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METAL-SUPPORT INTERACTIONS: THEIR EFFECTS UPON ADSORPTION, ELECTRONIC, AND ACTIVITY/SELECTIVITY PROPERTIES OF COBALT IN CO HYDROGENATION

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SUMMARY

The investigation of cobalt metal-support interactions and their effects upon adsorption and activity/selectivity properties of cobalt is described. The objectives of this research are to (i) determine the effects of cobalt-support interactions on dispersion, oxidation state and adsorption properties of cobalt; (ii) correlate the activity/ selectivity properties for hydrocarbon synthesis on cobalt with dispersion, oxidation state and behavior of adsorption of CO and H₂ and (iii) measure directly the extent of interaction of various supports with iron and cobalt using Moessbauer Spectroscopy. The proposed work features a comprehensive, quantitative experimental investigation of Co on Al₂O₃, SiO₂, TiO₂, MgO, and carbon supports with careful characterization of the physical and chemical, bulk and surface properties of each catalysts with BET, H₂ and CO chemisorption XRD, TEM, ESCA, TPD, and TPR measurements.

During the first year of investigation H₂ and CO adsorption uptakes and activity/selectivity data were obtained for Co supported on alumina, silica, magnesia, titania and carbon. The results provide evidence that supports and preparation methods can significantly influence adsorption and activity/selectivity properties. For example, Co/TiO₂ is significantly more active and more selective for C₈₊ hydrocarbons than Co/Al₂O₃ and Co/SiO₂; Co/carbon produces significantly higher fractions of CO₂ and C₂-C₃ hydrocarbons than cobalt on Al₂O₃, SiO₂ or TiO₂.

I. INTRODUCTION

Cobalt and iron catalysts find wide application in the oil, gas and chemical industries, particularly in catalytic hydrogenation and hydrotreating reactions. They are expected to find even broader application in future energy technologies such as production of synthetic fuels from coal and electric power from fuel cells.

Most commercial metal catalysts consist of a metal or metal oxide phase dispersed throughout a high surface area ceramic carrier or "support". The purpose of the support is basically two-fold: (i) to facilitate the preparation of a well-dispersed, high surface area catalytic phase and (ii) to stabilize the active phase against loss of surface area. Metal-support interactions are primarily responsible for this stabilization, the degree of which varies with the support metal system.

The effects of the support on activity and selectivity of the active catalytic phase have been assumed until recently to be of secondary importance. However, there is recent evidence that strong metal-support interactions can dramatically influence the activity/selectivity characteristics of noble and base metals in a number of reactions. They can likewise influence the manner in which reactant molecules adsorb on the metal. Particularly in base metal catalysts the metal-support interaction can determine the degree to which oxides can be reduced to the metallic state and the distribution of metal and metal oxide sites at the surface. Thus metal-support interactions can greatly influence the surface chemistry of a catalyst.

This report describes an investigation of the interaction of cobalt (and to lesser extent iron) metal(s) with a number of different supports, the strength of which is expected to vary over a wide range. The objectives are

to investigate the effects of metal-support interactions on adsorption and electronic properties, dispersion, oxidation state, and catalytic activity/selectivity behavior of cobalt for hydrogenation reactions.

II. OBJECTIVES AND APPROACH

A. Objectives

This work involves a comprehensive, quantitative investigation of the effects of metal-support interactions on the surface, electronic and catalytic properties of cobalt (and to a lesser extent iron), the objectives of which are:

1. Determine the effects of cobalt-support interactions on dispersion, oxidation state, and adsorption properties (i.e. adsorption stoichiometries and binding states for CO and H₂) of cobalt over a range of cobalt loading.
2. Correlate the activity/selectivity properties of hydrocarbon synthesis on cobalt with dispersion, oxidation state, behavior for adsorption of CO and H₂ and its strength of interaction with various supports.
3. Measure directly the extent of electronic interaction of iron, with various supports using Moessbauer Spectroscopy and correlate the degree of interaction with adsorption and activity/selectivity properties of the metal.

Cobalt has been chosen as the primary metal for study because of its importance in hydrotreating and coal-conversion reactions and because relatively little is known regarding its interaction with various supports. The materials to be used as supports include carbon, SiO₂, Al₂O₃, TiO₂, and MgO. These particular supports are emphasized because (i) their extent of interaction with metals is believed to span a wide range from weak to very strong and (ii) all have commercial significance.

B. Research Plan

In order to accomplish the above listed objectives the proposed work has been divided into four areas of study (four tasks) to be completed over a period of three years.

1. Determine the oxidation state and dispersion of cobalt as a function of support and metal loading.
2. Determine binding energies, binding states and adsorption stoichiometries for CO and H₂ on cobalt as a function of support and metal loading.
3. Measure specific activities and selectivities for hydrogenation of CO over cobalt on different supports.
4. Measure the effects of support on the electronic and chemical properties of iron (and cobalt to a limited extent) using Moessbauer Spectroscopy.

The experimental approach for each of these tasks is described below:

Task 1: Study of the Oxidation State and Dispersion of Supported Cobalt Catalysts. Catalysts containing 3 and 10 wt.% cobalt on high purity SiO₂, Al₂O₃, TiO₂, MgO, and carbon supports (and in addition 1 and 15% Co on Al₂O₃ and 10% Fe on TiO₂, MgO and carbon supports) will be prepared by simple impregnation of or pH-controlled deposition on the support with aqueous solutions of cobalt or iron nitrate, drying at 373 K and reduction in flowing hydrogen at 673 K.

For cobalt catalysts the extent of reduction of cobalt to the metal, the average oxidation state, and surface oxidation states will be determined by oxygen chemisorption of the reduced catalyst at 673 K, by temperature programmed reduction (or in selected cases by TGA), and by selected ESCA measurements of reduced catalysts.

Dispersion (fraction of metal exposed) of the cobalt and iron catalysts will be measured using hydrogen adsorption at 298 K and, in the case of 10% Co/SiO₂, Co/TiO₂, Co/MgO and Co/C, using X-ray line broadening and transmission electron microscopy.

Task 2: Study of Binding Energies and Stoichiometries for CO and H₂ on Supported Cobalt Catalysts. For the cobalt catalysts prepared in Task 1 above, CO adsorption uptakes will be measured at 298 K according to procedures previously developed in this laboratory. From comparison of the metal dispersions and hydrogen uptakes determined in Task 1 the H/Co_s stoichiometry (s denotes surface atom) will be determined. Comparison of CO and H uptakes will enable CO/Co_s stoichiometries to be determined as a function of support and of metal loading for each of the supports (especially Co/Al₂O₃) providing information on the distribution of different kinds of CO adsorption occurring (e.g. multiple, linear, and bridged).

Binding energies and binding states of CO and H₂ will be determined for each catalyst by means of temperature-programed-desorption (TPD). Attempts will be made to correlate the binding energies for the different catalysts with extents of reduction determined from Task 1 and with methanation activity and selectivity data from Task 3. An experimental apparatus for obtaining TPD data will be constructed as part of this task.

Task 3: Measurement of Specific Activities and Selectivities for CO Hydrogenation on Supported Cobalt Catalysts. Specific rates of CO hydrogenation for the 3% cobalt catalysts (and all of the Co/Al₂O₃ catalysts) described under Task 1 and the iron catalysts described under Task 4 will be determined using a single pass, differential reactor. Catalysts will be tested in powder form at 1 atm, H₂/CO = 2 and low conversions (3-5%) in the temperature range of 450-550 K in order to obtain intrinsic rates of reaction

and product selectivities in the absence of heat and mass transport influences. Gas samples will be analyzed chromatographically for CO, CH₄, CO₂ and hydrocarbons. Specific activities in the form of turnover numbers will be based upon hydrogen adsorption uptakes of the fresh catalyst.

The results in the form of turnover numbers, product distributions and activation energies for hydrocarbon synthesis will be correlated with binding energies of the reactants, metal dispersions, and metal-support interaction data from other tasks.

Task 4: Moessbauer Spectroscopy Study of Supported Cobalt and Iron Catalysts. Iron supported on SiO₂, Al₂O₃, TiO₂, MgO, and C as well as selected cobalt catalysts (Co/SiO₂, Co/TiO₂) will be examined by Moessbauer Spectroscopy. Samples of 10-15% Fe/Al₂O₃ and 1 Fe/SiO₂ have been prepared and characterized as part of a companion study sponsored by DOE Fossil Energy.

Since Moessbauer spectroscopy is most easily applied to the study of iron compounds we propose to investigate in situ reduced iron catalysts first to determine if changes in electronic structure of the metal crystallites due to metal-support interactions can be observed using the technique. If these experiments yield promising results we will prepare Co/SiO₂ and Co/TiO₂ catalysts using radioactive Co⁵⁷ for experimentation in source experiments

From the Moessbauer measurements in this study we expect to obtain electron densities at the nucleus, quadrupole splittings and magnetic fields of iron phases on various supports from which we will be able to determine effects of support on the reducibility of iron to the metal and on electronic and magnetic structures of metal clusters. We expect to obtain similar information for the cobalt catalysts, although the preparation of the radioactive catalysts and the Moessbauer experiments will be more difficult.

Mossbauer data in the proposed study will be obtained using a new Austin Science Associates spectrometer which was recently purchased through an NSF equipment grant.

III. ACCOMPLISHMENTS, DISCUSSION AND FUTURE WORK

A. Preparation and Measurement of Dispersion and Extent of Reduction of Supported Cobalt.

1. Catalyst preparation. It is well known that the method of catalyst preparation can affect dispersion, adsorption and activity/selectivity properties (1,2). The catalysts in this study were prepared by one of three methods i.e. impregnation, pH-controlled deposition, and evaporative deposition. Impregnation involved the addition of an aqueous metal salt to a dry powdered support to the point of incipient wetness. Each sample was dried in a force-circulating-air oven at 100°C and then the impregnation was repeated until the desired amount of metal was loaded on the support. In this study, cobalt nitrate was added to deionized-distilled water and impregnated on the supports three to four times.

A controlled pH deposition (1,2) was the second method employed to deposit cobalt on various supports. Urea was added to an aqueous suspension of support in cobalt nitrate at 95°C. The solution was well mixed while heating on a hot plate. The slow decomposition of urea in water deposits cobalt hydroxide on the support. The extent of reaction was determined by complexometric titrations using Murexide as an indicator. The deposition took about 20 hrs for the silica and alumina supports and 60 hrs for titania.

Evaporative deposition, the third method of catalyst preparation, was used for depositing cobalt on the carbon supports (3). A four to one mixture

of benzene and ethanol with support and cobalt nitrate was mixed continuously under a vacuum to dryness.

The following supports were used; silica (Cab-O-Sil Grade M-5 from Cabot Corp.), alumina (Dispal M Sample # 8032 H from Conoco Chemicals), titania (Oxide P25 from Degussa Inc.), Magnesia (Mg 700 from Dart Catalyst Division), and Carbon (Type UU from Barneby and Cheney).

Table 1 lists the catalyst codes, compositions, and preparation techniques. Three methods of controlled pH deposition were employed. Method 1 differed from Method 2 in that the initial pH of the second was adjusted to 2.5 and 60% more urea was added. Method 3 was not a urea deposition. In the case of magnesia, cobalt nitrate and water were mixed in a flask followed by the addition of MgO. Upon addition of magnesia support the pink cobalt solution immediately turned blue. Urea was not added and the solution was mixed for half an hour. An EDTA complexometric titration showed that 90% of the cobalt had deposited on the support. A titration the following morning indicated 100% deposition of cobalt onto the support.

Catalyst loadings of 3% and 10% were chosen because of their wide range of metal support interactions. The 3% cobalt was expected to show the stronger metal support effects.

Future plans include preparation of 3 and 10% cobalt catalysts supported on high purity Saran and Spheron carbons.

2. Catalyst reduction. From a previous study (4), it was shown that (i) carefully controlled decomposition of supported metal nitrates (at low heating rates) in pure hydrogen resulted in maximum metal dispersion, (ii) calcination in air at high temperature prior to reduction results in lower reducibility and metal surface area, and (iii) a slow heating rate during reduction of metal nitrates prevents exothermic temperature excursions which can sinter the

TABLE 1. Catalysts Prepared and Methods
of Catalyst Preparation

Code ^a	Cobalt Loading %	Preparation	Color of Reduced Catalyst
Co-S-104	3	impregnation	black
Co-S-105	10	impregnation	black
Co-S-106	3	pH controlled deposition ^b	violet
Co-S-107	3	pH controlled deposition ^c	violet-blue
Co-A-110	1	impregnation	violet-blue
Co-A-111	3	impregnation	violet-blue
Co-A-112	10	impregnation	black
Co-A-113	15	impregnation	black
Co-A-114	3	pH controlled deposition ^b	grey
Co-A-115	3	pH controlled deposition ^c	violet-blue
Co-T-100	3	impregnation	black
Co-T-101	10	impregnation	black
Co-T-102	3	pH controlled deposition ^c	dark grey
Co-M-100	3	impregnation	violet-pink
Co-M-101	10	impregnation	black
Co-M-102	3	pH controlled deposition ^d	black
Co-C-100	3	evaporative deposition	black
Co-C-101	10	evaporative deposition	black

^a A refers to alumina, S silica, T titania, M magnesia, and C carbon.

^b Method 1

^c Method 2

^d Method 3

metal. In view of these previous results, the prepared catalysts were not calcined before reduction and a slow heating ramp (less than 5°C/min) was maintained (see Fig. 1). The heating schedule also included holding the temperature constant for 15-20 min. at 100 and 200°C, the temperatures at which water is evaporated and the nitrates decompose slowly. All catalysts except cobalt on alumina were reduced at 400°C for 16 hours. The alumina supported catalysts were reduced at 375°C for 20 hours to avoid cobalt aluminate formation.

