BACKGROUND

Catalysts comprised of dissimilar metals, specifically the early and the late transition elements, exhibit unusual activity and selectivity in the conversion of synthesis gas ($CO+H_2$) to fuel alcohols and gasoline range hydrocarbons. Method of preparation, nature of support, and presence of other elements in the catalyst composite are known to govern the behavior of the catalyst. Though much experimental data on catalytic yields are available, little effort has been devoted to correlating the physical and chemical characteristics of these intermetallic composites. Very little is understood about the specific roles of the different elements in a catalyst and the underlying mechanisms in achieving the distinct functions of association, dissociation, and insertion of syngas for the production of alcohols.

Bimetallic catalysts have been receiving considerable attention in recent years by virtue of their potential for converting synthesis gas to mixed alcohols. The continued threat of oil shortages and the consequent effects on national and global economies make these studies critical [1-3]. Stringent regulations on the percentage of methanol in gasoline blends increase the attractiveness and incentive to develop processes for the efficient production of longer chain alcohols; which in turn can be blended in greater proportion with gasoline. Blended fuels are not only cleaner sources of energy but also improve driveability and boost octane number.

The catalyst systems developed and patented by several investigators [4-8] differ widely in method of preparation and composition of constituent elements. A wide variety of preparation techniques, combinations of transition elements, alkali metals, and supports seem to have the potential to fulfill the functionality requirements for production of alcohols. It is believed that dissimilar transition metals distributed at atomic distances function synergetically, accomplishing three functions: dissociation (C-O bond breaking), association (hydrogenation/chain growth), and insertion (CO insertion/hydrogenation) [9]. The effectiveness of the catalyst seems to be influenced by the composition, size, and morphology of the metal cluster. Cluster physics reveals [10] that small aggregates of metal atoms behave like "giant atoms" with electron energy levels that exhibit a "shell structure" similar to atomic nuclei. The number of atoms and the nature of interactions between the cluster atoms determine the energy of the delocalized electrons. These itinerant electrons are believed to be responsible for the chemical and magnetic properties of the cluster. Since the position and nature of the constituent atomic cores determine the number of itinerant electrons, the cluster character and consequently the behavior of the composite catalyst is sensitive to the method of preparation. The pH, temperature, sequence of precipitation, drying, calcination, and reduction temperatures are known to influence the structure and properties of the catalyst. Keeping all other parameters constant, a detailed investigation of the effect of sequence of precipitation on the catalyst character is carried out in this study.

Although extensive valuable information is available on catalytic yields such as conversion efficiency, selectivity, product distribution, etc., relatively few studies have been made to analyze the nature of interactions between the transition metal atom and carbon monoxide/hydrogen gas molecules. A complete description of gas-metal interactions requires information both on the adsorbate and adsorbent simultaneously. In this investigation we examined the changes in the magnetic character of the ferromagnetic metal due to CO adsorption by Zero-field NMR of cobalt, magnetization study of the composite catalyst by Vibrating Sample Magnetrometry (VSM) and FTIR study of the adsorbed CO molecule. Many questions regarding these catalysts need to be answered. For example, does an electronic interaction occur between the ferromagnetic metal (Co/Fe) and copper or chromium /zinc such that there is an enhancement of the electron density at the transition metal surface thus changing the strength of the metal - CO/H_2 bonds? Is a particular crystalline phase such as hexagonal close packed (hcp) cobalt or face centered cubic (fcc) cobalt favored based on the preparative techniques. Is a rhombohedric phase of hydro-talcite structure or spinel structure or oxidic matrix structure predominate in the catalyst system? Does a change in the intermetallic ratio alter the strength and character of CO/H_2 adsorption? The techniques employed in this work, both ZFNMR and magnetization studies are sensitive to the crystalline phase and to changes in the electronic charge distribution around the transition metal nuclei and provide information on the adsorbent metal atom. The FTIR studies provide information on the adsorbate gas molecule and the changes in the stretching frequencies of the adsorbate reveal the nature of gas-metal interactions in the catalyst. The main focus of this study is to examine the subtle changes that occur in the character of adsorbate and adsorbent due to gas-metal/intermetallic interactions and their relation to the observed selectivity character of the catalyst.

