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QUARTERLY TECHNICAL PROGRESS REPORT

Submitted to U.S Department of Energy

GRANT TITLE:	Investigation of Syngas Interaction in alcohol Synthesis Catalysts
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*U.S. / DOE Patent Clearance is not required prior to the publication of this document

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Aug 23, 1996
Date

MASTER

Quarterly Technical Progress Report
(Period April 1 to June 30.)

This report presents the work done on " Investigation of Syngas Interaction in Alcohol Synthesis Catalysts" during the last three months. In this report the results of the work on the metal precursors of copper, cobalt and chromium using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) are presented.

Introduction: The technique of diffuse reflection spectroscopy has been used successfully in many fields as an adjunct to more well known spectroscopic methods and is often found more useful where traditional methods fail. This technique has become more popular and recently employed by several researchers [1-3] to study surface structures of metal oxides, opaque carbons and carbon supported catalysts. Due to the relative ease of the sample preparation and the high sensitivity of DRIFT, we have employed this technique to investigate the effect of CO adsorption on metal precursors.

Experimental Studies:

Description of the FTIR Spectrometer and DRIFT System:

The experimental set up consists of Mattison Research series FTIR spectrometer, equipped with an MCT detector operable in the mid IR region (4000-600 cm^{-1}), a diffuse reflectance accessory, an environmental chamber and an automatic temperature controller.

An optical diagram of the diffuse reflection attachment is shown in Fig.1. The praying mantis design incorporates two 6:1, 90° off -axis ellipsoidal mirrors, M_3 and M_4, which subtend 20% of the 2 pi solid angle. These ellipsoids are arranged with a common focal point S. Mirrors M_1 and M_2 transfer the IR beam from the spectrometer to the first of these ellipsoids M_3. This ellipsoid focuses the beam onto the sample, S. The second ellipsoid (M_4) collects the radiation diffusely reflected from the sample. This radiation is then directed by mirrors M_5 and M_6 towards the detector. The environmental chamber (fig.2), a stainless steel reaction chamber, consists of a sample cup to load the sample, two windows at the entrance and exit positions for the incident and reflected infrared radiations. A third window is provided at the back of the chamber to illuminate or view the sample. In addition two entry ports are provided for evacuation and gas entry and another two for water circulation. The environmental chamber is also provided with an automatic temperature controller and can be heated up to 600°C.

Sample preparation:

One molar solution of nitrate of copper is precipitated in Sodium hydroxide at 80°C and a pH of 7-8. The precipitate is washed and air dried overnight at 100°C and calcined at 350°C for 18 hrs. This precursor is loaded in to the sample cup of the environmental chamber .

Sample is evacuated at 80°C for about an hour and DRIFT spectra of the metal precursor are obtained at various temperatures up to 350°C to serve as reference. A fresh sample is again loaded and evacuated at for about an hour at 80°c and then CO is admitted and spectra were taken while continuously flowing CO as the temperature raises to 350°C. The same procedure was repeated for Co and Cr precursors.

Results and Discussion:

Copper Pre-cursor:

The infrared absorption spectrum of cuprous oxide was investigated earlier by Pastrniak[4], Lisistsa and Kholodar [5] and O'Keefee[6]. Pastrniak obtained the absorption spectra of Cuprous oxide using cuprous oxide films and powdered Cu_2O pressed into KBr. Two absorption maxima were recorded at 1124 and 794 Cm^{-1}. The results of our studies on the absorption spectra of copper pre-cursor and precursor + CO recorded at a resolution of 4 cm^{-1} using DRIFT at various temperatures is shown in Fig.3 and 4. The measured frequencies along with Lisitsa data for comparison are presented in Table 1. We observed two absorption peaks at about 1150 and 1082 cm^{-1} which average to 1120 cm^{-1} in agreement with earlier observations. The vibrational frequencies of a given mode do not show significant dependence on temperature. In addition, we observed absorption bands at 1256, and 1557 and 2075 cm^{-1}. Based on the assignments of Pastrniak, both 1557 and 2075 could be mixed vibrational mode frequencies. The closest possible assignment is shown in Table 1.

