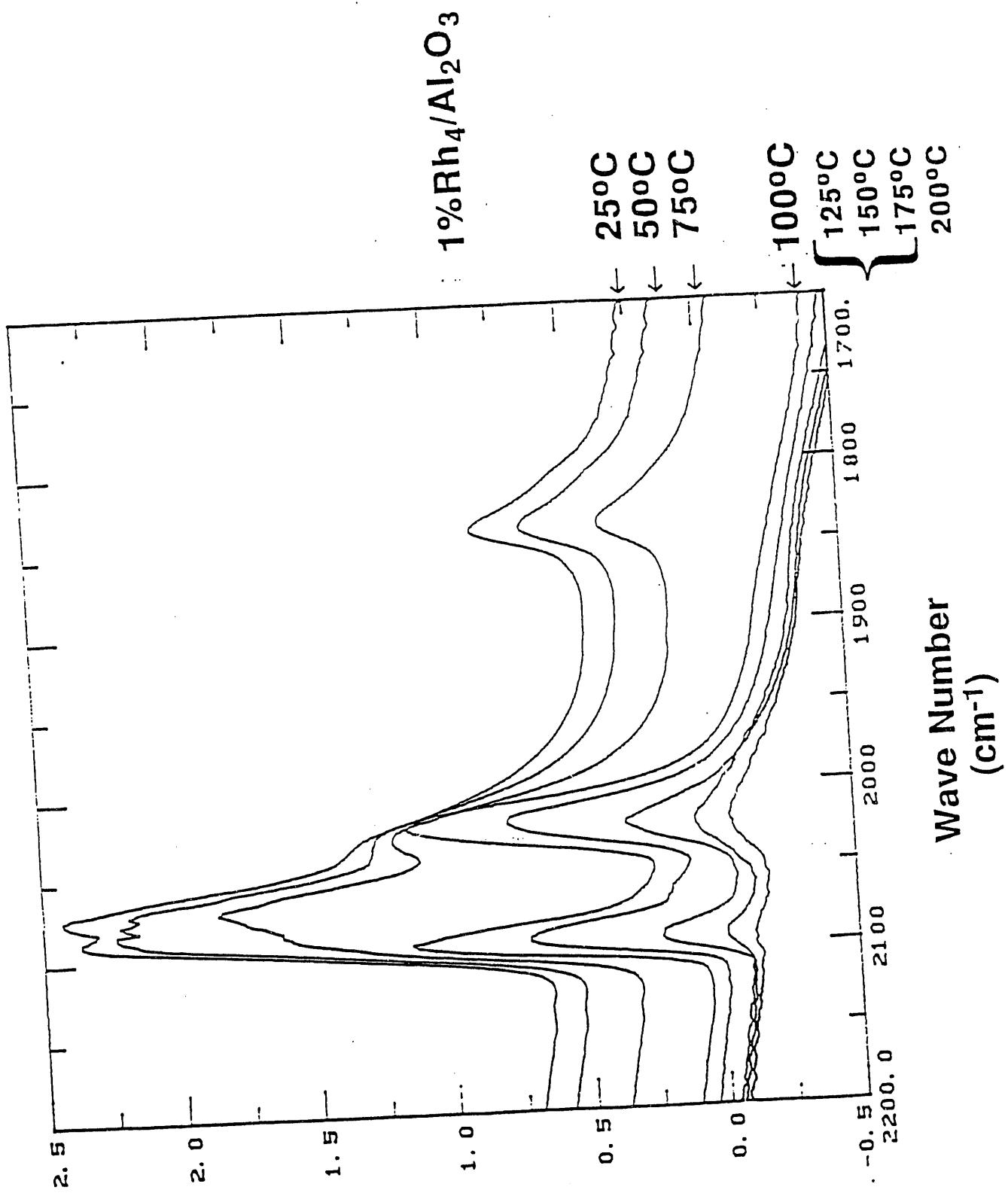


Figure 4
Spectra for $[\text{Rh}_4(\text{CO})_{12}]$ Adsorbed on $\text{Nb}/\text{Al}_2\text{O}_3$