PROJECT OBJECTIVES

The primary objectives of the project are to

a) synthesize, by controlled sequential and co-impregnation techniques, three distinct composition metal clusters (consisting of Cu-Co-Cr and Cu-Fe-Zn): rich in copper (Methanol selective), rich in ferromagentic metal (Co or Fe - Hydrocarbon selective) and intermediate range (mixed alcohol catalysts);

b) investigate the changes in the magnetic character of the systems due to interaction with CO, through

   i) Zero-field Nuclear Magnetic Resonance (ZFNMR) study of cobalt

   ii) Magnetic character (saturation magnetization and coercive field) analysis of the composite catalyst by Vibrating Sample Magnetometry (VSM);

c) examine the changes in syngas adsorption character of the catalyst as the composition changes, by FTIR Spectroscopic analysis of CO stretching frequencies;

d) determine the nature and size of these intermetallic clusters by Scanning Electron Microscopy (SEM); and

e) perform catalytic runs on selected samples and analyze the correlations between the physical and chemical characteristics.

The catalysts chosen have a greater promise for industrial application than the Rh and Mo based catalysts. Several groups preparing catalysts [4-9] by synthetic routes have reported divergent results for activity and selectivity. Generally the research has followed an empirical path and less effort is devoted to analyze the mechanisms and the scientific basis. The primary intent of this study is to analyze the nature of the intermetallic and gas-metal interactions and examine the correlations to catalytic properties.

EXPERIMENTAL: INSTRUMENTAL

A. Zero-field NMR Studies

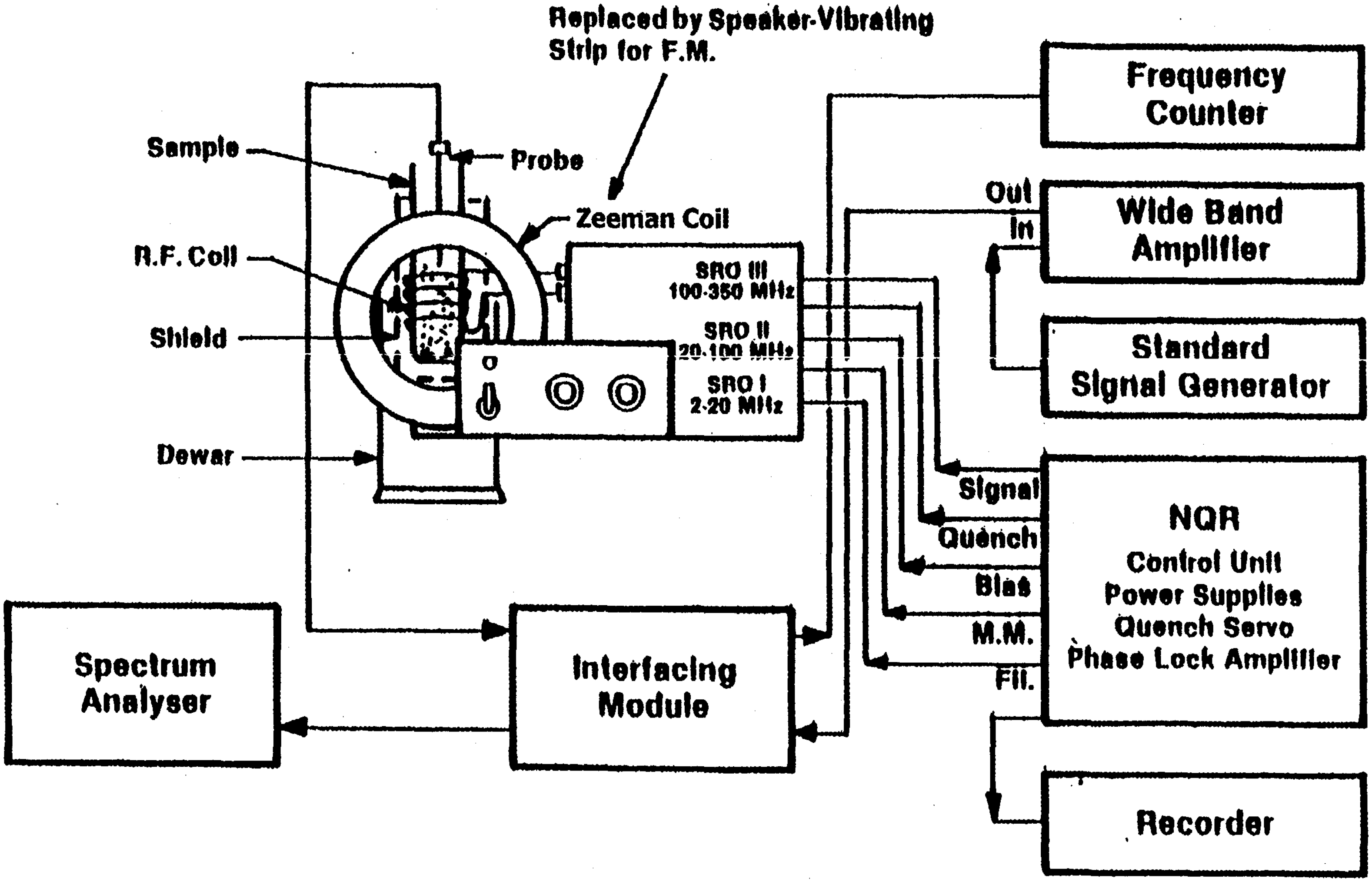
Since its discovery by Gossard and Portis in 1959, nuclear magnetic resonance in ferromagnetic materials has provided information concerning hyperfine fields, and nuclear spin relaxation. Using this technique it is possible to characterize multi-domain, and superparamagnetic particles [11].