Cobalt Pre-cursor:

Earlier studies[7] on CoO infrared absorption spectra indicate one peak at 846 cm^{-1}. In our studies we did not observe any absorption band around 846 cm^{-1} but absorption maxima were seen at 1032, 1431 and 1580 cm^{-1}. Measured frequencies of CoO and CoO + CO are included in Table 2.

Also we have investigated the effect of CO adsorption on cobalt metal after reducing the precursor in a flowing stream of hydrogen. We did not observe any of the vibrational modes in metal + CO (Co + CO) which were observed in the metal precursor adsorbed with CO (CoO + CO). This observation supports the view of Xiaoding[8] that CO adsorption occurs only on Cu or Co ion but not on the metal.

Chromium Precursor: Earlier studies by Davydov[9], report six absorption bands assigned to chromium oxide in the region 700 - 1100 cm^{-1}. Our results indicate only two absorption bands in this region and are shown in Table 2.

Observed vibrational frequencies for meal precursor and metal precursor + CO are presented in Table 2. CO adsorption on the metal precursor could lead to a drop in frequency. Using the basic equations,

$$\nu = \sqrt{\frac{k}{\mu}} \qquad \text{and} \qquad \frac{\nu}{\nu_0} = \sqrt{\frac{\mu_{MO+CO}}{\mu_{MO}}}$$

we estimate for CO adsorbed on metal oxide , the maximum possible shift could be about $0.6\nu_0$ if strong bond formation occurs between the adsorbate CO and the adsorbent lattice point. ν_o is the frequency of the metal oxide. We believe that the drop in the lattice vibrational frequency is indicative of adsorption bond strength . As such the analysis of the new frequencies observed in the adsorbed species becomes very complex, in the absence of a detailed knowledge of all possible lattice vibrational modes of the metal oxide. We also find certain modes of vibration remain unaffected due to CO adsorption such as 1256 cm^{-1} line copper oxide, 1125 & 1032 cm^{-1} lines in cobalt oxide and 936 cm^{-1} line of chromium oxide. The data and analysis presented on these samples in this report is preliminary and further investigation is necessary to make any conclusive statements.

Future Plans:

The present studies provide some interesting results which are worthy of further exploration . We plan to extend our studies to Cu/Cr, Co/Cr and Cu/Co/Cr metal ratios during the next quarter. The present data serves as a reference for comparison.

Student Training:

One of the objectives of this project is to provide research training for minority undergraduate students at a school with predominant African American enrollment. Out of the three students involved in the project during this summer, one is an engineering major and two are physics majors. All these students have been trained in the catalyst preparation techniques. Two of the students worked with the FTIR instrument and acquired the needed skills to operate the instrument, collect and analyze the data independently with minimum supervision. One of the Xavier students spent about four weeks of summer at Grambling state University working with Dr. A.N. Murty , the Co-PI , and a Grambling State University physics student . They received training in the operation of ZFNMR spectrometer during the summer and acquired the needed skills to collect and analyze the data on the samples investigated.

