

WORK PERFORMED: RESULTS AND DISCUSSION

A. Sample preparation methods:

Since the surface composition and morphological character of the catalyst is sensitive to the method of preparation, we employed three distinct protocols to control the structure of the metal clusters. The methods are very close to those suggested by the earlier investigators. Alerasool and Gonzalez [37] reported that when $\text{Pt}(\text{NH}_3)_4 (\text{NO}_3)_2$ and $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ were used as metallic precursors, the structure of the resulting bimetallic catalysts was strongly dependent on the method of preparation. On co-impregnation the surface composition of the resulting bimetallic catalysts was slightly enriched in Pt. In sequential impregnation the order in which the impregnation is carried out was crucial in the resulting structure of the bimetallic particles. When the sequence $\text{Pt}(\text{NH}_3)_4 (\text{NO}_3)_2$ was followed by drying and exposure of reduced Pt/SiO_2 to a solution of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, bimetallic catalysts were not formed. Only mono dispersed Pt and Ru particles were observed. However, when the impregnation sequence was reversed bimetallic particles were clearly observed. These bimetallic particles had a surface composition which was enriched in Pt. To investigate the effect of sequence of precipitation, a series of Cu-Co-Cr/Cu-Fe-Zn catalysts were prepared following two protocols (a) and (b).

a.) Co-Precipitation

One molar aqueous nitrate solutions of the three metals Cu/Co/Cr or Cu/Fe/Zn are mixed in the desired ratios. The mixed nitrate solution is added slowly, drop wise, to a solution of sodium carbonate/hydroxide maintained at a constant temperature of 75-80°C and pH between 7-8, while stirring continuously. At the end of precipitation the mixture

is thoroughly washed in warm water to remove the sodium nitrate. The precipitate is air dried at 80°C for 18hrs, calcined at 350°C for 18 hrs and reduced at 350°C for 18 hrs in a flowing stream of hydrogen. These are designated as type A catalysts.

b.) Sequential precipitation

In this procedure, desired amount of 1M aqueous solution of copper nitrate and chromium nitrate are mixed and added slowly drop wise to a 7-8 pH sodium carbonate/hydroxide solution at a temperature of 75-80°C., while continuously stirring. At the end of precipitation, the washed precipitate is resuspended in a 7-8 pH sodium carbonate/hydroxide at 75-80°C, and desired amount of cobalt nitrate/iron nitrate solution is precipitated on top. The precipitate is dried, calcined and reduced as in protocol (a). These are designated as type B catalysts - Co atop Cu.

Maintaining identical intermetallic ratios, a third sample is prepared reversing the sequence of precipitation and repeating protocol (b). These are designated as type C catalysts -Cu atop Co. Since the intermetallic ratios are constant in the three samples, any changes in the syngas interaction character should reflect the changes in the surface composition/intermetallic interaction produced by the preparative technique. Further, since the three protocols could yield a wide variety of possible compositions and structures of metal clusters for a given ratio, our characterization studies are expected to provide a comprehensive picture of the syngas interaction character.

Cu/Co Ratio:

It has been established by Courty, *et al* [38, 39] that the main product obtained in the copper rich field ($\text{Cu/Co} \geq 5$) is methanol, while in cobalt rich field hydrocarbons are

produced ($\text{Cu}/\text{Co} \leq 1$). Intermediate compositions in the range $1 < \text{Cu}/\text{Co} < 3$ yield a mixture of light alcohols ($\text{C}_1\text{-C}_6$) with hydrocarbons ($\text{C}_1\text{-C}_6$) as by-products.

Figure 7 is reproduced from the above publication for the purpose of explaining the basis of our choice of the specific ratios. We investigated twelve distinct composition catalysts to cover the three regions of selectivity suggested by the IFP group [38].