At the nuclei of atoms of ferro-, antiferro-, and ferrimagnetic materials there exists a strong internal magnetic field due to the partial polarization of s-electrons by the magnetic state of the material. This field, referred to as the hyperfine field, is the same field as described in Mossbauer spectroscopy. The interaction of the nuclear spin with the hyperfine field gives rise to a set of quantized energy states which lead to the well-known resonance condition $\omega = \gamma \mathbf{H_{hf}}$ where γ is the nuclear gyromagnetic ratio and $\mathbf{H_{hf}}$ is the hyperfine field. Thus, resonance conditions exist without the application of an external magnetic field, and through resonance techniques the internal field can be determined. It should be noted that the polarization of the s-electrons is a result of the electrostatic coupling of 3d (or 4f) electrons and s-electrons (both inner and outer s-band). As such the hyperfine field reflects the 3d electronic structure and behavior, and can provide valuable information if significant perturbations in the charge distribution occur due to syngas adsorption on the ferromagnetic metal, or because of intermetallic interactions with in the metal cluster due to compositional changes or preparative techniques.

Adsorption of a molecule on the surface of ferromagnetic solid produces a change in the magnetization of the solid. If the adsorption process involves appreciable electronic interaction and if the ratio of surface to volume in the adsorbent is large, then the fractional change of magnetization becomes substantial and lends itself to convenient measurement and interpretation [12]. The NMR line frequency can be represented by $\omega = \gamma (\mathbf{H_{hf}} \pm \Delta \mathbf{H_{hf}})$ where $\Delta \mathbf{H_{hf}}$ represents the resulting modifications in the charge distribution in the vicinity of the cobalt nucleus due to the adsorbed molecule.