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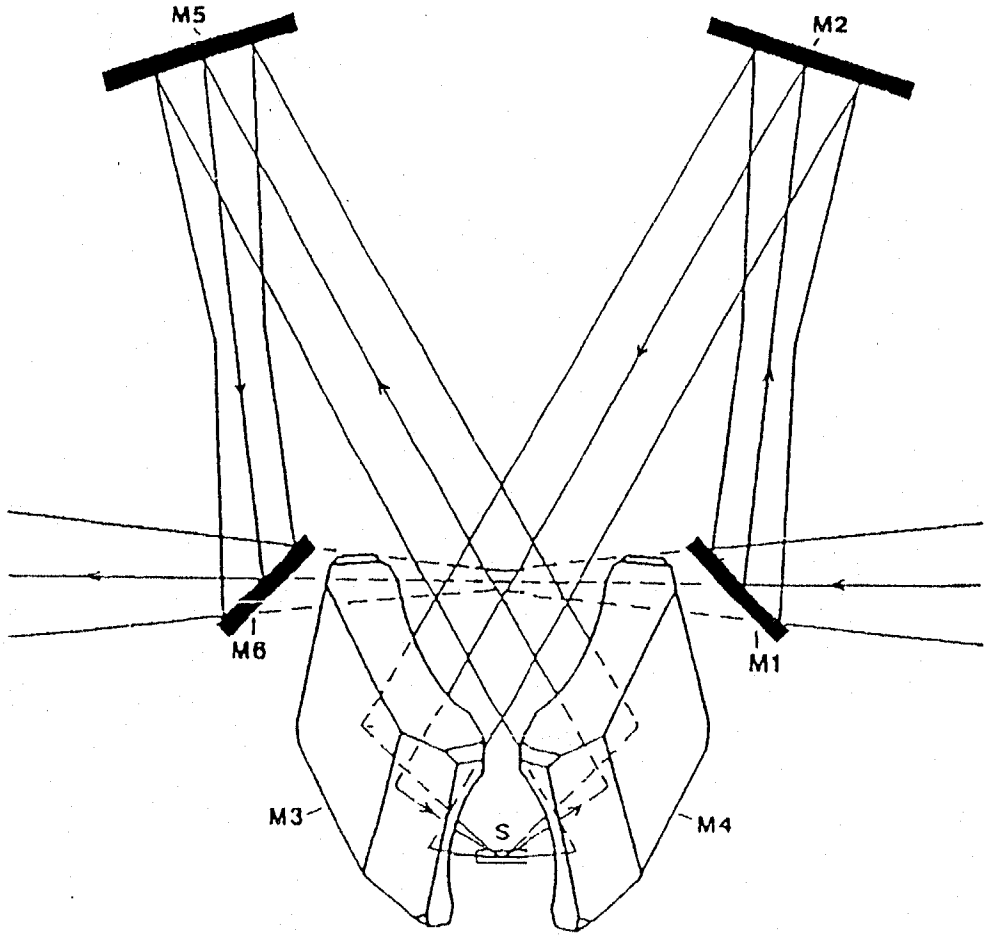

Figure 1. Optical Diagram of the Praying Mantis Diffuse Reflection Attachment.