The catalysts were placed in a flow-through reactor cell (see Fig. 2) and reduced in flowing hydrogen gas (99.99%, Whitmore) at a GHSV of 2,000 h⁻¹. The hydrogen was purified by passing through an Engelhard palladium Deoxo catalytic purifier and a molecular sieve trap in a dry ice-acetone bath. Reduction temperatures were maintained using a tube furnace coupled to a temperature controller/programmer.

Following reduction in the Pyrex cell, it was possible to observe the color of each catalyst. The catalysts with lower weight percentages of cobalt were more difficult to reduce as evidenced by their lighter colors after reduction (see Table 1). The more reduced catalysts were black, as in the case of all 10% cobalt supported catalysts. Results for Co/Titania and Co/silica supports show that an impregnated catalyst is easier to reduce than a precipitated one. These preliminary results suggest that precipitated catalysts or those with lower metal loadings involve strong metal support interactions which prevent complete reduction of cobalt to the metallic state.

Future plans for catalyst reduction include reduction of 3% cobalt on Al₂O₃, MgO, TiO₂ at 600°C in flowing H₂ for 8-12 hours. These catalyst were difficult to reduce at 400°C and elevated temperatures should enhance their reduction to the metallic state.

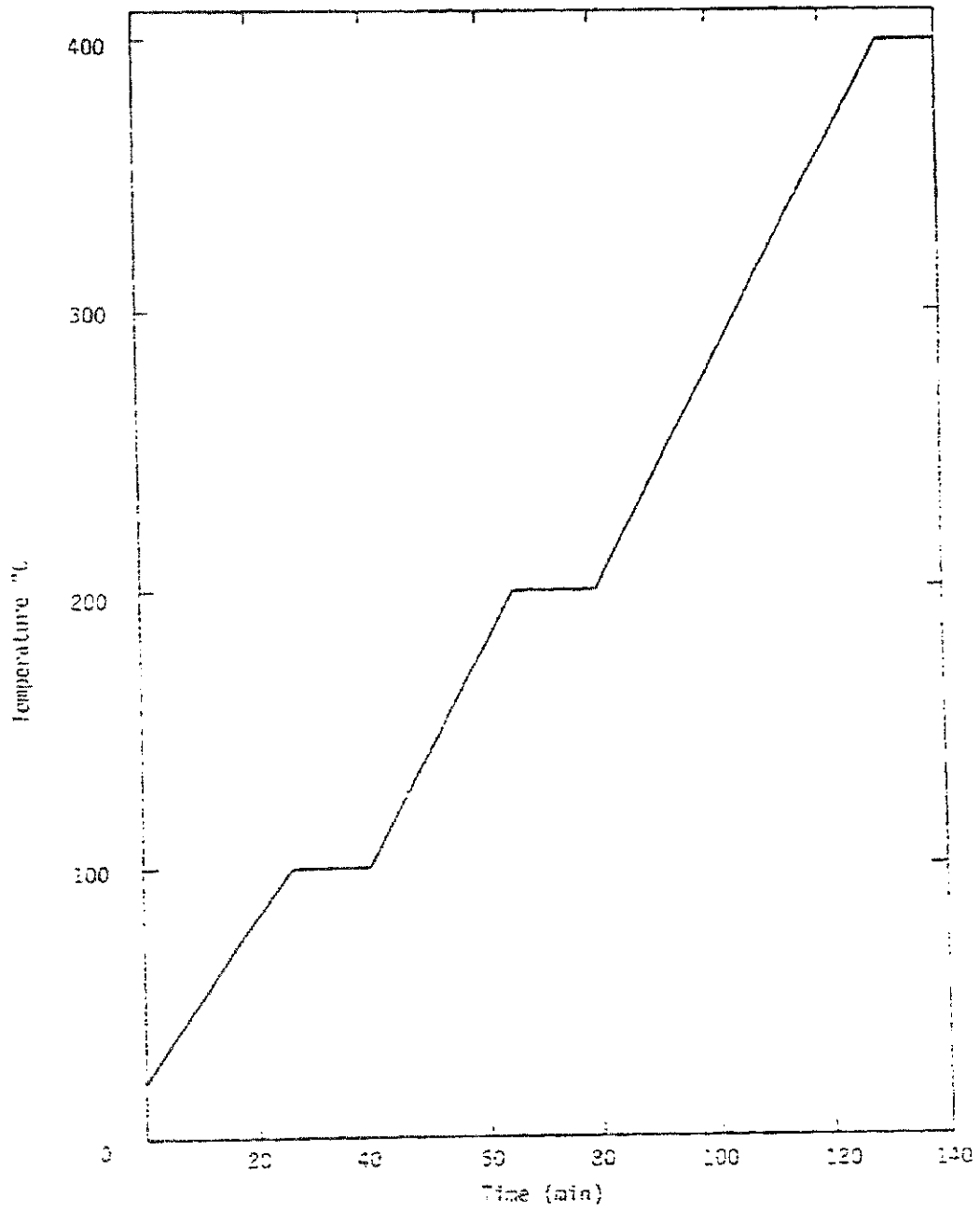


Figure 1. Temperature schedule for reduction

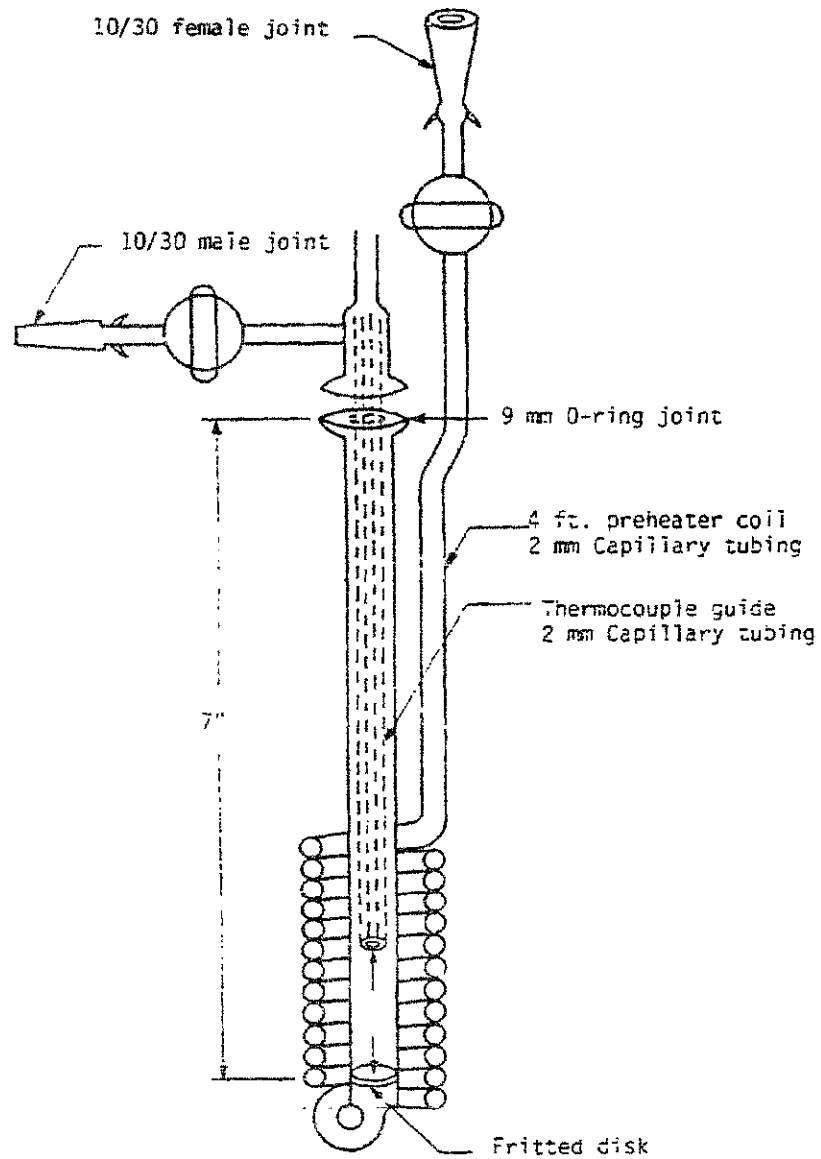


Figure 2. Laboratory Pyrex Reactor.

3. Chemisorption measurements. CO and H₂ adsorption uptakes provide a means of measuring metal surface areas and observing effects of metal-support interactions on reactant adsorption properties. Titration with O₂ at 400°C is a means of determining the extent of reduction of cobalt to the metal. The chemisorptive uptakes of hydrogen, carbon monoxide, and oxygen were measured using a volumetric glass system evacuated by mechanical and oil diffusion pumps, isolated by a liquid nitrogen trap. The reactor cell containing a reduced catalyst sample was evacuated to 5×10^{-5} Torr at the desired temperature and a measured volume of gas was allowed to adsorb on the catalyst surface. The amount of adsorbed gas was measured after 45 min by means of a calibrated gas buret connected to a manometer backed with a metrically calibrated mirror.

Following evacuation at 400°C the cobalt surface areas were measured using hydrogen chemisorption at room temperature. Typical room temperature isotherms for H₂ (see Fig. 3) were determined by plotting micromoles of H₂ adsorbed vs. pressure. The uptake due to chemisorption was then determined by extrapolating the straight-line portion of the isotherm to zero pressure. Carbon monoxide chemisorption measurements were performed in a similar manner. The total gas uptake was measured at room temperature following evacuation to 5×10^{-5} Torr at 400°C. The physically adsorbed carbon monoxide was measured after evacuation at room temperature to 5×10^{-5} Torr. The difference between the total uptake and the physical uptake was the chemisorbed CO (see Fig. 4). The extent of reduction was measured by oxygen titration at 400°C following evacuation to 5×10^{-5} Torr at 400°C. A typical oxygen titration isotherm is shown in Figure 5.

All the prepared catalysts, except the 1 and 15% cobalt on alumina were characterized by hydrogen and carbon monoxide chemisorptions (see Table 2).