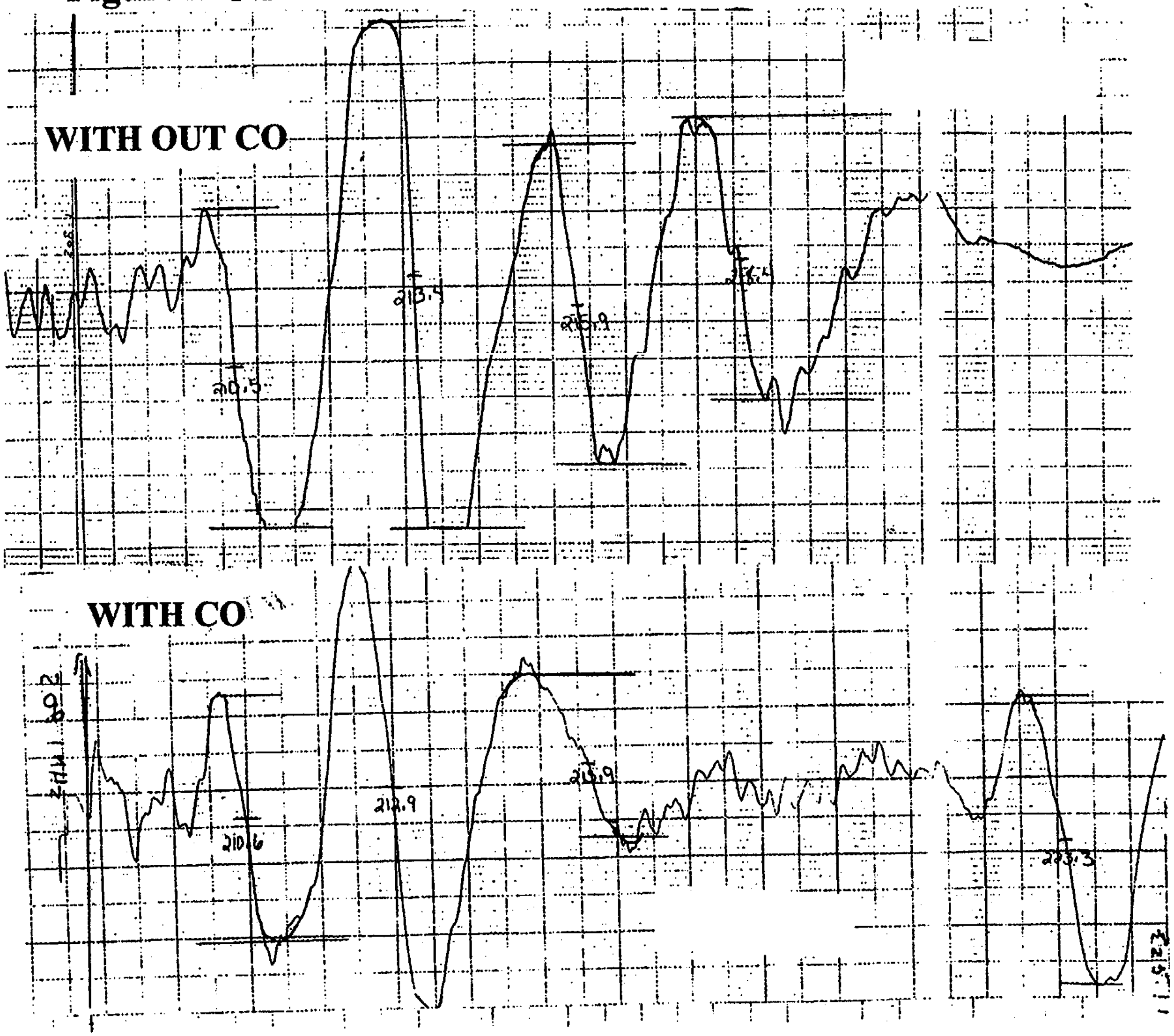
Figure 1 is a block diagram of the NQR/ZFNMR spectrometer system. The spectrometer is a conventional Superregenerative oscillator (SRO) with Zeeman modulation and phase sensitive detection. It was designed by WILK's scientific corporation as a Nuclear Quadrupole Resonance spectrometer with a servo controlled self quenching system for auto scan operation in the frequency range 2-350 MHz. Since Zeeman modulation is not suitable for ferromagnetic materials, frequency modulation was employed. This was easily accomplished using a woofer (low frequency) speaker to vibrate a small metal strip near the oscillator tank circuit.

The spectra were scanned in the 205-230 MHz region. The carrier frequency of the SRO was determined by displaying the oscillator output on a Tektronix Model 2712 spectrum analyzer/frequency counter. The NMR spectra were scanned at a flow rate of 0.1MHz/min and the resonance frequencies were ascertained with an accuracy of ±0.3 MHz. A typical NMR spectrum of a catalyst sample is shown in Figure 2.



NMR/NQR SPECTROMETER SYSTEM BLOCK DIAGRAM

Figure 2 NMR SPECTRA OF Cu/Co/Cr SAMPLES



B. Magnetic Measurements

Substances composed of atoms or ions with permanent magnetic moments arising from unpaired electron spins can be classified as para-, ferro-, antiferro-, or ferrimagnetic depending on such factors as exchange interaction between neighboring species, chemical composition, crystalline structure, crystal field effects, particle size, and temperature [13].

For paramagnetic behavior the magnetic susceptibility (χ) defined as the ratio of magnetization (M) to Field (H), can be adequately described by the Curie Weiss law: $\chi = C/(T-\theta)$ where C and θ are the Curie and Weiss constants. When neighboring atoms or groups of atoms interact strongly and behave in a cooperative fashion, a ferromagnetic state exists with all spins 'parallel' in its domain.

Highly dispersed metals with metal crystallite sizes of less than single magnetic domain size exhibit unique magnetic properties [14]. Although the atoms which comprise these single domain particles are ferromagnetically coupled, the particles themselves behave like paramagnetic particles with very large magnetic moments. This gives rise to a behavior known as super paramagnetism. The magnetic moment associated with these superparamagnetic particles is directly proportional to the particle volume. The particle size can be determined from magnetization measurements [15]. Such analysis has been used to determine average particle size and particle size distribution for many highly dispersed metal catalysts [16-17]. Most heterogeneous catalysts are comprised of transition elements, their oxides or compounds, and often include various supports. The important characteristics of the transition elements are their incomplete d-electron shell and their unpaired electron spins. These features are responsible for their specific magnetic as well as their valuable catalytic properties.