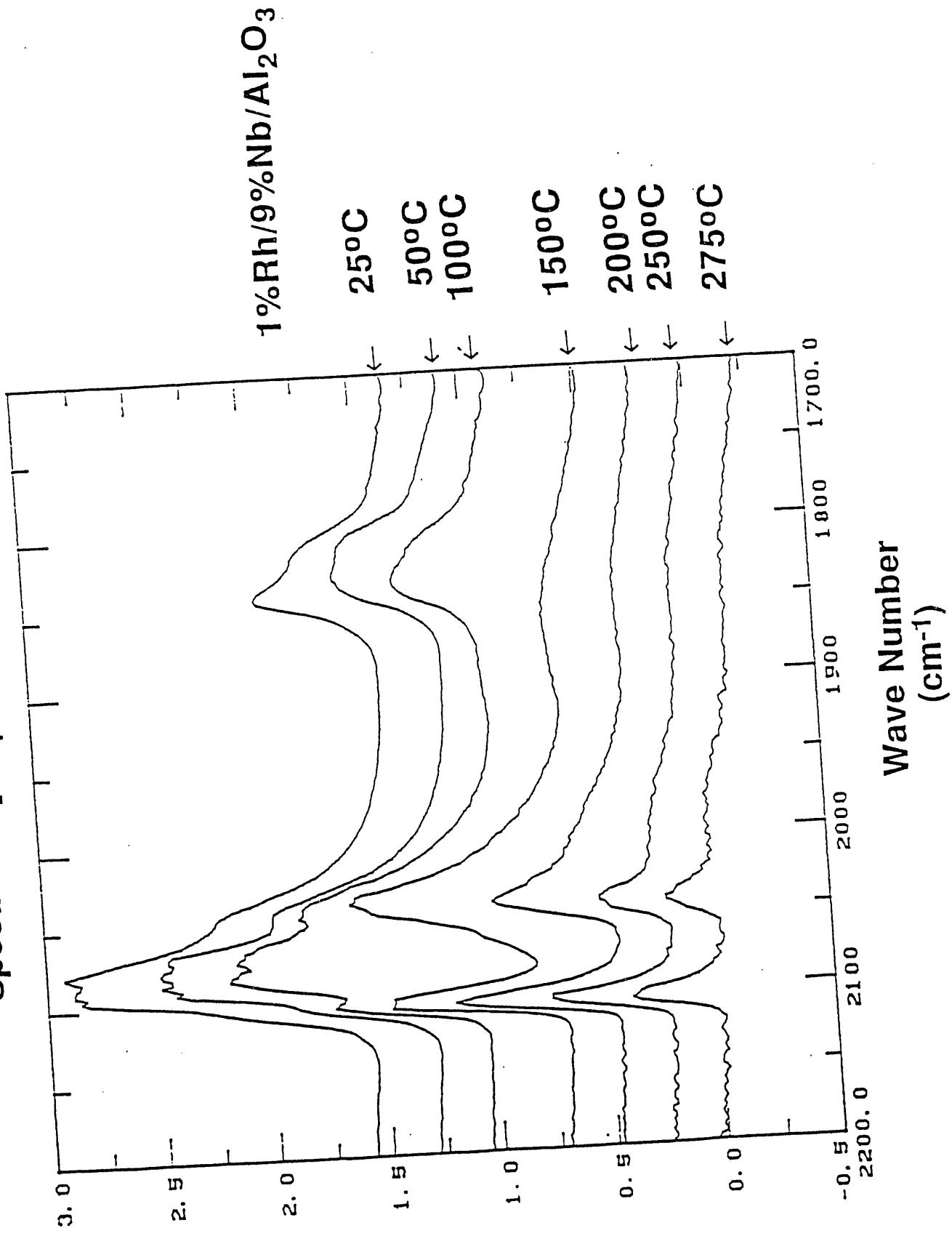


Figure 5
FTIR Spectra for CO Adsorbed on Rh/Al₂O₃

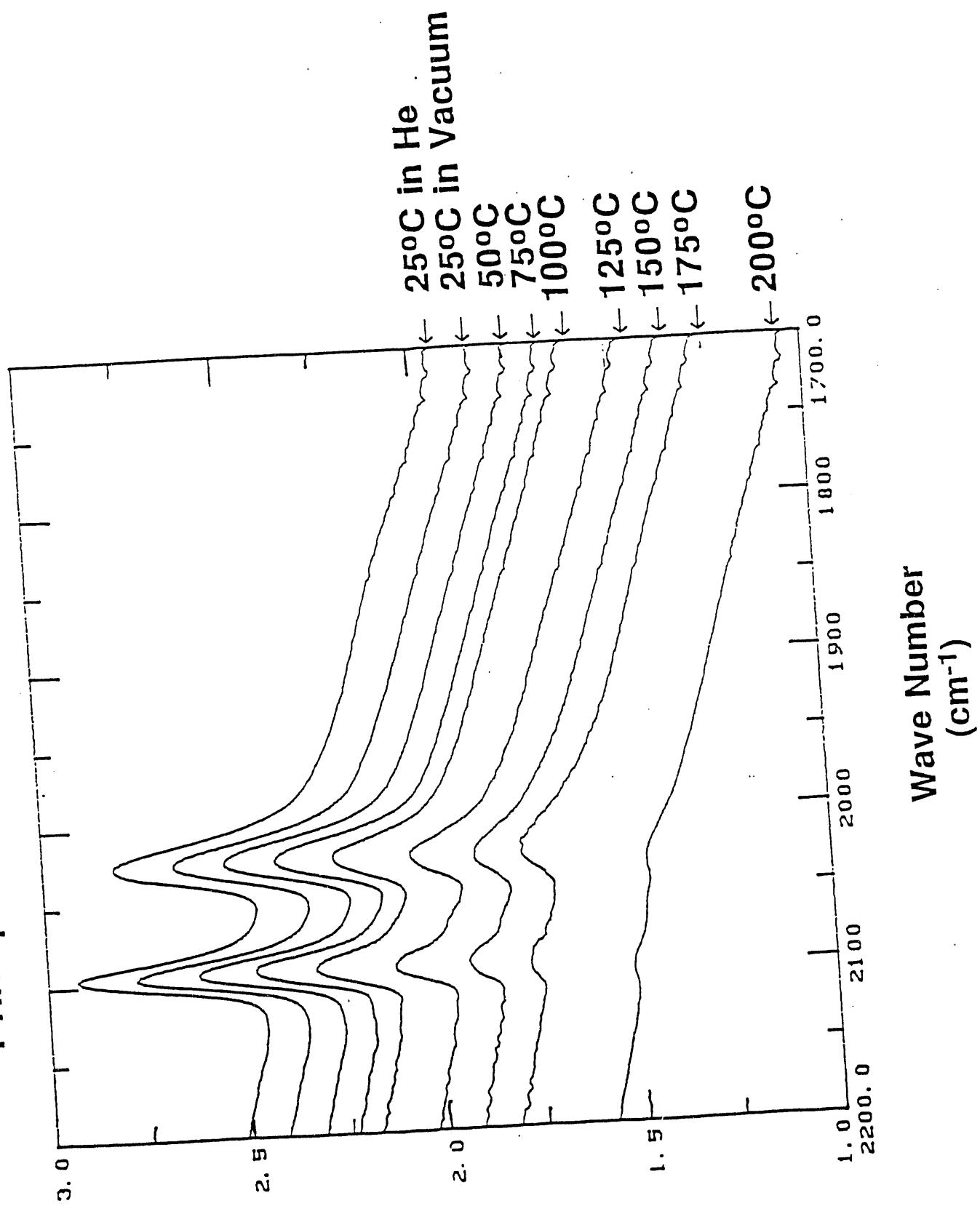