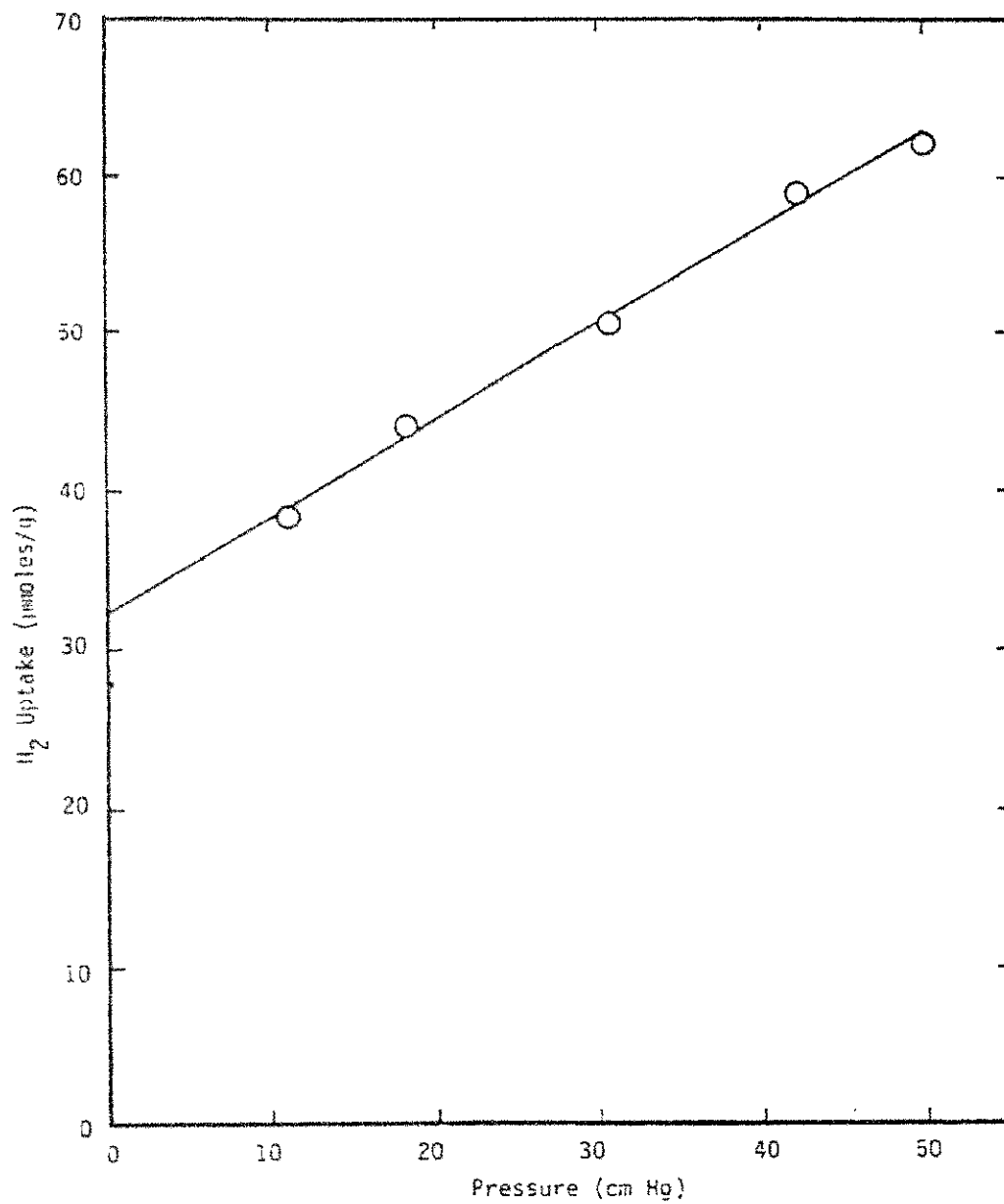


Figure 3. Total H₂ adsorption on Co-S-105 at 25°C

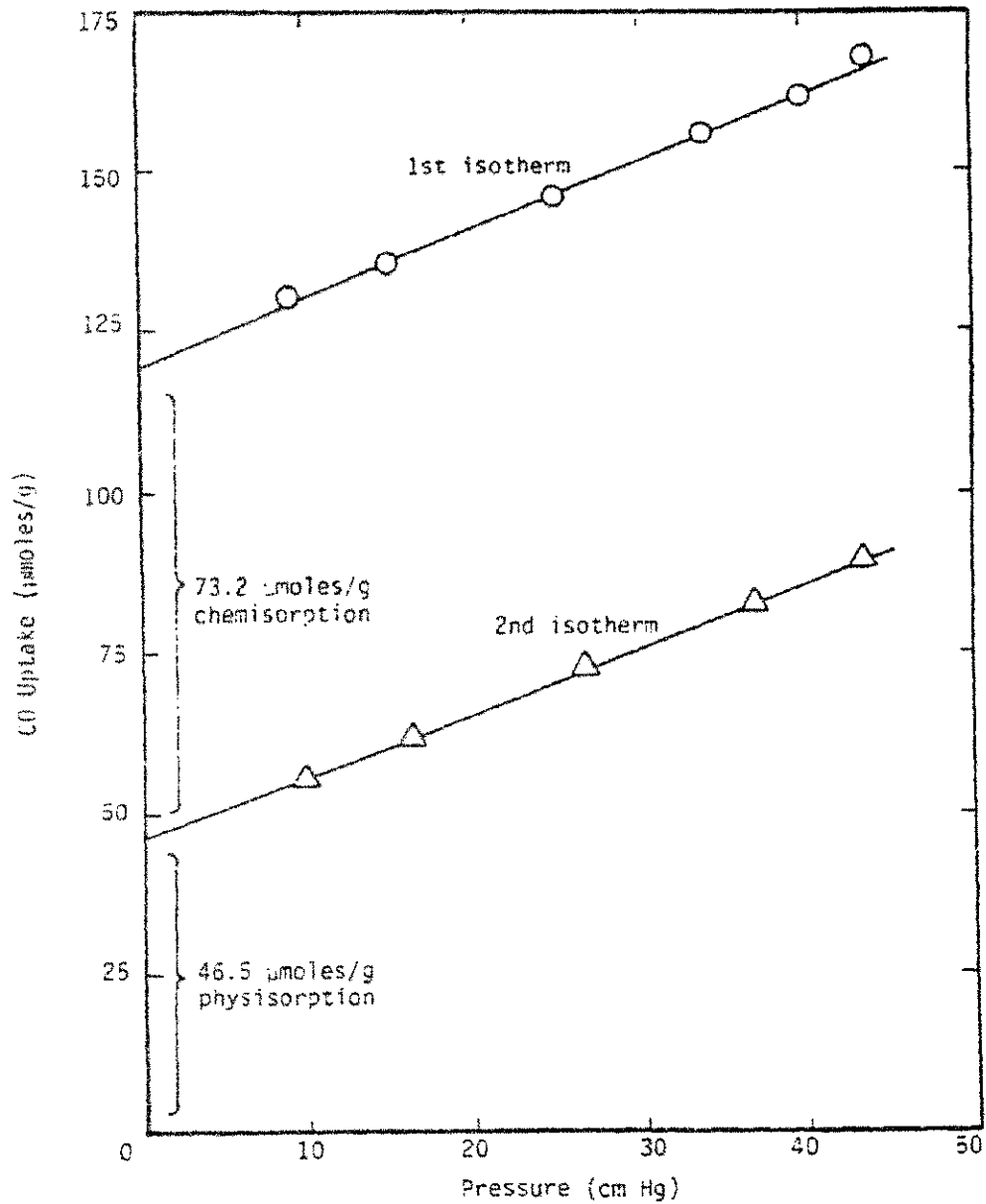


Figure 4. CO Physisorption and Chemisorption on Co-S-105 at 25°C.

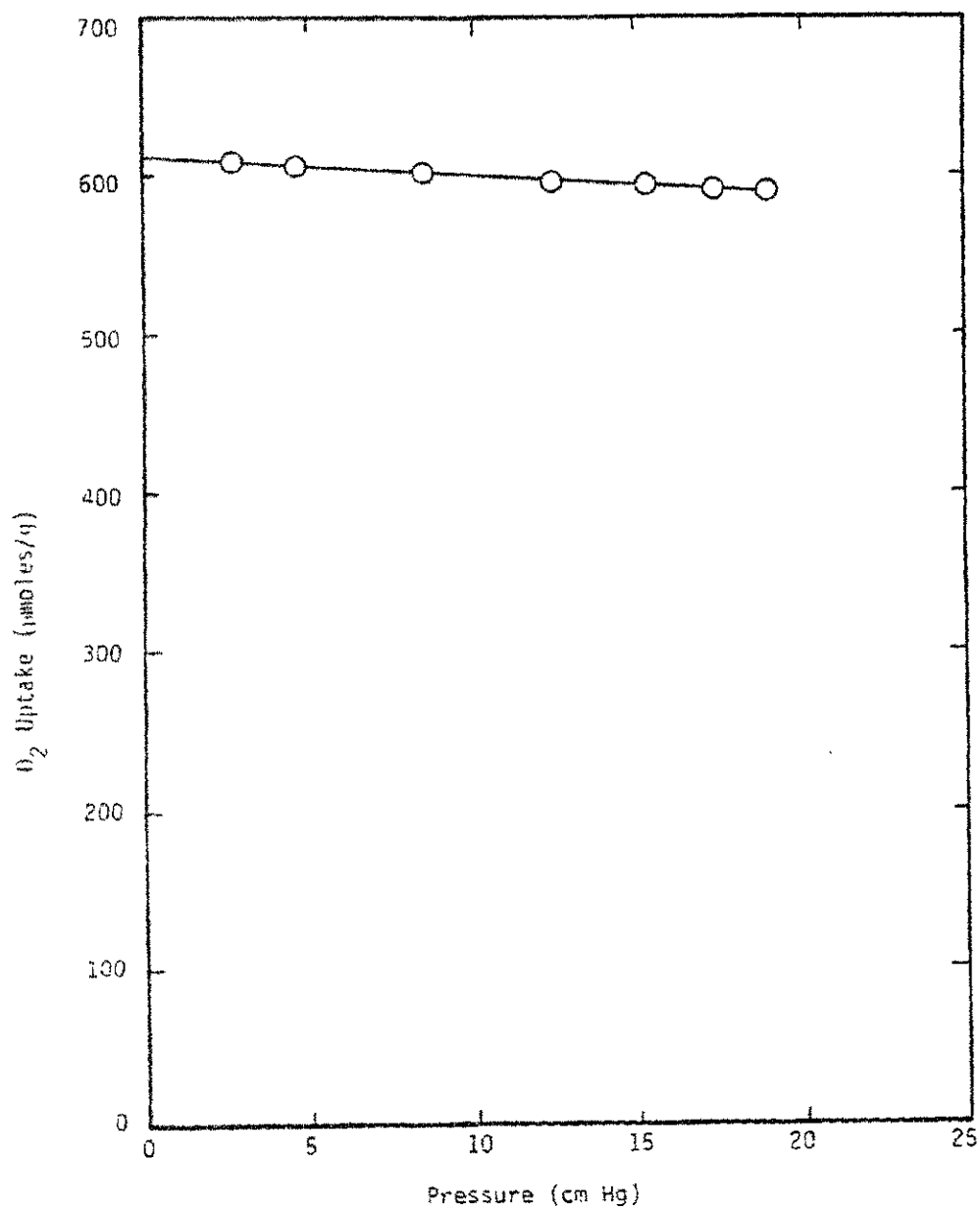


Figure 5. O₂ Titration on Co-S-105 at 400°C

TABLE 2. Adsorption Data

Catalyst	wt% Co	H ₂		CO		O ₂	
		Total Uptake	Chemisorption	Total Uptake	Chemisorption	Total Uptake	Chemisorption
Co-S-104	3	*11.2		*57.7	*17.1	40.6	193.9
Co-S-105	10	*37.6		119.7	46.5	73.2	*620.1
Co-S-106	3	10.8		80.0	45.7	34.3	
Co-S-107	3	8.5		26.1	21.0	5.1	
Co-A-110	1						
Co-A-111	3	4.3		*34.8	*23.6	11.2	
Co-A-112	10	*15.2		82.5	51.3	31.2	267.3
Co-A-113	15						
Co-A-114	3	5.8		14.8	11.3	3.5	
Co-A-115	3	9.1		94.0	54.3	39.7	134.4
Co-T-100	3	6.1		*65.7	*55.5	10.2	
Co-T-101	10	11.9		*61.2	37.7	23.5	
Co-T-102	3	*6.2		*73.2	*53.1	20.1	
Co-M-100	3	0.2		5.3	1.5	3.8	
Co-M-101	10	1.2		3.1	1.9	1.2	
Co-M-102	3	2.5		35.8	14.7	21.1	
Co-C-100	3	*14.5		*51.5	22.5	29.0	
Co-C-101	10	93.4	6.7	218.5	67.7	150.8	
			44.8				
			7.8				
			48.6				

Repeated with error > 10%
 * Repeated with error < 10%

O₂ titration uptakes were measured for 4 catalysts samples. The reproducibility of CO adsorptions was generally satisfactory ($\pm 10\%$) but a few of the H₂ adsorptions were repeated with an error greater than 10%. Reversible adsorption of H₂ on carbon, SiO₂ and Al₂O₃ supported cobalt was significant (see Table 2). The reversible adsorption of hydrogen on Co-C-101 was the largest (up to 48% of total H₂ uptake), while that for Co-A-114 (29%) and Co-S-105 (19%, see Fig. 6) was considerable.

In order to determine accurately the amount of carbon monoxide chemisorbed on the metal it is necessary to correct for the carbon monoxide chemisorbed on each support (5). The chemisorptions in Table 2 are a combination of chemisorption on the metal and support. The amount of chemisorption on the support should be determined by repeating the same procedure used for the catalysts. Blank supports were prepared by impregnation or evaporative deposition without any cobalt in solution. The same drying and reduction procedure was followed. Table 3 lists the chemisorption uptakes of hydrogen and carbon monoxide on each support. The hydrogen uptakes are small (less than 3 $\mu\text{moles/g}$) for all supports. The carbon monoxide uptakes on titania and carbon are large, but mostly due to large physical adsorption. Titania had the largest chemisorption of 4.4 $\mu\text{moles/g}$, while the others were less than 2 $\mu\text{moles/g}$.

The metal uptakes, calculated by subtracting out the support adsorptions from the adsorption data of Table 2, are presented in Table 4 along with some literature values (6-8) for comparison. The H₂ uptake of 11.2 $\mu\text{moles/g}$ for 3% Co/SiO₂ (Co-S-104) compared quite favorably with the value of 13.2 $\mu\text{moles/g}$ reported by Bartholomew (8) for 3% Co/SiO₂. The CO uptake for 3% Co/SiO₂ (Co-S-104) of 40.6 $\mu\text{moles/g}$ was closer to the value of 24.8 reported by Bartholomew (8) than the value of 12 $\mu\text{moles/g}$ reported by Vannice (5).