Significant changes in the saturation magnetization M_s have been reported for a number of ferromagnetic catalysts due to chemisorption of H_2(H_2/Ni-Cu, H_2/Co, H_2/Fe). The change in magnetic moment per adsorbate molecule, ε, in general can be represented by , where ΔM_s change in saturation magetization, M_s saturation magnetization, n_{metal} number of moles of the metal or gas, and β is the Bohor magneton number of the metal. All the ferromagnetic metals were found to yield appreciable ε values: ε (Ni/H_2) = -0.37, ε (Co/H_2) = -0.54, ε (Fe/H_2) = +1.85. Very few studies have been made with CO as adsorbate. For adsorbates other than H_2 the magnetization studies yield ζ what is known as bond number ζ(x) = ε(x)/ ε(H), where x is the adsorbate molecule. Thus the bond number indicates the number of adsorbent atoms involved in the interaction per adsorbate molecule, and one could postulate the possible nature of bonding.

The characteristic magnetic properties; M_S (saturation magnetization), M_r (remanent magnetization) and H_C (coercive field) have been determined using Digital Measurement Systems Vibrating Sample Magnetometer. Figure 3 is a block diagram of the experimental system. This is a Model 880A DMS VSM, with an accuracy of 1%, and a sensitivity of 50 micro EMU with one average. The sensitivity can be increased to 5 micro EMU with 100 averages. The system is microprocessor controlled and auto ranges full scale measurement from 0.04 EMU-4000 EMU. In the present arrangement a maximum magnetic field of 13.5 k.Oe can be applied and it can be programmed to make temperature dependent measurements in the range –192°C to +740°C. A typical hysteresis curve of a catalyst sample is shown in Figure 4.

ZFNMR studies along with magnetic measurements have provided an excellent approach in our investigations of the magnetic nature of the inter-metallic interactions in the higher alcohol synthesis copper-cobalt catalyst systems [18-24].