Figure 6
FTIR Spectra for CO Adsorbed on Rh/9%Nb/Al₂O₃

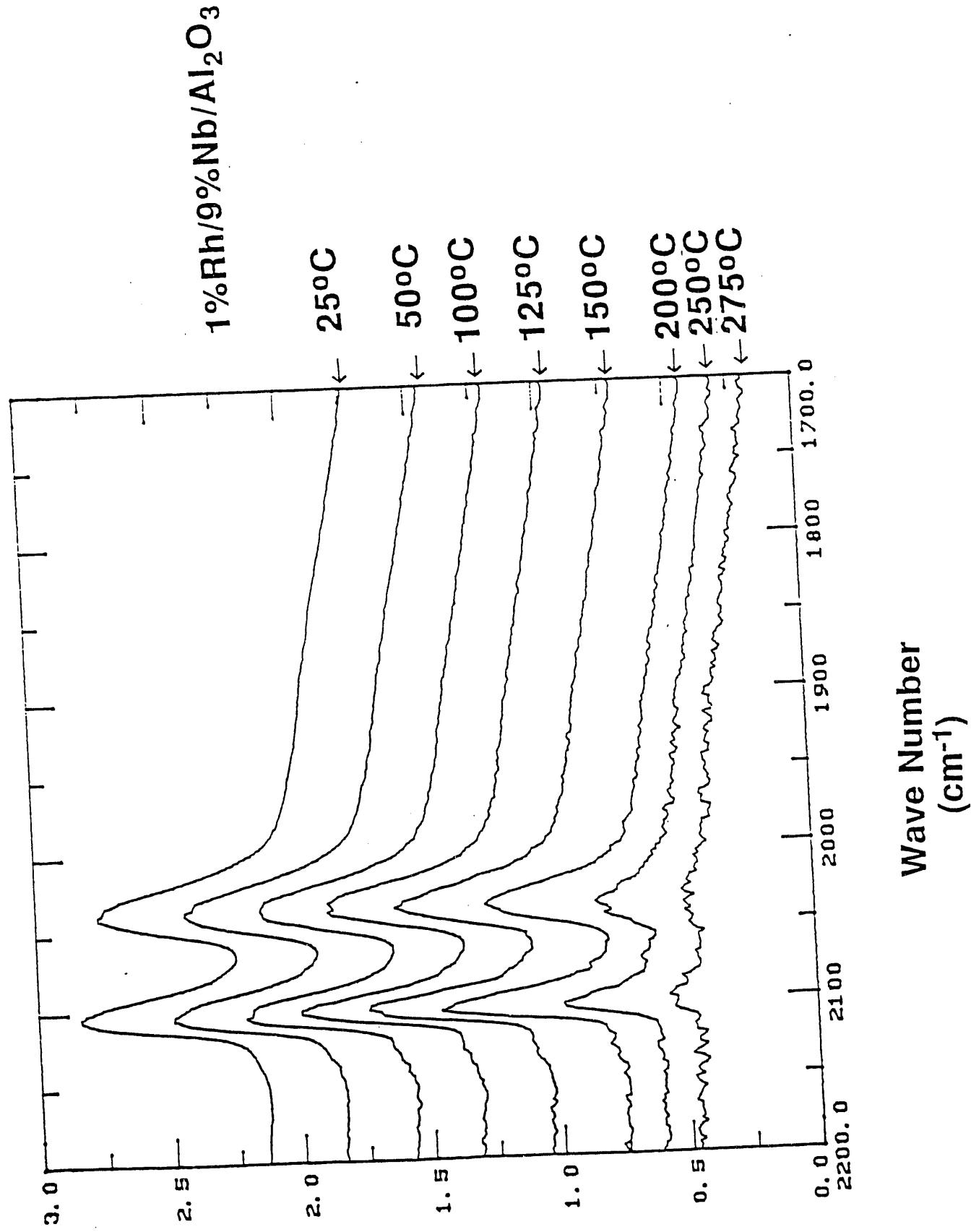