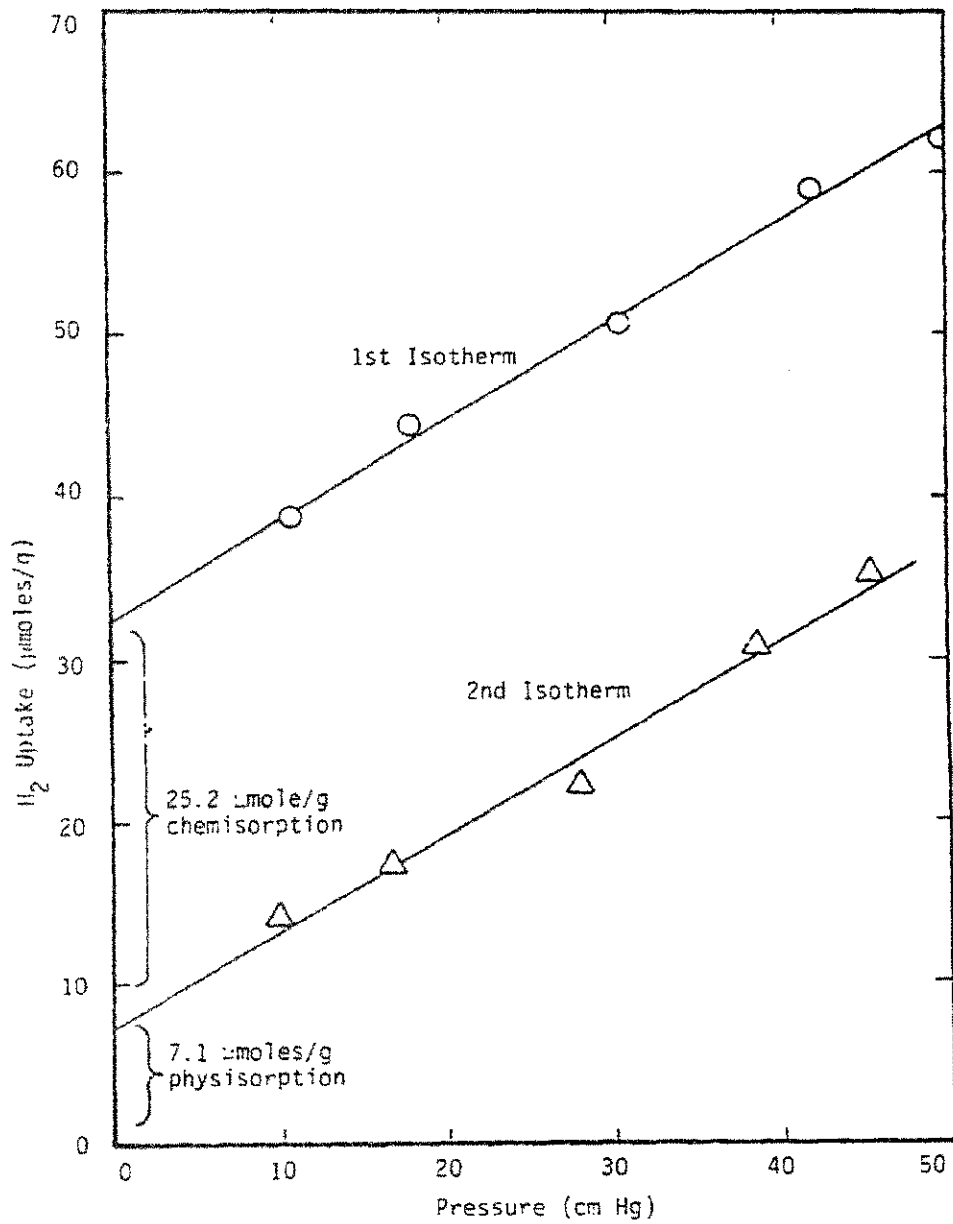


Figure 6. H₂ Physisorption (or reversible chemisorption) and chemisorption (irreversible) on Co-S-105 at 25°C.

TABLE 3. Support Chemisorption Micromoles/gram

support	H ₂ uptake	H ₂ physisorbed	H ₂ chemisorbed	CO uptake	CO physisorbed	CO chemisorbed
SiO ₂						
Al ₂ O ₃	1.2	-1.2	2.4	5.3	4.0	1.3
TiO ₂	2.7	0.9	1.8	34.0	29.6	4.4
MgO	0.8			5.5	4.6	0.9
Carbon	1.2	4.3	-3.1	33.8	32.0	1.8

TABLE 4. Corrected Chemisorption Uptakes on
Metallic Cobalt (Micromoles)

Catalyst	wt% Co	H ₂	CO	CO/H ₂ ^{a,b} (ref)
Co-S-104	3	11.2	40.5	1.81
Co-S-105	10	37.6	73.2	0.97
Co-S-106	3	10.8	34.3	1.59
Co-S-107	3	8.5	5.1	0.30
Co-A-111	3	3.1	9.9	1.60
Co-A-112	10	14.0	29.9	1.07
Co-A-114	3	4.6	2.2	0.24
Co-A-115	3	7.9	38.4	2.43
Co-T-100	3	3.4	5.8	0.85
Co-T-101	10	9.2	19.1	1.04
Co-T-102	3	3.5	15.7	2.24
Co-M-100	3	0	2.9	
Co-M-101	10	0.4	0.3	0.38
Co-M-102	3	1.7	20.2	5.94
Co-C-100	3	13.3	27.2	1.02
Co-C-101	10	92.2	149	0.81
Co/SiO ₂	4	26	12 ^c	0.231 (6)
Co/Al ₂ O ₃	2	1	16	8.00 (7)
Co-S-101	3	13.2	24.8	5.94 (9)
Co-S-102	15	40.0	31.9	0.40 (8)
Co/ThO ₂ /Al ₂ O ₃	23			(15)

a) ratio of chemisorbed CO to hydrogen atoms adsorbed

b) based on total H₂ uptakes

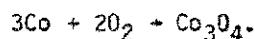
c) used catalyst

From the data in Table 4 it is clear that the method of preparation significantly influenced adsorption of CO on alumina-, titania-, and magnesia-supported cobalt, whereas hydrogen uptakes on the 3% cobalt catalysts were nearly the same for different preparations involving the same support. The differences in CO adsorption due to preparation are evidently complex and thus far no trends are evident.

Table 4 shows that the type of support also affected the H₂ and CO adsorption properties of cobalt. Indeed the H₂ chemisorption of cobalt on various supports increased in the following order: Co/MgO < Co/TiO₂ < Co/Al₂O₃ < Co/SiO₂ < Co/C. The hydrogen uptake of magnesia supported cobalt was nearly zero for both 3 and 10% loadings. This is consistent with Boudart's (9) observation that iron supported on magnesia does not adsorb H₂. At the other extreme 10% cobalt supported on carbon adsorbed 92.2 μ moles of H₂ per gram of catalyst. The chemisorption of CO on different supported cobalted catalysts followed the same order as H₂. The values range from 0.3 μ moles/g for Co/MgO to 149 μ moles/g for Co/C (10% Co loadings).

Chemisorption measurements in the near future will include the redetermination of some apparently spurious data, the analysis of the 1 and 15% cobalt on alumina catalysts, and the analysis of cobalt on Saran and Spheron carbons (yet to be prepared). For some of the cobalt catalysts the adsorptions were small (less than 10 μ moles). Since the chemisorption apparatus has an inherent error of ± 1 μ mole, more accurate data will be obtained using larger samples.

4. Extent of reduction. The extent of reduction was determined from the oxygen titrations at 400°C according to the method of Bartholomew and Farrauto (4). It was assumed that the reaction of cobalt with oxygen is as follows:



and that the supports do not adsorb oxygen. The extent of reduction to metallic cobalt was 55% for both 3 & 10% Co/SiO₂, 24% for the impregnated 10% Co/Al₂O₃, and 39.5% for the 3% pH-deposited Co/Al₂O₃. The values found in literature (15-17) range from 24.4 to 100% reduction for alumina supported cobalt catalysts, although the catalyst with 100% reduction was reduced at 600°C, while the catalysts in this study were reduced at 350-400°C.

During the next few weeks we plan to obtain oxygen titration data for the remaining catalysts to determine the extent of reduction to cobalt metal as a function of support and metal loading and for the supports to determine if any support corrections are necessary.

5. Dispersion. The calculations for dispersion were based on the assumptions that (i) cobalt metal is present as spherical particles and (ii) the unreduced cobalt is present in a separate dispersed layer in intimate contact with the support (5). Thus, in calculating metal dispersion (or the fraction of metal atoms exposed), the metal loading was multiplied by the fraction of cobalt reduced to the metallic state. The site density of 7.05×10^{-2} nm²/atom used in these calculations was based on the arithmetic average of the three lowest index planes of cobalt (hcp). Accordingly the percentage dispersion was calculated from total H₂ adsorption uptakes according to the equation

$$\% D = 1.179 \frac{X}{Wf}$$

where X = total H₂ uptake in micromoles per gram of catalyst, W = weight percentage of cobalt, and f = fraction of cobalt reduced to the metal determined from O₂ titration. Average crystallite diameters (in nm) were calculated from %D assuming spherical metal crystallites of uniform diameter d. Thus

$$d = 93.5/(\%C).$$

Dispersions and average crystallite diameters are listed in Table 5. The dispersions are disappointingly low but nevertheless comparable with cobalt dispersions reported by other workers (7, 8, 15-17). The dispersion of 8% for Co-S-105 is the same that Hossain found by x-ray diffraction. The dispersion of 5% for Co-A-114 is a little lower than the literature values of 7% (Hossain by XRD) or 8% (Vannice by CO chemisorption). The crystallite diameter for Co-S-105 (11.6 nm) is in good comparison with Bartholomews data (11.5 nm) and Hossain's data (11.2 nm) determined by magnetic studies. However the average crystallite diameter for Co-A-114 (20.4 nm) is larger than the literature values (11.4 to 16.2 nm).

Since we are desirous of obtaining higher cobalt dispersions, our preparation work during the coming year will focus on 3 areas with significant potential for obtaining improvements: (i) reduction of the catalysts prepared by the conventional techniques over a range of temperatures, with and without calcination, to determine the optimum condition for maximum dispersion, (ii) preparation of catalysts on dehydroxylated alumina supports, since Brenner (10) has shown that a greater extent of reduction to the metal and higher dispersions are possible by this technique and (iii) preparation of catalysts on dehydroxylated supports using cobalt carbonyls, since this has been demonstrated as a route to highly dispersed metals (10). Future work will also include preparing samples for transmission electron microscopy. The TEM values of crystallite diameter will be used to determine the H/Co (surface) stoichiometry. From previous experience (11) we expect that only the catalyst with higher metal loadings (e.g. 10% Co) are suitable for TEM.

TABLE 5. Dispersion and Crystallite Size

Catalyst	wt% Co	% reduction	H ₂ uptake	% Dispersion	Crystallite diameter (nm)
Co-S-104	3	54.2	11.2	8.12	11.5
Co-S-105	10	54.8	31.6	8.09	11.6
Co-A-112	10	24.4	15.2	7.3	12.8
Co-A-114	3	39.5	4.6	4.58	20.4
Co/SiO ₂	8	100		7.8 (XRD)	13.3 (XRD) ^a
Co/Al ₂ O ₃	8	100		9.2 (magnetic)	11.2 (magnetic)
Co/Al ₂ O ₃	2			6.7 (XRD)	15.5 (XRD)
Co/Al ₂ O ₃	8	33		8	11.4 (magnetic)
Co/Al ₂ O ₃ /ThO ₂	24	24.4			16.2 (XRD)
Co-S-101	3	71.2	13.2	7.2	13.0
Co-S-102	15	30.6	35.0	7.1	12.8

a) No correction for instrument broadening

B. Study of Binding Energies and Stoichiometries for CO and H₂ on Supported Cobalt Catalysts.

1. Stoichiometries of CO and H₂ Adsorption on Supported Cobalt Catalysts

The chemisorptions were performed as described in Task 1 and the data are presented in Table 4. Hydrogen adsorbs dissociatively (18) on cobalt and presumably with a stoichiometry of one hydrogen atom to one cobalt atom (19) while the adsorption of carbon monoxide is more complex. The latter can adsorb linearly (one molecule per metal site), form a bridged complex (one molecule bonded to two sites), or form a subcarbonyl (two or three molecules per site) (20). Assuming that hydrogen adsorbs with a 1:1 (CO/H) stoichiometry, the CO/H ratios in Table 4 should correspond to the number of CO molecules adsorbed per cobalt surface atom. This number apparently varies from 0.24 to 5.95 (see Table 4) for cobalt on different supports.

The CO/H ratios for the 10% Co/SiO₂, Co/Al₂O₃, Co/TiO₂ and 3% Co/C were very close to one indicating a linear carbon monoxide adsorption. The lower CO/H ratios of 0.81 and 0.85 for 10% Co/carbon and 3% Co/TiO₂ (impregnation) suggests that a combination of linear and bridged species was adsorbed. CO/H ratios of greater than 1 were obtained for 3% impregnated cobalt on silica and alumina suggesting a combination of linear and subcarbonyl CO species. CO and H₂ uptakes for 3 and 10% Co/MgO prepared by impregnation were unexpectedly low possibly as a result of suppression of the CO and H₂ adsorptions on cobalt due to a strong cobalt-magnesia interaction or due to low extents of reduction to cobalt metal. The pH deposited cobalt on magnesia showed a very large CO/H ratio possibly due to suppression of hydrogen adsorption as a result of a strong metal support interaction.

The pH deposited catalysts showed generally a wider variation in CO/H ratios than those prepared by other techniques. For example the pH deposited

catalysts prepared by method 1 has a CO/H ratio greater than one for cobalt on silica and less than one for cobalt on alumina while catalysts prepared by pH deposition method 2 showed the opposite trend.

2. Studies of Binding Energies: A System for Thermal Desorption Mass Spectroscopy

As outlined in Task 2 of the work statement for this contract, a Mass Spectrometer Temperature-Programmed-Desorption (TPD) System was designed and installed to facilitate the determination of binding energies, binding states, and orders of desorption. An equipment schematic of the overall system, which was assembled in the last six months, is shown in Figure 7. Because of the complexity of the overall system its description will be divided into three component systems: (i) The Flow System, (ii) The Sampling and Detection System, and (iii) The Data Gathering and Processing System.

Flow System. The flow system (see Figure 8) was designed to purify, regulate, and monitor all of the gases handled in the TPD studies. Hydrogen gas is provided to allow all catalyst samples to be reduced in situ. Provision is presently made for one adsorbate (H_2 in N_2); a CO adsorbate line will also be added in the next few months.

Recent experience with a thermal conductivity cell TPD system in this laboratory (21) indicates that the small catalyst samples (typically on the order of tens of milligrams) used in TPD studies are very susceptible to contamination by impurities in the gases. Due to the elevated temperatures used in TPD runs, catalysts samples are especially vulnerable to surface oxidation and for this reason each gas is cleaned in a two stage process comprised of a deoxygenation trap (specific for each gas) and a molecular sieve trap.