FIGURE 3. DMS VIBRATING SAMPLE MAGNETOMETER

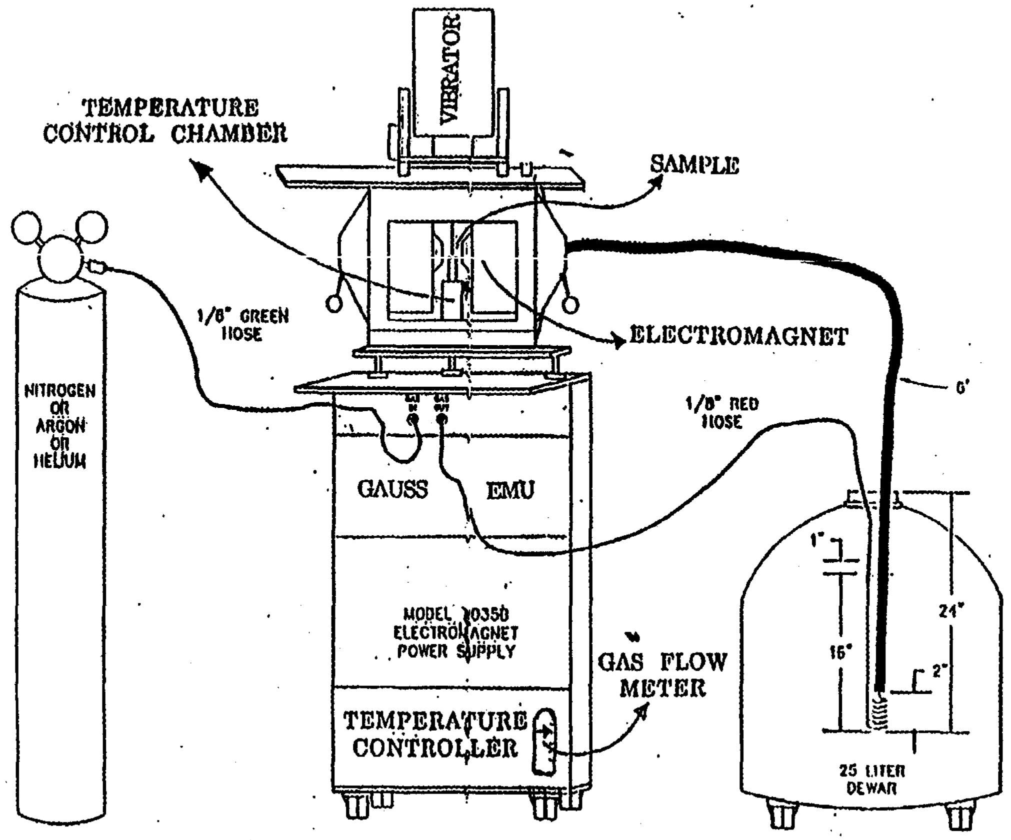
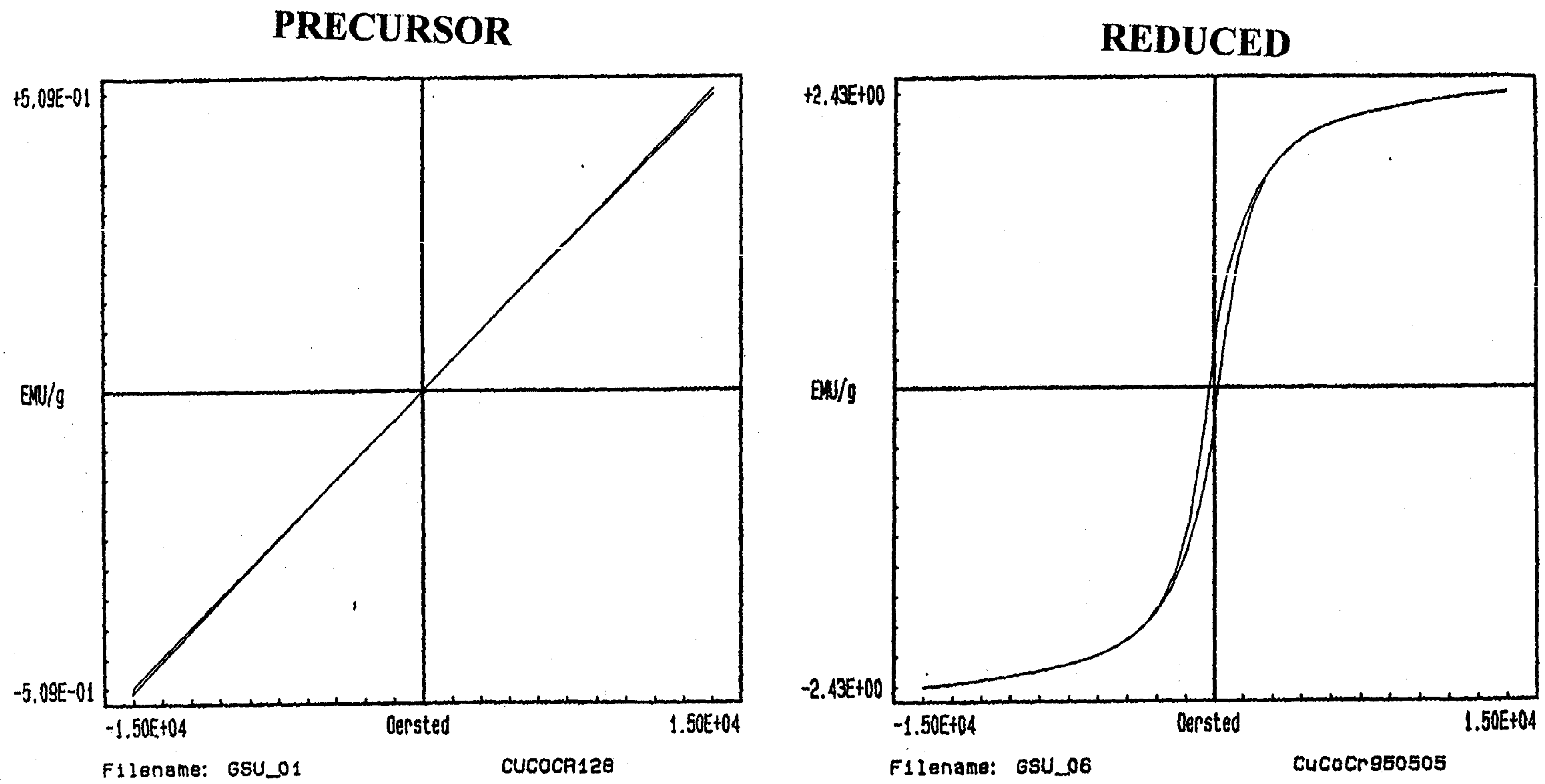


FIGURE 4. HYSTERISIS CURVE OF A SAMPLE CATALYST


PRECURSOR

REDUCED

C. Fourier Transform Infrared Spectroscopy (FTIR)

Several investigators have successfully employed FTIR and IR spectroscopy techniques for the surface characterization of Cu/Co catalysts using CO as a probe molecule [25-29]. In general, spectroscopic techniques are found to be most precise in the analysis of vibrational and rotational structures of molecules [30, 31].