Figure 7
Spectrum for $[\text{Rh}_4(\text{CO})_{12}]$ Adsorbed on Nb/SiO_2

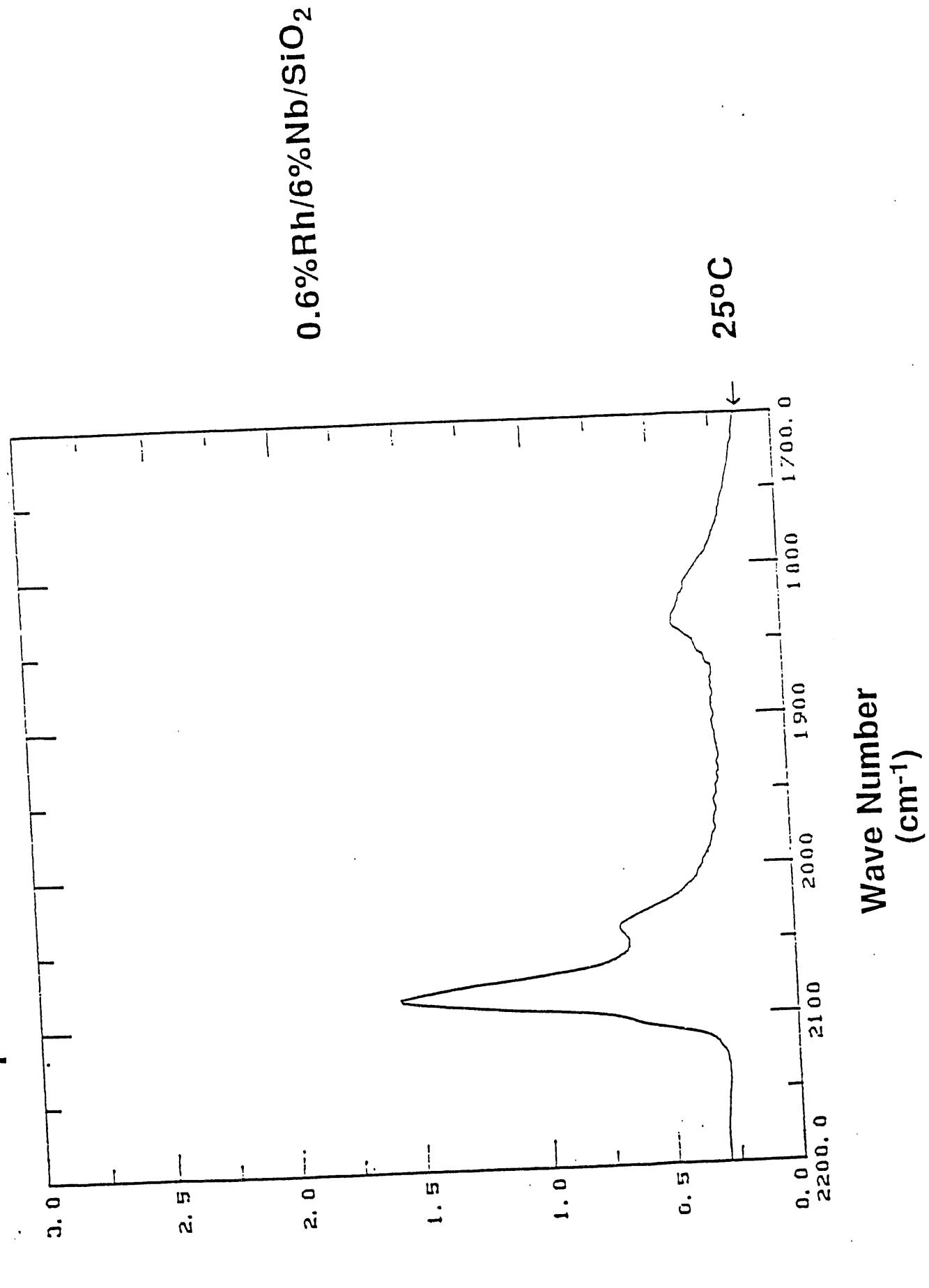