For the carrier and reduction gases flow is monitored by means of

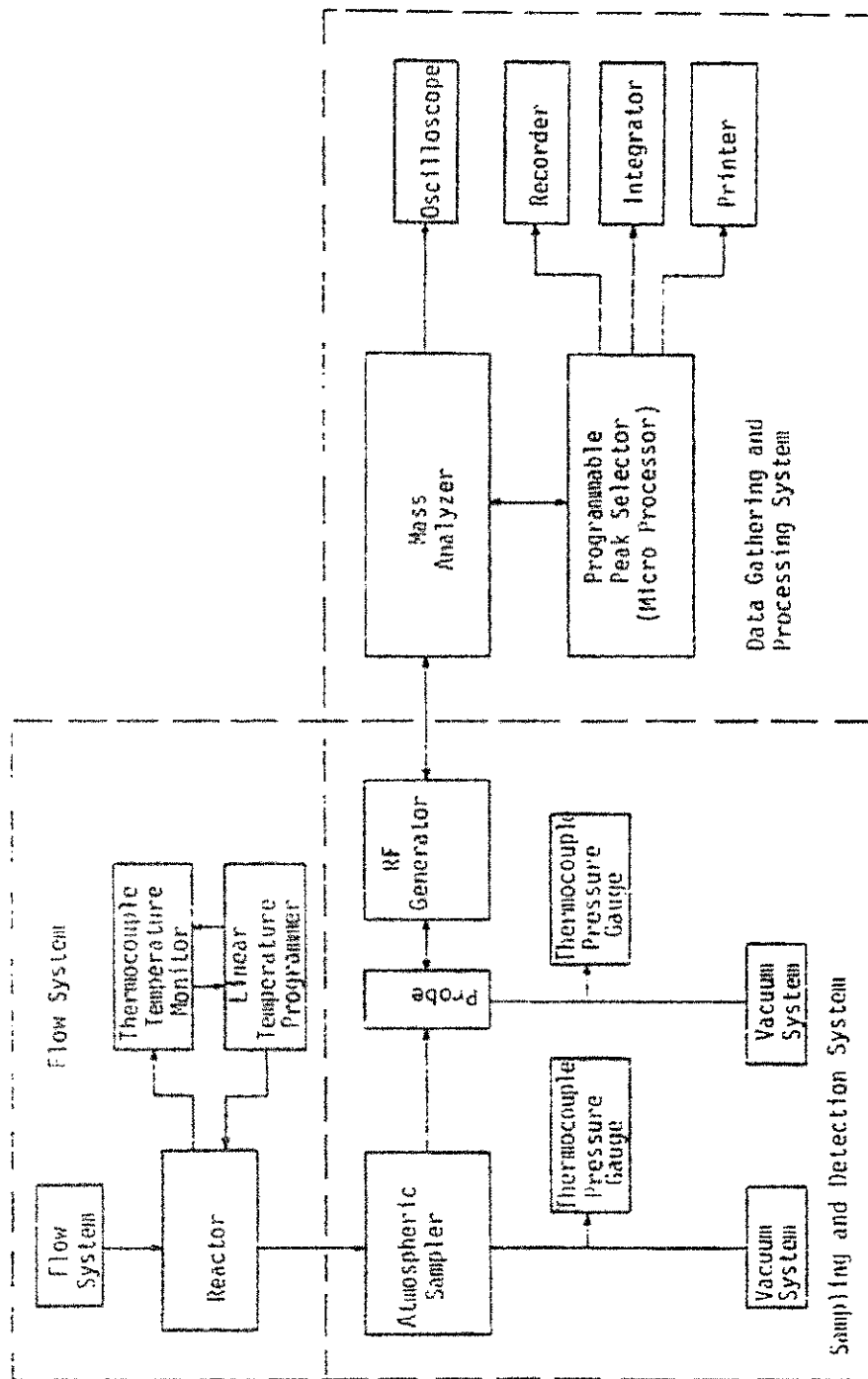


Figure 7. Mass Spectrometer - Temperature Programmed Desorption System

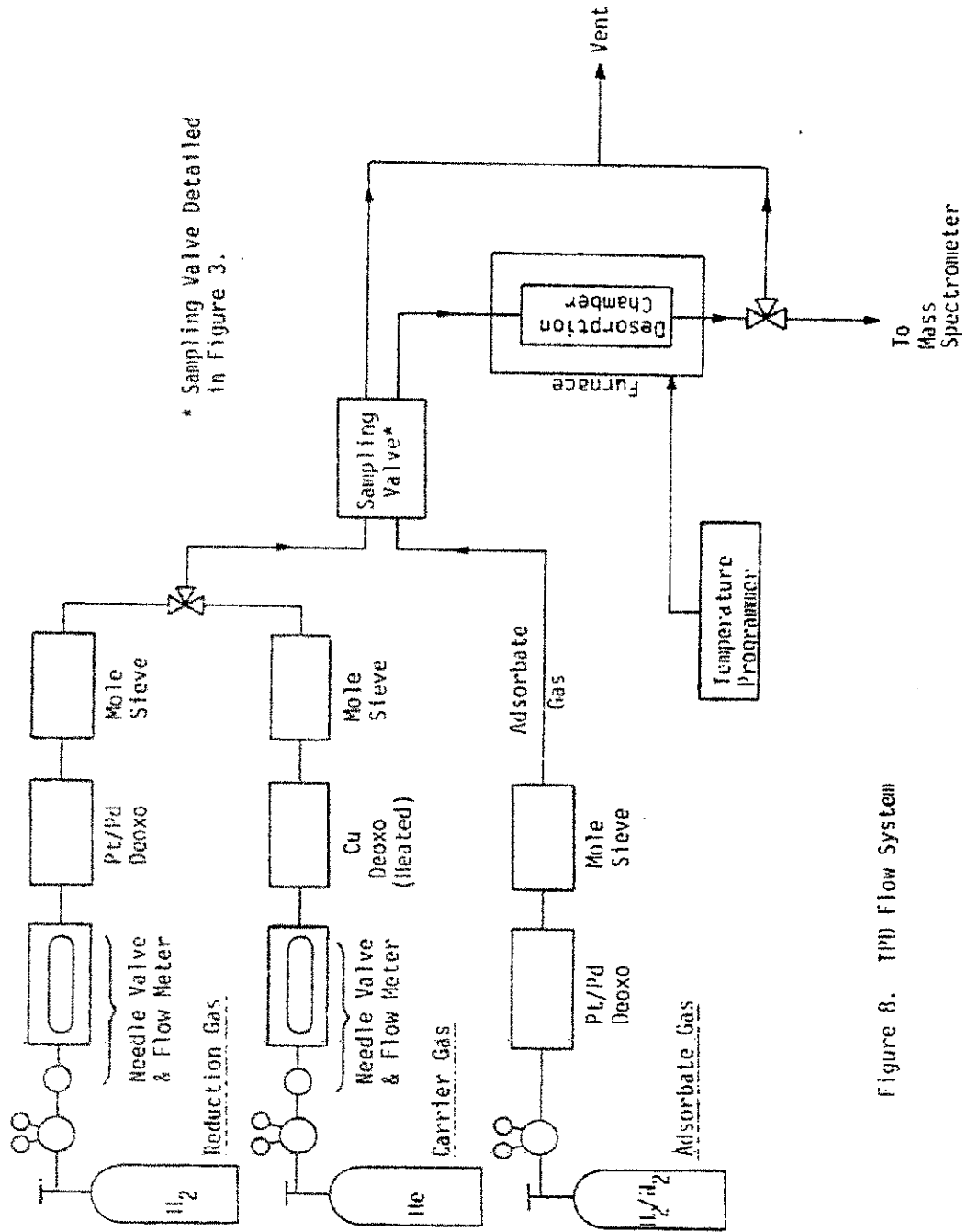


Figure 8. TPD Flow System

calibrated rotameters and regulated through needle valves. Monitoring of the adsorbate gas is accomplished with a bubble flow meter as the adsorbate gas is introduced into the carrier stream via a sampling valve (see Figure 9), and only small flows (10-50 cm³/min) are maintained. The actual amount of adsorbate introduced is determined through PVT relationships given the volume of the sample loop and the number of such volumes introduced during an experiment.

The adsorption/desorption chamber for the system is a quartz reactor tube fitted with a sintered quartz frit to support the catalyst. Since catalyst bed temperatures must be carefully monitored during desorption runs, the flow system in the vicinity of the desorption chamber has been designed to allow a chromel-alumel thermocouple to be inserted directly into the catalyst sample. The quartz desorption chamber is surrounded by a concentric quartz tube which has been wound with nichrome wire, and, as such, serves as a high temperature, fast response furnace providing the energy for desorption. The temperature attained by the furnace is controlled by a linear temperature programmer (designed and constructed at BYU) capable of delivering temperature ramps in the range from 1°K/minute to 100°K/minute.

Sampling and Detection system. Detection of the desorbed species is accomplished with a UTI 100 C Mass Spectrometer equipped with a quadrupole mass filter (range capability from 1 to 300 AMU) and a Faraday cup backed by a sixteen stage electron multiplier. Gases from the flow system, at a pressure slightly above atmospheric, are passed through a two-stage sampling system to reduce the pressure to about 10⁻⁵ to 10⁻⁶ Torr before introduction to the mass filter (see Figure 10). Reactant gases pass by an orifice and are vented; simultaneously a small portion of gas is drawn by vacuum through the orifice into the first stage of the atmospheric sampler. The vacuum (0.35 Torr) in