When the probe molecule is adsorbed on the surface of the catalyst there are two possible electronic interactions between the adsorbent and the adsorbate. One is electron donation (s-electron) from the probe molecule to the empty d-orbital of the metal cation, the effect is strengthening of C-O bond of CO. Then CO vibrational frequency shifts to a higher value. The other interaction is the back- donation of the d-electron from the metal cation to an antibonding orbital of CO. The effect is weakening of the C-O bond of CO and ν_{CO} shifts to a lower frequency. A knowledge of the change in the stretching frequency of CO reveals the nature and extent of intra and intermolecular interactions in the catalyst. The differences in the frequency shifts from one catalyst to the other which differ either in composition or preparative procedure would shed light on the catalytic character. The FTIR and magnetization studies complement each other in the development of a picture of adsorbate and adsorbent interactions and their relation to observed selectivity character.

Several FTIR studies of CO adsorbed Cu-Co catalysts were performed [28, 29] using transmission spectroscopy. This technique seems to have several disadvantages. Most metal catalysts supported on metal oxides are opaque to IR radiation and the use of pressed discs, provides less surface area per gram of adsorbent available to adsorbate molecule. In recent years, Diffuse Reflectance Infrared Fourier Transform Spectroscopy

(DRIFT) has been widely used [32-36] for powdered samples due to a) it's ease in sample handling, b) enhancement in percentage of adsorption, and c) increase in the area of contact of the adsorbent with the gas. In our FTIR investigation of CO adsorption character, we have employed the DRIFT technique.

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

A block diagram of the optics of the diffuse reflection attachment is shown in Figure 5. The praying mantis design incorporates two 6:1, 90° off-axis ellipsoidal mirrors, M_3 and M_4, which subtend 20% of the 2π 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 (Figure 6), a stainless steel reaction chamber, consists of a sample cup to hold 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. Spectra can be recorded in the Mid-IR region at resolutions of 1, 2, or 4 cm^{-1}. The noise level can be decreased by increasing the gain and the number of scans.