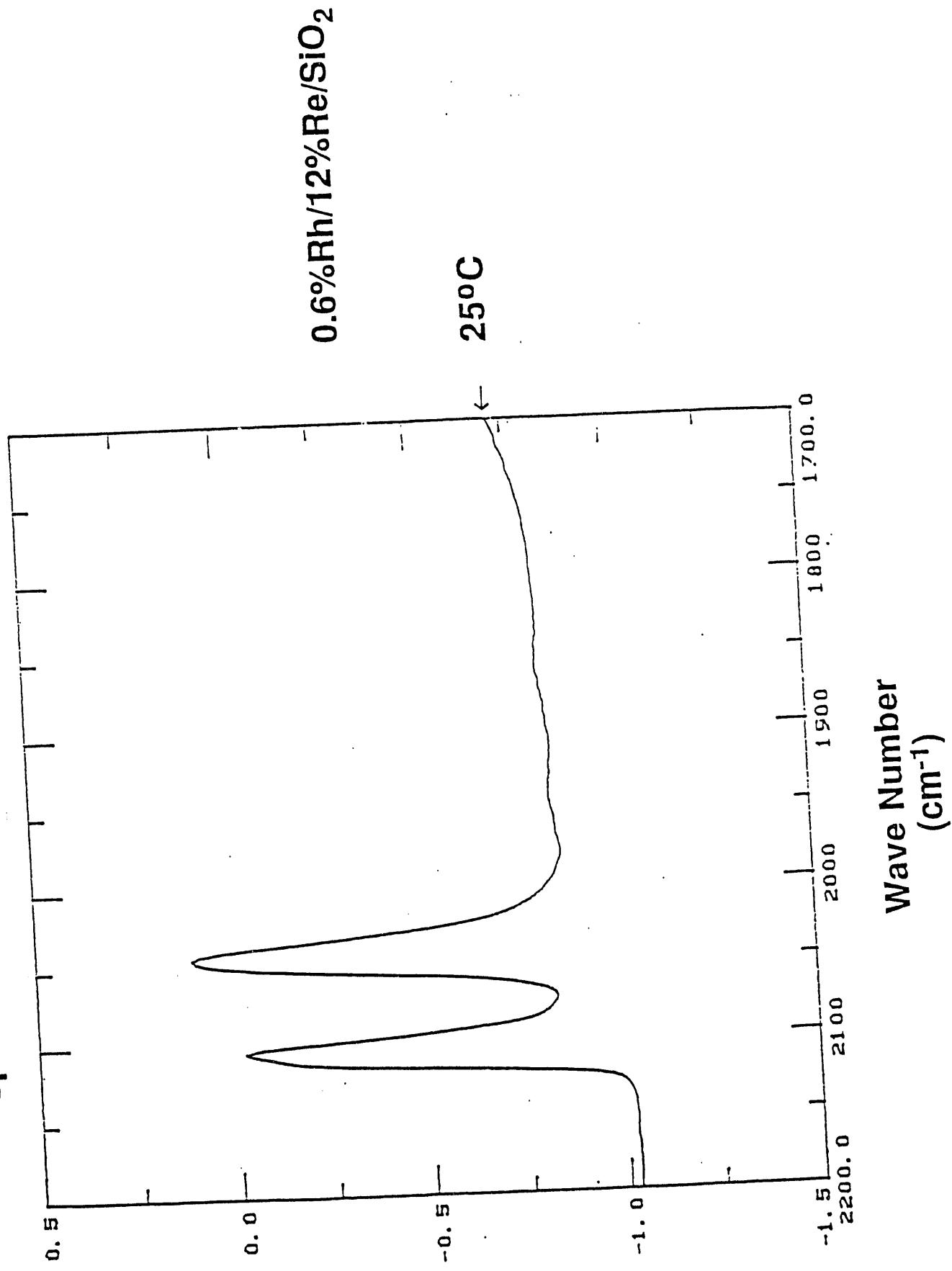


Figure 8
Spectrum for $[\text{Rh}_4(\text{CO})_{12}]$ Adsorbed on Re/SiO_2



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8/30/93

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