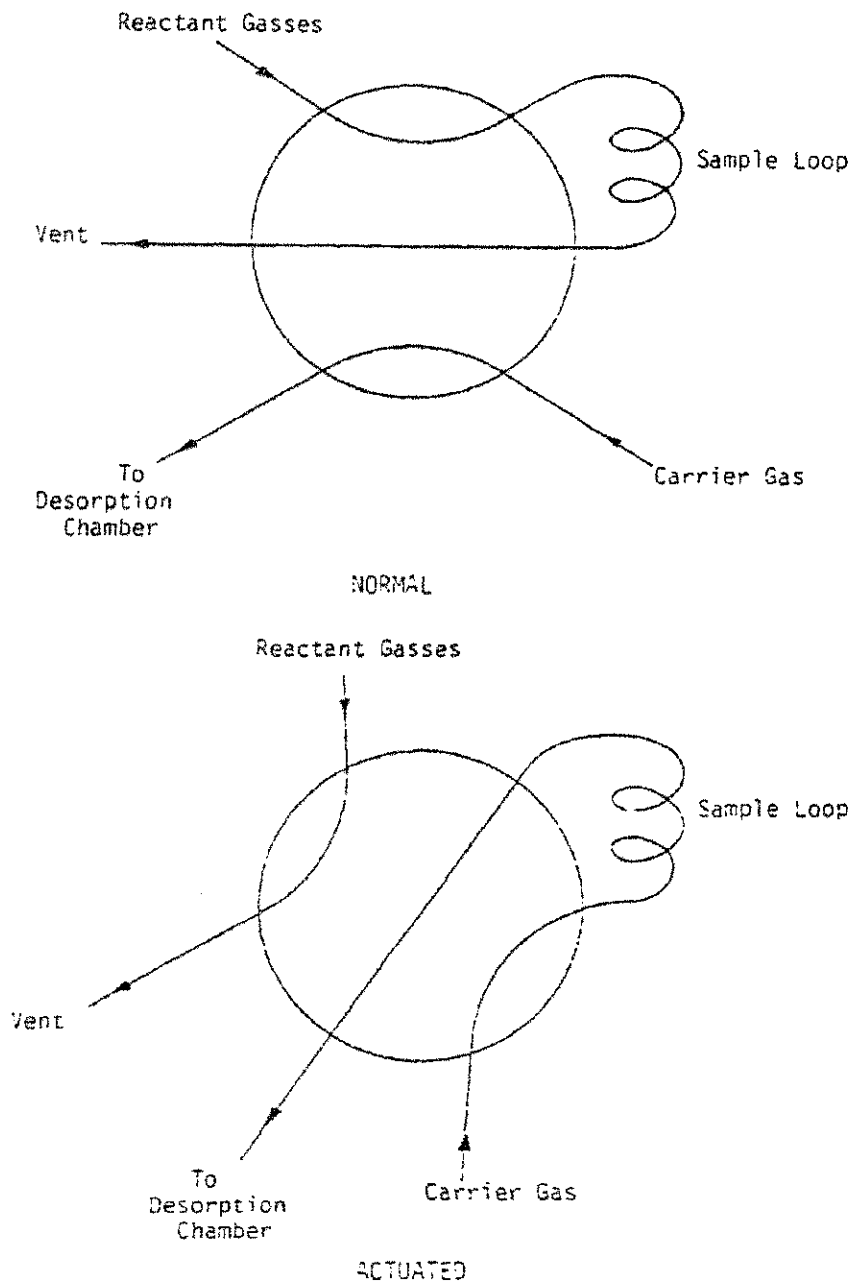


Figure 9. Sampling Valve Detail

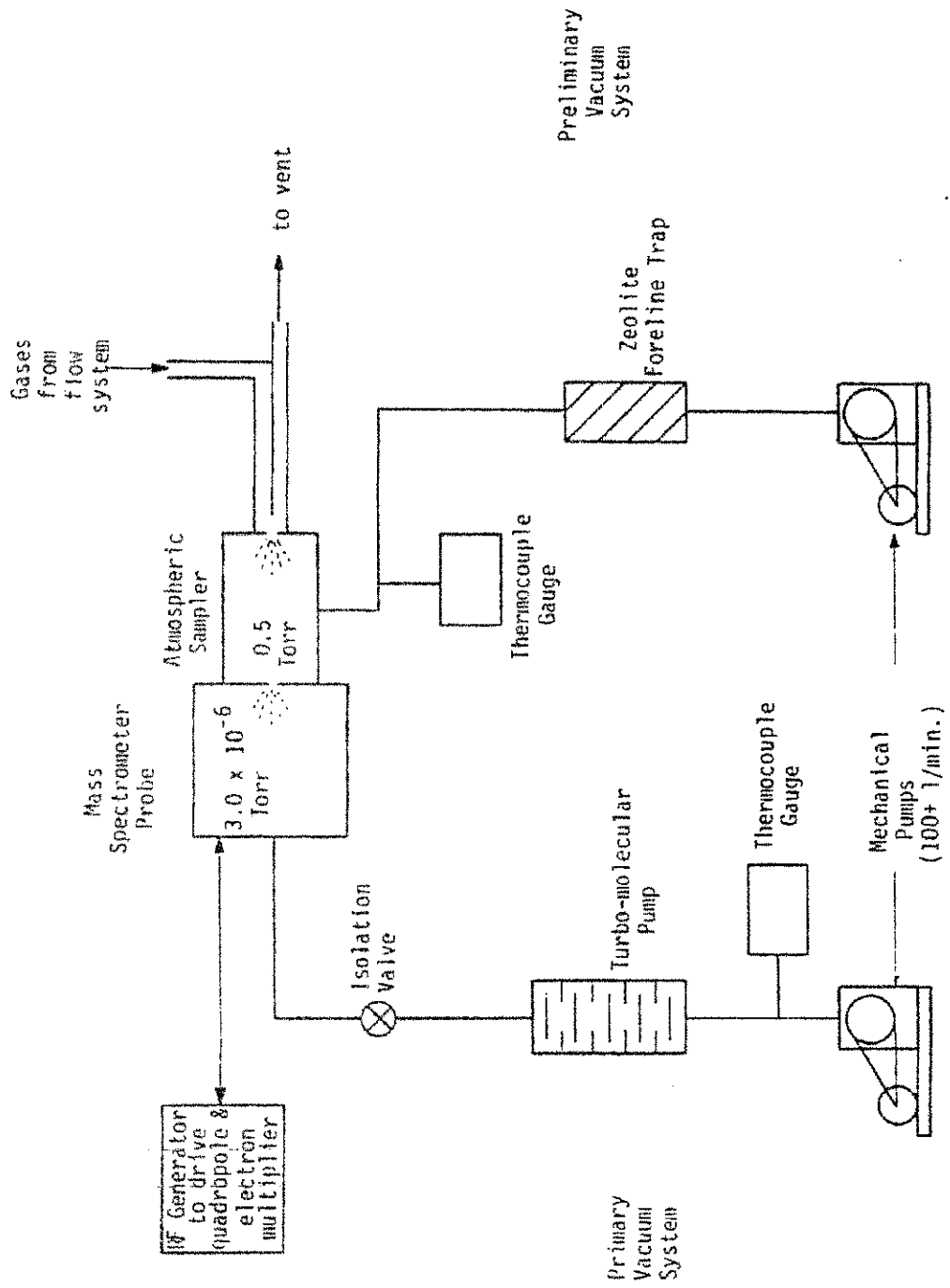


Figure 10. Mass Spectrometer Sampling and Detection System.

the first stage sampling chamber is obtained with a two-stage, direct-drive, 90 liter/minute Directorr mechanical pump, pressure is monitored with a Hastings DV-6 thermocouple vacuum guage and controller, and the pump oil vapors are prevented from contaminating the sampling chamber by a Varian Zeolite foreline (bakeable) trap. Only a small portion of gas from the first stage of the sampler is admitted into the high vacuum chamber (second stage) which houses the mass filter and electron multiplier. The high vacuum system for the mass spectrometer probe was originally designed and installed with a CVC Diffusion pump and liquid nitrogen trap combination which turned out to be unsatisfactory for two reasons:

1. The diffusion pump, while capable of pulling a good vacuum, was simply unable to maintain a sufficient vacuum under flow conditions to allow experimentation to occur in the pressure range ($2-6 \times 10^{-6}$ Torr) recommended by other investigators and factory specifications.
2. Operating costs, in terms of liquid nitrogen requirements, were unreasonably high.

Because of the relatively large volume requirements on the vacuum system which result from the dynamic sampling characteristics, sorption, ion, and sublimation pumps were also unsatisfactory for the application presented here. For these reasons the primary high vacuum pump selected was a Balzers O40 turbo-molecular pump. This pump has the capacity (40 liters/second) necessary to remove gases from the probe chamber while still maintaining operating pressures in the range needed for careful experimentation. In addition, the eleven stage operation of the pump selected maintains the partial pressure of oil on the high vacuum side of the pump in the range of 10^{-14} Torr thus eliminating the need for a liquid nitrogen trap. Pressure in the high vacuum chamber is monitored by an integral ionization (Bayard-Alpert)

gauge and in the region between the turbomolecular and mechanical pumps by a Hastings DV-8 thermocouple vacuum gauge. A shut-off valve is located between the turbomolecular pump and the high vacuum chamber to facilitate routine maintenance without exposing the chamber to unnecessary contamination.

Data Gathering and Processing System. The data gathering and processing system is comprised of the following electronic hardware and software (see Fig. 7):

1. A UTI 100C Mass Analyzer which contains all of the electronic hardware that actually drives the mass filter, monitors the pressure, and scans the mass spectrum as directed by the operator. All internal and external electronic parameters can be adjusted on this unit.

2. UTI Programmable Peak Selector (PPS) which is a microprocessor and data storage instrument. When properly programmed, the PPS can "instruct" the mass analyzer to scan selected mass peaks (up to nine separate peaks simultaneously), record information about peak intensity, and store all of this data over time. The data can be output in real time mode or from memory in either analog or digital form to any of a variety of other instruments (oscilloscopes, strip chart recorders, x-y plotters, computers, etc.).

3. A Hewlett Packard Model 120 AR Oscilloscope for monitoring real time output.

4. A Hewlett Packard Model 7132 (2 pen) Strip Chart Recorder which receives a real time signal from either the Mass Analyzer or the PPS (or a delayed signal from the PPS) and graphically plots that signal against time.

Current Direction of Work on TPD System. The entire desorption - mass spectroscopy system as described is presently installed and fully operational. Work is currently being done to calibrate, adjust, fine tune, and trouble shoot all parts of the system so that the system will respond as needed to

carry out the TPD studies outlined in Tas. 2 of this project. Some of the problems currently under investigation are:

1. Baseline stabilization has proven difficult because of the small background signals being tracked. This problem is being attacked on two fronts: (i) Proper stabilization of background pressure through pumping system adjustments, and (ii) Dynamic electronic filtering of high frequency noise signals.
2. Optimization of sampling pressures and flows to obtain higher signal-to-noise ratios for the hydrogen peak which is currently one of the most difficult to analyze by the mass spectroscopy technique.

Direction of future work. Now that the TPD system is installed work will proceed in the following areas:

1. Hydrogen desorption from cobalt-silica catalysts (see Table 1) will be the first area of investigation because studies on these catalysts have already been done in our laboratory and can therefore provide a basis for comparison of the mass spectrometry system with the TC-Chromatograph system.

2. Other catalysts, as outlined in Table 1, will be investigated for H₂ and CO desorption. Hydrogen desorption is of initial interest because in our previous study of nickel on different supports (22) the hydrogen desorption peaks were well-defined and clearly affected by the support.

C. Measurement of Specific Activities and Selectivities for CO Hydrogenation on Supported Cobalt Catalysts.

1. Turnover numbers. The most meaningful way to compare catalytic activities for different catalysts is to base them on metal surface areas determined from H₂ chemisorption. A turnover number represents the number of

specific molecules that react per active metal site per second. The carbon monoxide turnover number was used to compare the catalytic activity of various cobalt supported catalysts.

A single-pass differential reactor (see Fig. 2) was used to test the powdered catalyst samples over a range of temperatures. The reactor system is shown in Figure 11. High purity hydrogen (99.99%) and carbon monoxide (99.99%) tanks were connected to the system through high-pressure two-stage regulators. To insure reliable and reproducible reactor data the gases were further purified in deoxo and molecular sieve traps. Automated mass flow controllers were used to adjust the H₂ and CO flow rates. Before any gases were directed into the reactor, the system was evacuated to purge any contaminants that may have been in the lines. A tubular furnace supplied heat to the reactor cell and its temperature was regulated by a laboratory controller. The product gases were passed through heated lines to a chromatograph sampling valve for on-line analysis. A Hewlett-packard HP5834A gas chromatograph equipped with fixed gas and hydrocarbon capillary columns (see Fig. 12-14) was used to analyze gas samples.

During the first few minutes of CO hydrogenation most of the cobalt catalysts showed a sharp drop in initial activity; steady state values could be obtained after one hour of operation. Accordingly the carbon monoxide turnover numbers in Table 6 were obtained from chromatographic analysis of the fixed gas products after approximately one hour of reaction in the temperature range of 175-225°C (see Fig. 13). Heat and mass transfer resistances were minimized by maintaining low conversions of 5 to 10%. Some literature values are listed at the end of Table 6. The turnover number for 3% cobalt on silica of 8.6×10^{-3} at 200°C is in good agreement with the value of 5.9×10^{-3} at 190°C reported by Bartholomew et al. (23) and somewhat higher than the value of