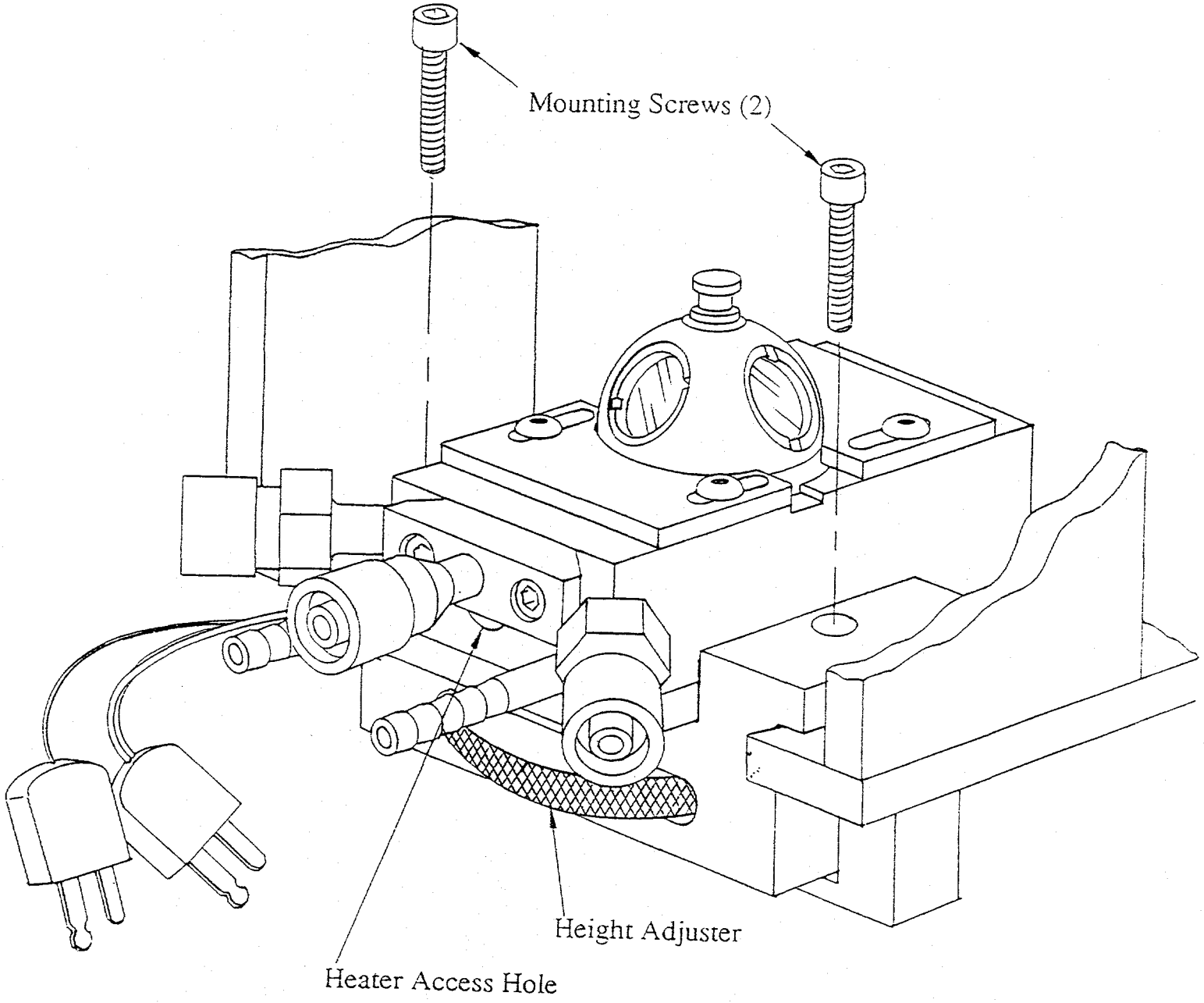

Figure 2. The HVC Installed in the Two-Dimensional DRA.