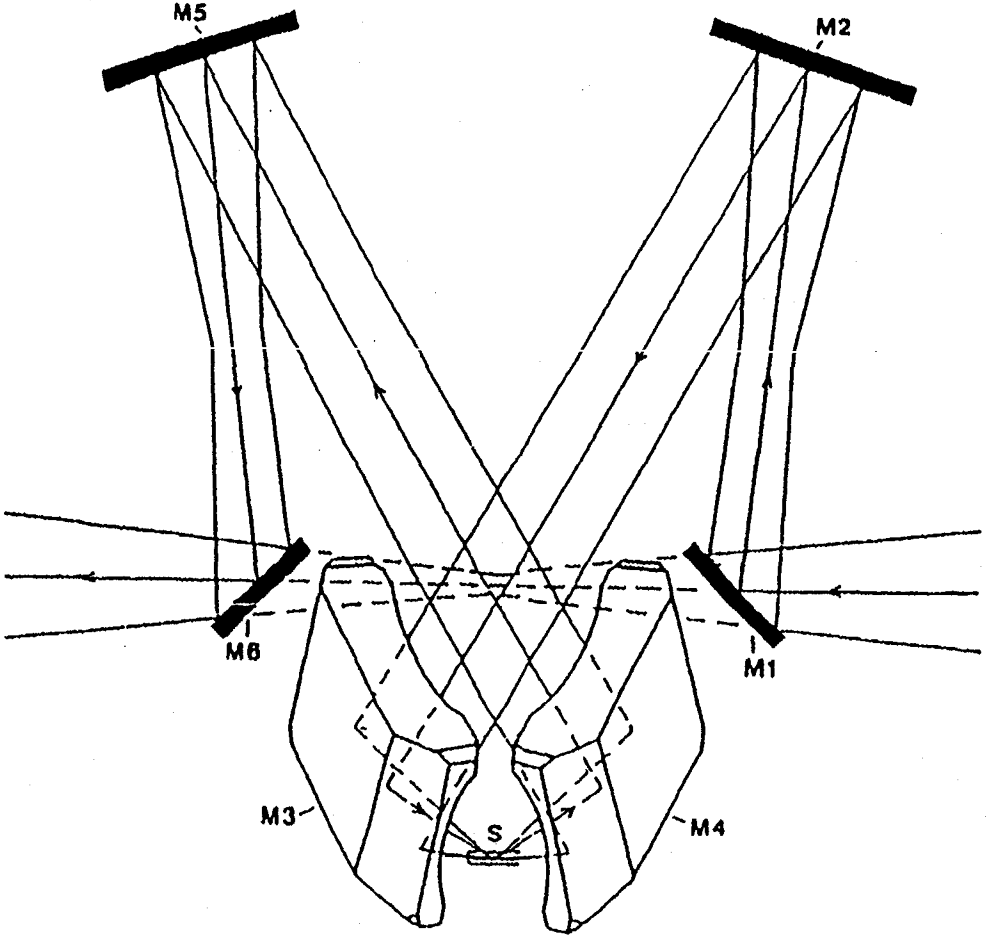


Figure 5. Block Diagram of the Optics of Diffused Reflection Attachment

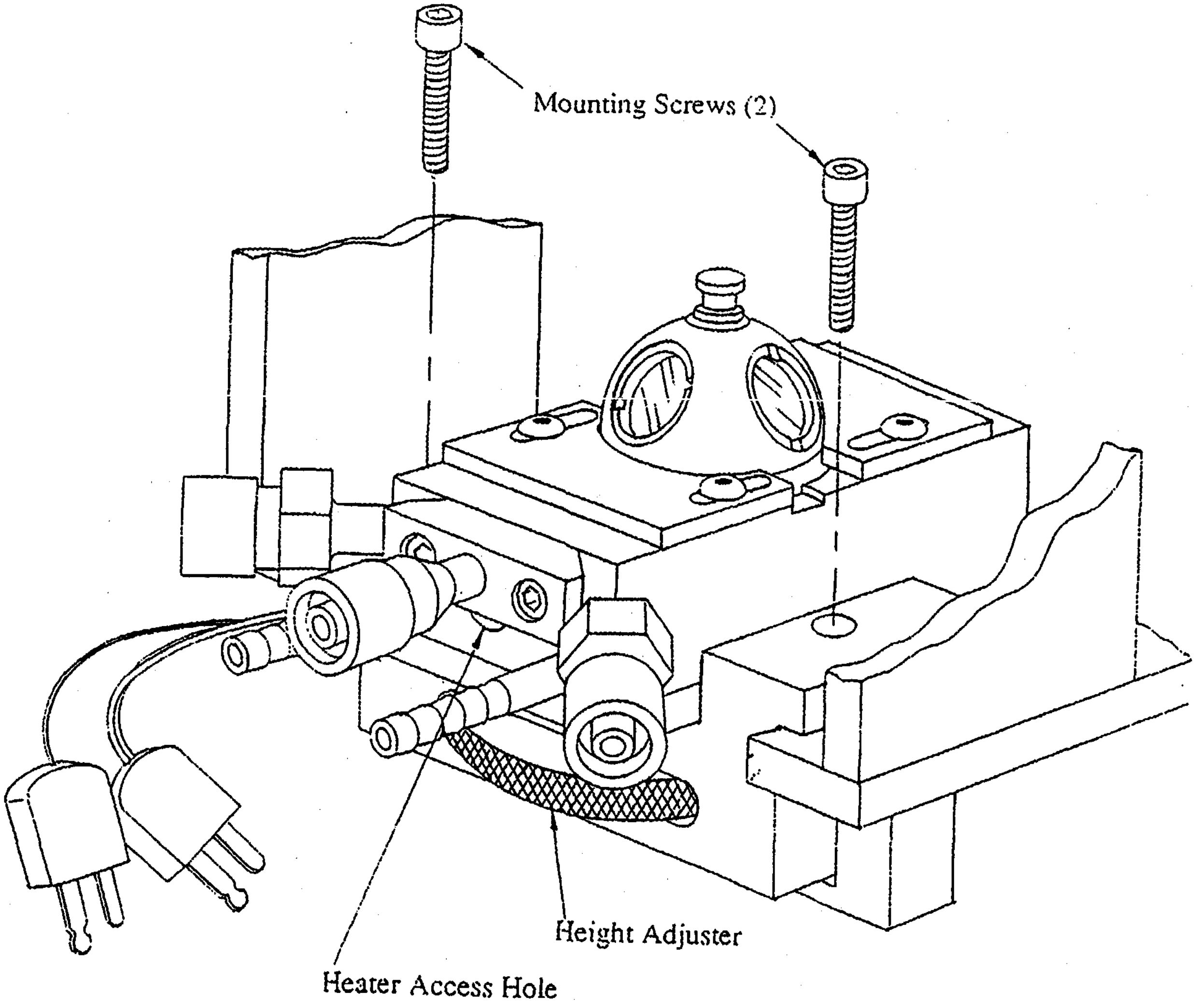


Figure 6. High Vacuum Environmental Chamber