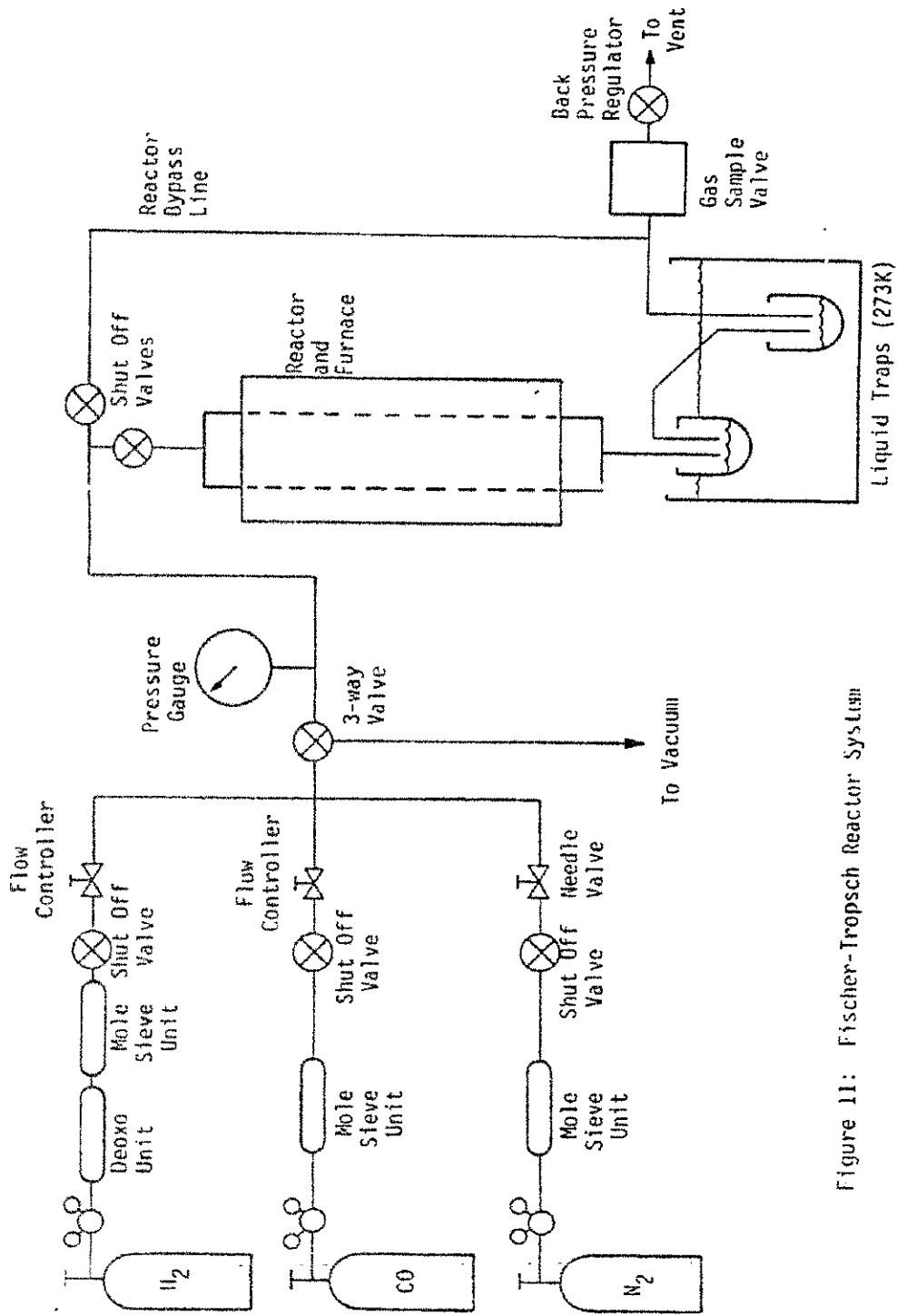


Figure 11: Fischer-Tropsch Reactor System

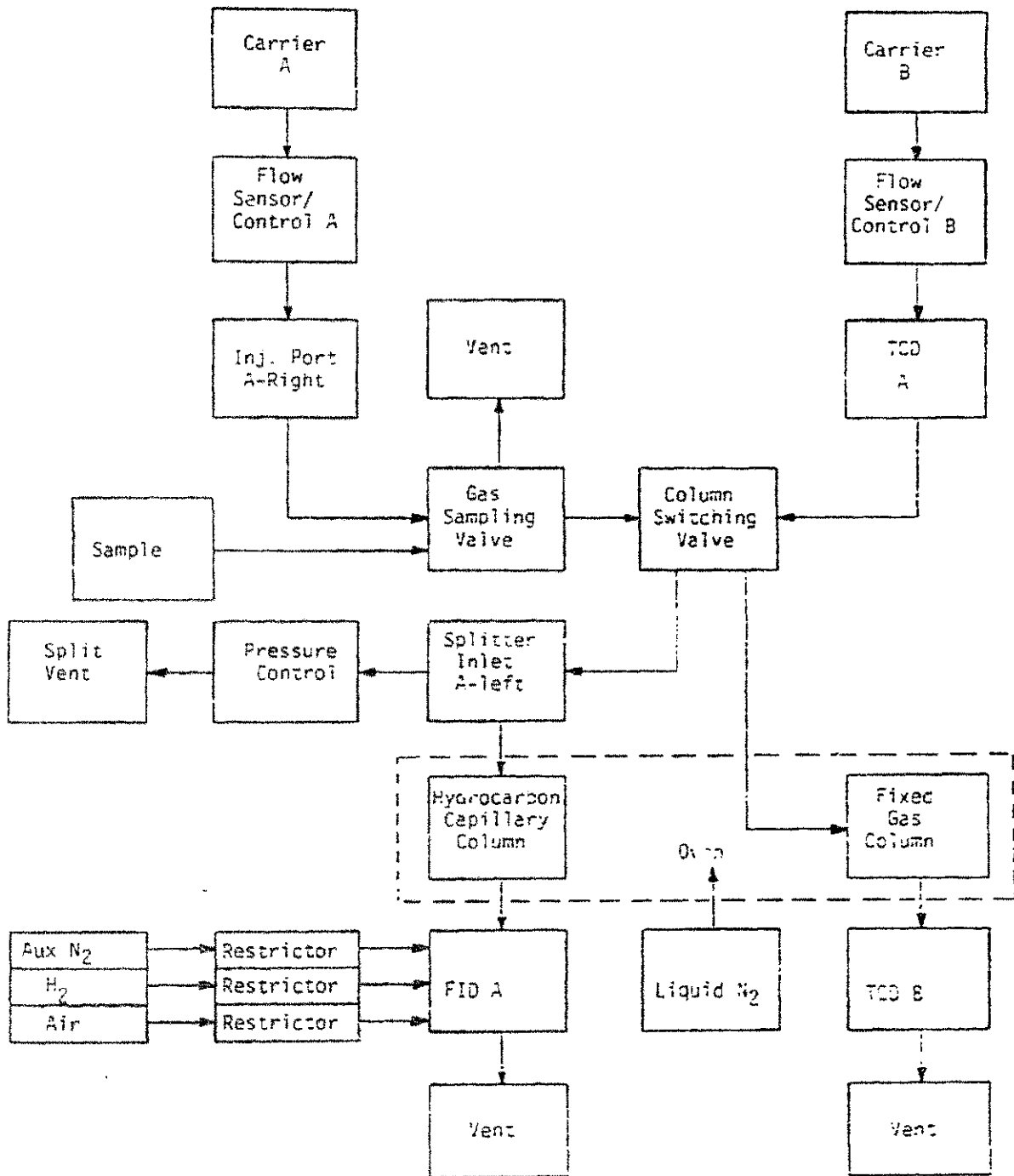
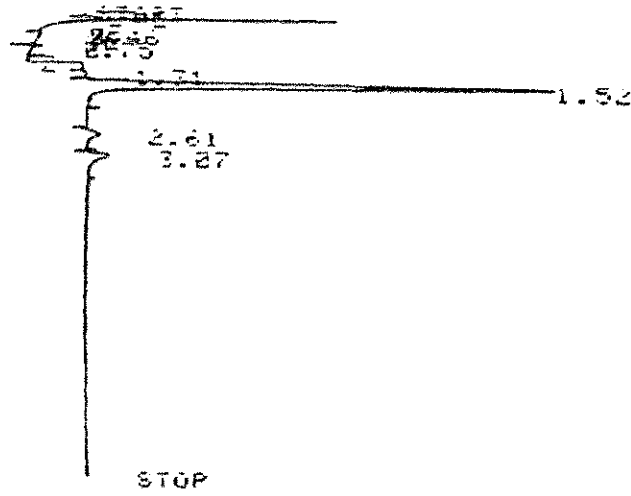


Figure 12. Basic Chromatograph Interconnections



28 5838A
 10 11 11 11

	AREA	AREA %
N ₂	17000	10.000
CO	21000	12.500
CH ₄	21000	12.500
H ₂ O	41000	24.375
	170000	100.000

Figure 13. Fixed gas analysis of Co-S-105

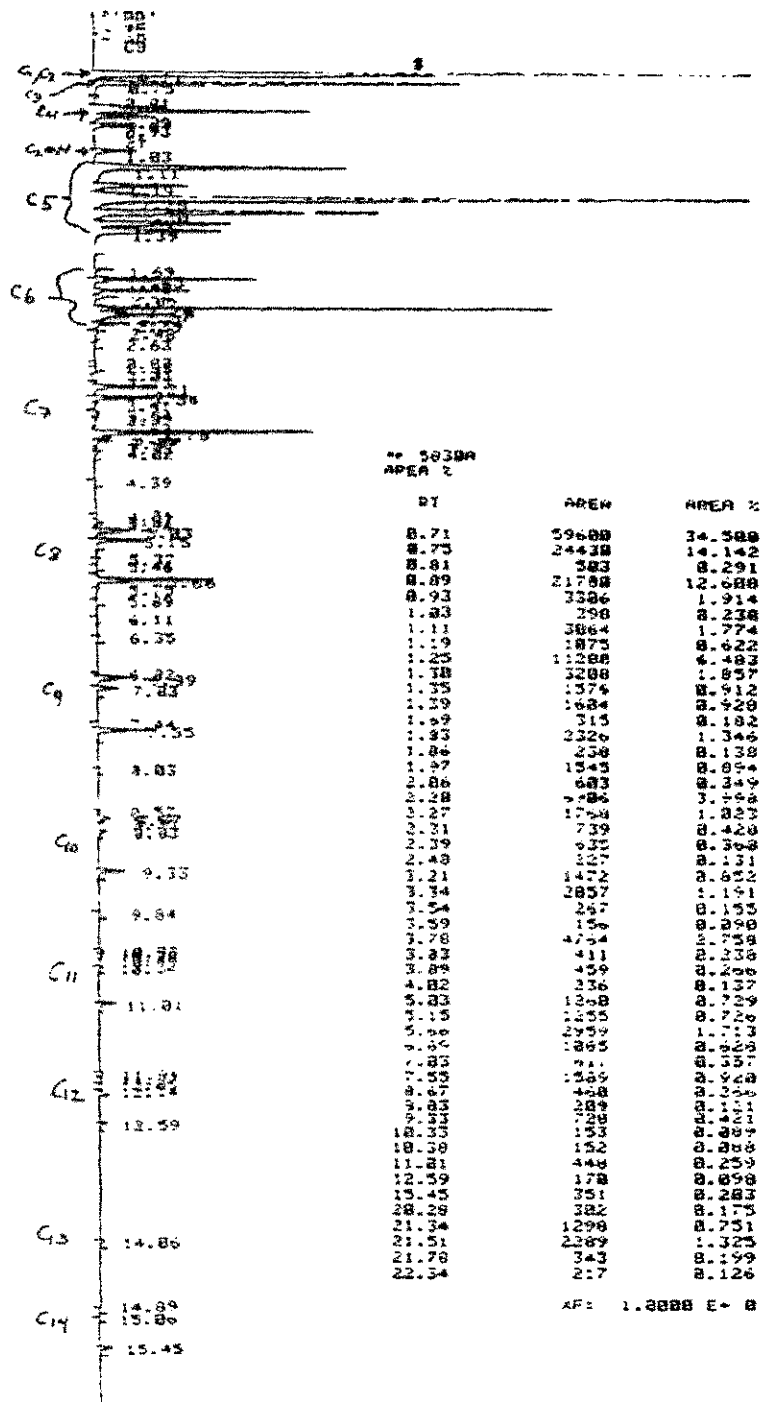


Figure 14. Capillary column analysis of Cc-S-105

TABLE 6

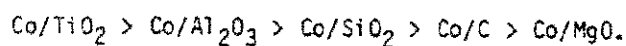
Turnover Frequencies^{a, b} for CO Hydrogenation of Supported Cobalt Catalysts

Catalyst	wt. %	175°C	200°C	$\frac{N_{CO}}{275^\circ C} \times 10^3$	250°C	275°C	$\frac{\xi_{CO}}{(kJ/mole)}$	misc.
Co-S-104	3	5.92	8.56	10.14			20	
Co-S-105	10	2.19	3.15	8.51			50	
Co-S-106	3							inactive @ 400°C
Co-S-107	3							4.70 @ 325°C
Co-A-111	3		9.2	14.7			33	
Co-A-112	10	6.30	18.4	28.3			56	
Co-A-114	3				17.8			
Co-A-115	3	3.32	5.31	16.0			58	
Co-T-100	3	10.2	17.9	41.0			51	
Co-T-101	10	2.00	3.32	8.27			52	
Co-T-102	3			5.31				inactive @ 400°C
Co-M-100	3							inactive @ 320°C
Co-M-101	10			21.5				
Co-M-102	3							
Co-C-100	3			1.99	5.6	15.6	93	
Co-C-101	10							
Co/SiO ₂	4	0.93 ^c	3.6 ^c	12.2 ^c		100	95	(6)
Co/Al ₂ O ₃	2		0.57 ^c	2.4 ^c		28	112	(7)
Co-S-101	3		5.9					(23) at 190°C
Co-S-102	15	0.64						(12)

a. Turnover frequency is the number of CO molecules converted per cobalt surface site (measured by irreversible adsorption) per second
 b. at 85 kPa; H₂/CO = 2/1, at 5-10% conversion after 1 hour
 c. extrapolated

3.6×10^{-3} at 200°C reported by Vannice (6) but still in fair agreement. However, the turnover numbers for 3% cobalt on alumina were much higher than those reported by Vannice (7).

The observed order of activity of supported 3% cobalt catalysts was as follows:



It is interesting that the cobalt catalysts show the same trend in activity according to support as in a study of 3% nickel on similar supports (2,13).

The data in Table 6 show that metal loadings significantly affected activity. For example, the impregnated catalysts of 3% loading were more active than the corresponding catalysts of 10% loading for silica and titania while the opposite was true for magnesia and alumina. This is also consistent with the data for supported Ni of Bartholomew et al. (2,13). The fact that cobalt/titania shows the highest activity at a 3% cobalt loading and that this drops off dramatically at a 10% loading suggests that the titania cobalt metal-support interaction is optimal for Fischer-Tropsch synthesis at 3% and at higher loadings the cobalt cannot interact intimately enough with the support. However, if the metal-support interaction is too strong, as in the case of 3% Co/MgO, the catalyst is apparently quite inactive. Although the 10% Co/MgO (Co-M-101) had a large turnover number at 225°C , this was based on a very small surface area and thus the overall activity per gram of catalyst was very small.

The data in Table 6 also show that the method of preparation significantly affects the activity for CO hydrogenation; indeed, all of the catalysts prepared by pH-deposition except Co-A-115 were less active than their impregnated counterparts.

Activation energies for the rate of carbon monoxide conversion were

calculated from an Arrhenius plot of $\ln N_{CO}$ versus $1/T$ and are listed in Table 6 along with some literature values. The activation energies from Vannice's studies are three to four times larger than those from this study in the case of Co/SiO_2 and Co/Al_2O_3 while E_{act} for $Co/Carbon$ is in the same range as previously reported values (6,7). We are suspicious that our low values, esp. 20 and 33 kJ/mole for Co-S-104 and Co-A-111, may reflect the effects of more severe deactivation at the higher temperatures. Accordingly we intend to repeat the runs for these two catalysts with the addition of a hydrogen regeneration between each measurement so as to ensure that the rates are measured under comparable conditions at each temperature. This procedure will also be used in all subsequent measurements.

2. Hydrocarbon Analysis. Fischer-Tropsch Synthesis on cobalt and iron catalysts typically yields a wide range of hydrocarbons consisting of paraffins, olefins, and alcohols along with water and carbon dioxide as by-products. The selectivities (wt.%) to hydrocarbons, H_2O , and CO_2 are listed in Table 7. The data indicate that increased loading causes a decrease in the hydrocarbon fraction accompanied by an increase in the water fraction. The pH deposited catalysts had smaller hydrocarbon fractions and larger H_2O fractions than their impregnated counterparts. The CO_2 fraction for cobalt on all supports except carbon was small (less than 10%). However, 3% cobalt on carbon produced 53.3% CO_2 a behavior most unusual for cobalt (more typical of iron)! The 3% Co/SiO_2 and Co/Al_2O_3 catalysts prepared by impregnation had nearly identical hydrocarbon, water, and carbon dioxide yields.

The hydrocarbon product gases were analyzed by capillary chromatography. The analysis time was short and the graphs were well defined (see Fig. 14). The selectivity data in Table 3 were obtained using a two to one ratio of hydrogen and carbon monoxide at temperatures from 225-275°C.