Figure 3: FTIR Spectra of Copper Oxide: Temperature Range 80°C - 350°C

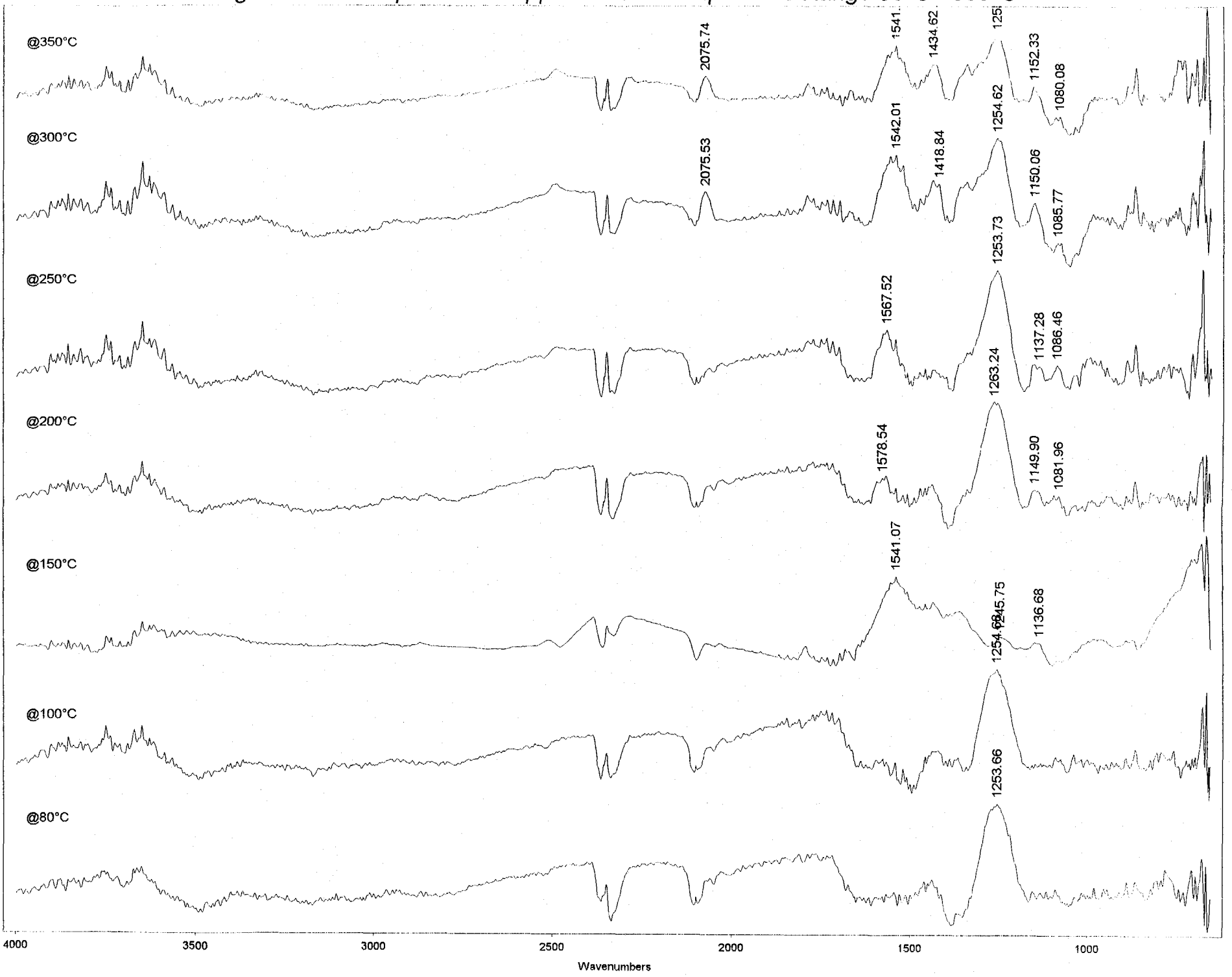

Figure 4: FTIR Spectra of Copper Oxide + CO: Temperature Range 80°C - 350°C

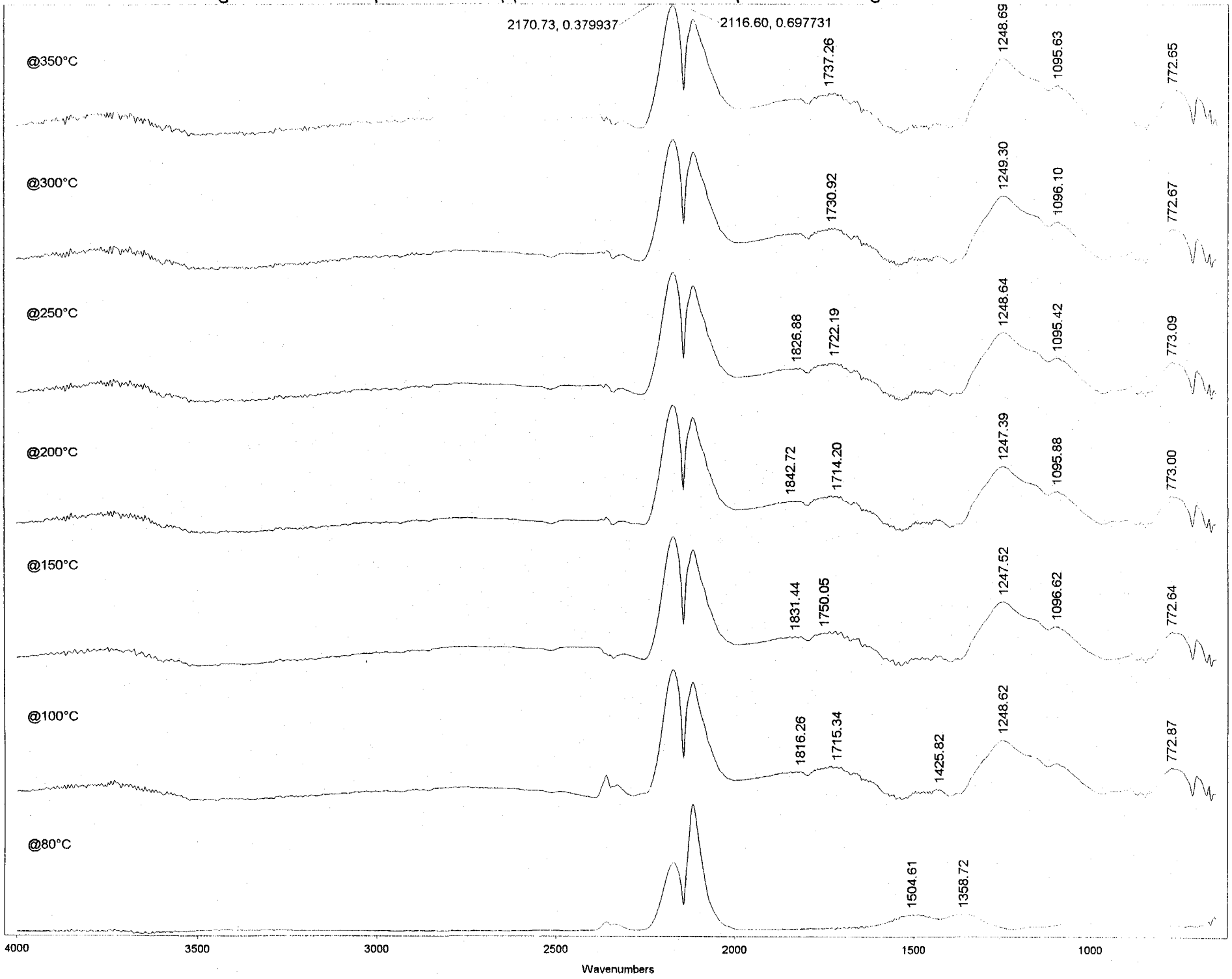

Table 1

Adsorption Maxima of Copper Oxide/Cuprous Oxide

Present (ν cm^{-1})	Pastrnyak (ν cm^{-1})	Lisitsa (ν cm^{-1})	Designation
2075	-	-	$(\nu_1+\nu_2+\nu_6)$
1557	-	-	$(\nu_1+(\nu_4-\nu_6))$
1256	1307	1268	$(\nu_1+\nu_6)$
1120	1124	1127	ν_1
-	699	715	ν_2
-	662	662	ν_3
-	610	610	ν_4
-	518	518	ν_5
-	182	182	ν_6

Table 2

Adsorption Frequencies (cm-1) of Metal Oxides

Copper Precursor		Cobalt Precursor		Chromium Precursor	
CuO	CuO + CO	CoO	CoO +CO	CrO	CrO + CO
2075	-	-	1939	-	1575
-	1726	1581	1583	-	1452
1557	-	1431	-	1046	-
1436	-	-	1339	-	998
1256	1249	1257	-	936	933
1120	-	1125	1129	-	724
-	1096	1032	1030	-	-
-	773	973	-	-	-
-	-	-	855	-	-