TABLE 7
Hydrocarbon, water, and Carbon Dioxide Selectivities^{a,b}

Catalyst	wt.% Co	HC	H ₂ O	CO ₂
Co-S-104	3	87.1	2.6	10.2
Co-S-105	10	61.6	38.4	0
Co-S-107	3	72.6	18.3	9.1
Co-A-111	3	86.8	3.2	10.0
Co-A-112	10	55.0	36.1	8.9
Co-A-114	2	60.0	40.0	0
Co-A-115	3	65.2	34.8	0
Co-T-100	3	63.4	36.6	0
Co-T-101	10	50.6	49.4	0
Co-T-102	3	61.6	38.1	0.3
Co-C-100	3	33.6	11.1	55.3

a. Weight percent to product gas stream

b. At 85 kPa, H₂/CO = 2

TABLE B

Selectivity Data^{a,b} in CO Hydrogenation on Supported Cobalt

Catalyst	wt.% Co	T°C	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₈₊	Alcohols
Co-S-104	3	225	48.6	9.0	14.3	10.8	6.4	4.1	2.0	1.3	1.4	3.9
Co-S-105	10	225	28.8	1.0	8.2	18.2	13.7	12.3	7.8	4.6	4.2	1.3
Co-S-107	3	325	98.3	1.0	0	0	0	0	0	0.5	0.2	0
Co-A-111	3	225	41.3	7.4	16.3	12.7	7.8	5.2	2.4	1.5	1.3	4.0
Co-A-112	10	225	32.4	4.3	14.7	11.9	10.4	8.2	5.7	4.3	6.8	1.3
Co-A-114	3	250	11.8	19.9	15.7	13.7	12.2	9.6	7.0	5.2	3.6	1.2
Co-A-115	3	225	26.9	6.2	13.3	11.9	9.9	8.9	7.0	5.4	8.0	2.7
Co-T-100	3	225	30.6	5.9	16.1	13.3	9.7	8.5	5.4	2.6	4.4	3.5
Co-T-101	10	225	15.5	8.4	10.6	10.5	11.3	10.2	8.8	7.3	16.0	1.1
Co-T-102	3	225	11.8	15.8	14.4	13.8	14.3	10.4	8.4	6.7	4.5	0
Co-C-100	3	275	26.7	24.8	21.1	11.3	8.1	4.3	2.8	0.8	0	0

a. Highest percent of hydrocarbons in product

b. At 80 kPa, H₂/CO=2, after 1 hour of reaction

Figures 15 and 16 show the hydrocarbon product distribution (wt.%) as a function of carbon number for all 3 and 10% impregnated cobalt catalysts.

There are significant differences in hydrocarbon product distribution as a function of support. For example, the Co/TiO₂ catalysts (impregnated) produces more C₂₊ hydrocarbons than Co/Al₂O₃ or Co/SiO₂. However, the most significant support effect was observed with cobalt on carbon. The 3% Co/C produced unusually high C₂ and C₃ fractions compared to the other cobalt catalysts. It is interesting that the 3% impregnated Co/SiO₂ and Co/Al₂O₃ catalysts had nearly identical hydrocarbon yields (Table 7 shows same result), yet the Co/Al₂O₃ was more than twice as active.

The effect of preparation technique on selectivity is evident from the data in Table 8. The 3% cobalt on silica prepared by pH deposition produced 98% methane opposed to the impregnated catalyst that produced 49% methane. However, the increased methane production could also be explained in part, at least, by the elevated temperature of 325°C needed to activate the catalyst. The opposite effect is observed for cobalt on alumina and titania. The pH deposited Co/Al₂O₃ and Co/TiO₂ produced much smaller fractions of methane than the impregnated catalysts. This is consistent with the results of Bartholomew et al. (2) for nickel on SiO₂, Al₂O₃, TiO₂ prepared by impregnation and pH deposition.

In previous work with Ni on different supports, Bartholomew, et al. (2,13) observed a correlation between C₂₊/CH₄ production ratio and CO/H adsorption ratio. Table 9 lists the corresponding ratios for supported cobalt catalysts from this study. At this point it is hard to see any correlation between the CO/H chemisorptions ratio and the C₂₊/CH₄ ratio for supported Co. It would seem that if more carbon monoxide were chemisorbed, then more carbon would be present on the active metal surface for chain lengthening.

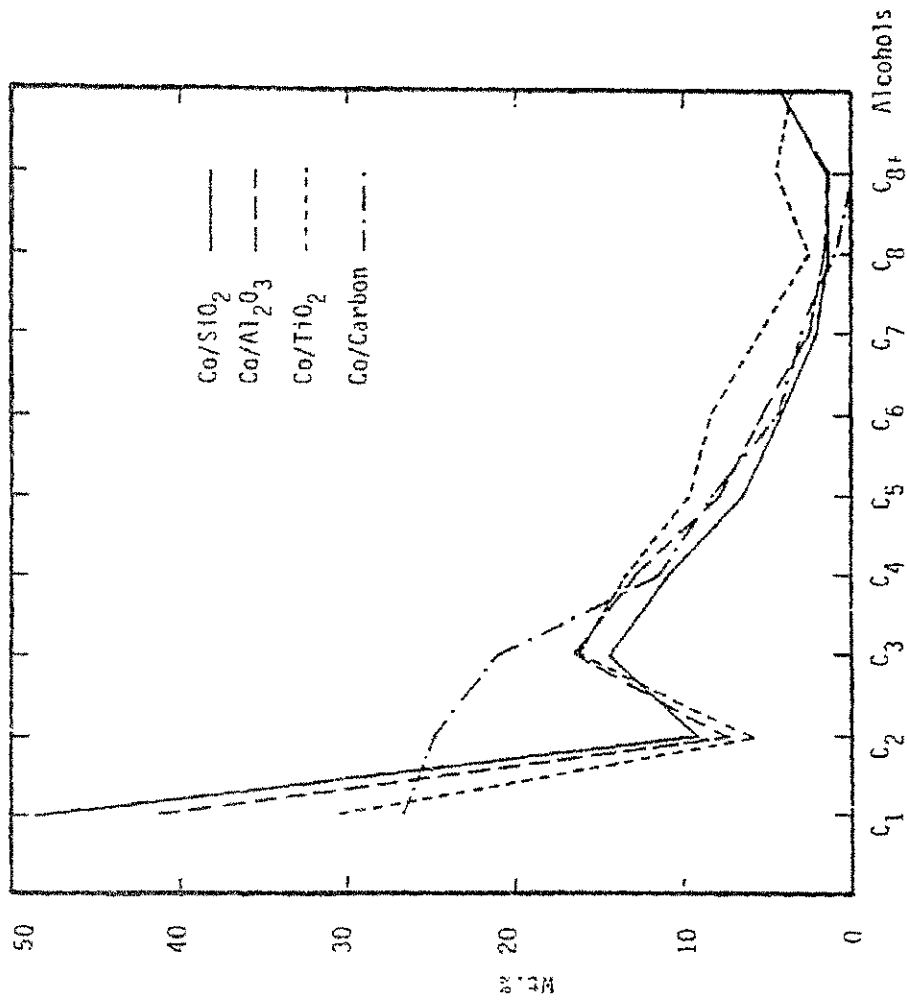


Figure 15. Hydrocarbon Yield for impregnated 3% Supported Cobalt

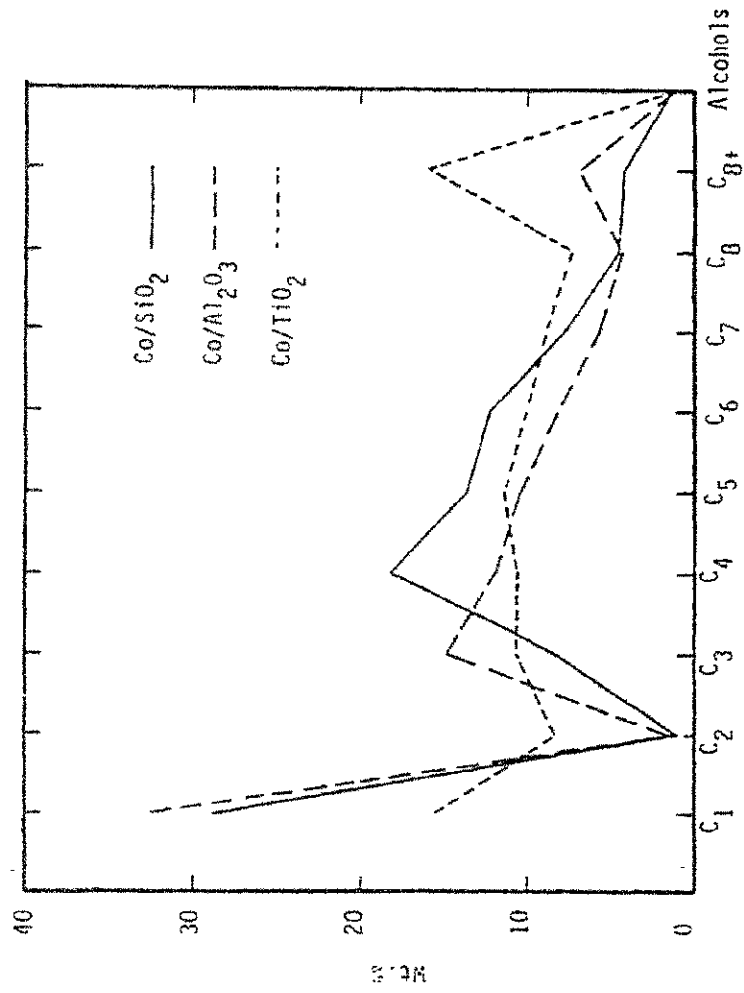


Figure 16. Hydrocarbon Yield for impregnated 10% Support Cobalt.

TABLE 9

Correlation of Selectivity with CO/H Adsorption Ratio

Catalyst	CO/H ^a Chemisorbed	C ₂₊ /CH ₄ ^b	C ₂₊ /CH ₄ ^c
Co-S-104	1.81	1.04	0.36
Co-S-105	0.97	2.47	0.58
Co-S-107	0.30	0.02	0.0057
Co-A-111	1.60	1.42	0.44
Co-A-112	1.07	2.09	0.54
Co-A-114	0.24	7.47	2.32
Co-A-115	2.43	2.72	0.71
Co-T-100	0.85	2.27	0.63
Co-T-101	1.04	5.45	1.31
Co-T-102	2.24	7.47	2.15
Co-C-100	1.02	2.75	1.02

a. Molecules of CO adsorbed per atom of H adsorbed (Total)

b. Mass of C₂₊ hydrocarbons produced per mass of methane

c. Mole fraction basis

Therefore a higher CO/H adsorption ratio would yield higher selectivities for higher molecular weight hydrocarbons. This was true for cobalt on titania, but the reverse was true for silica and alumina supported cobalt.

IV. CONCLUSIONS

1. Alumina- and silica-supported cobalt catalysts prepared by conventional impregnation and deposition techniques have dispersions in the range of 5-10%. Percents reduction to the metal are in the range of 40-60% for catalysts reduced at 350-400°C. Unconventional preparation methods such as the use of carbonyls with potential for preparing more highly dispersed, highly reduced catalysts should be investigated.
2. Adsorption stoichiometries of H₂ and CO on cobalt are significantly influenced by support and preparation history. Adsorption of bridged CO species is apparently favored in some systems (e.g. Co/Al₂O₃ prepared by controlled pH deposition) linear or subcarbonyl CO species in other systems. Suppression of H₂ adsorption is apparent in several Co/support systems, especially Co/MgO.
3. Specific activities for cobalt in CO hydrogenation are significantly influenced by support, metal loading and preparation method. For the 3% loading catalysts and the same preparation method the order of decreasing specific activity is Co/TiO₂, Co/Al₂O₃, Co/SiO₂, Co/C, Co/MgO.
4. Product distributions for Co catalysts in CO hydrogenation are also significantly affected by support, metal loading and preparation method. For example, Co/TiO₂ produces more C₃- hydrocarbons than either Co/Al₂O₃ or Co/SiO₂; Co/carbon produces unusually high C₂, C₃ and CO₂ fractions compared to the other cobalt catalysts. Hence the Co/carbon system shows promise for production of chemicals feedstocks.

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APPENDIX A. Schedule for Testing of Catalysts

1. Reduce sample according to program

0-10 min	50°C
10-20 min	80-90°C
40-60 min	100°C
40-50	140°C
50-60	180°C
60-70	200°C
80-90	240°C
90-100	280°C
100-110	320°C
110-120	360°C
120-130	400°C

stop @ 375 for Al_2O_3 for 20 hours
 stop @ 400 for others for 16 hours

2. Evacuate @ 400°C decreasing to 375°C to 10^{-5} torr for Al_2O_3 @ 375°C decreasing to 350°C to 10^{-5} torr
3. Chemisorb H_2 for 45 min. @ 25°C
4. Evacuate @ 75°C to 5×10^{-5} torr
5. Chemisorb H_2 for 45 min. @ 75°C
6. Evacuate @ 400°C decreasing to 375°C to 5×10^{-5} torr
7. Chemisorb CO for 45 min @ 25°C
8. Evacuate @ 25°C to 5×10^{-5} torr
9. Chemisorb CO for 45 min. @ 25°C
10. Reactor runs
 - a. pretreat in H_2 @ 300°C for 1 hour
 - b. at reactor temp. introduce H_2 & CO in 2/1 ratio
 - c. measure CO conversion, C , H_2 and CO_2 , H_2O Production at 175, 200, & 225°C
 - d. measure entire product distribution @ 225°C
11. Passivate catalyst: fill with N_2 and crack to air
12. Remove TEM sample
13. Reduce for 6 hours at reduction temp.
14. Evacuate to 5×10^{-5} at reduction temp
15. O_2 chemisorb at reduction temp
16. Save sample