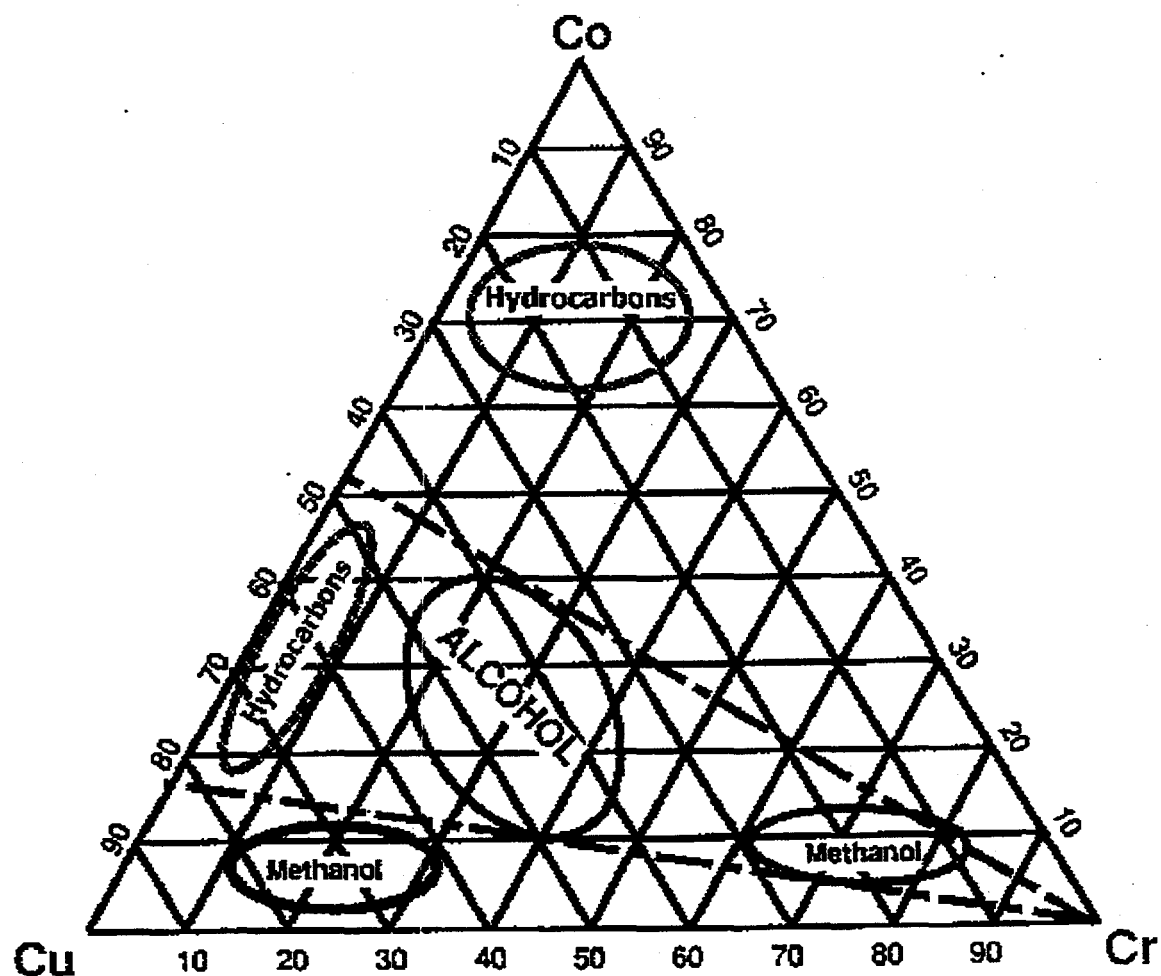


Figure 7. Selectivity Phase Diagram

CO adsorption studies were performed using DRIFT technique. Calcined samples are loaded into the sample cup of the DRIFT accessory and evacuated for 1 hour at 80°C. Then hydrogen is passed through the sample for 18 hours at a rate of 20 cc/min while increasing the temperature to 350°C. After reduction, hydrogen was pumped out while cooling the sample to room temperature and CO is admitted at room temperature at the same rate. Spectra are recorded at temperature increments of 50°C up to 250°C. Then CO was desorbed and spectra are recorded in the reverse order while continuing evacuation.

B. Effect of Sequence of Precipitation

1. NMR and Magnetization Studies

A number of catalysts with Cu/Co ratio spanning the complete range from 0.1 to 37 were prepared carefully using the co-precipitation (type A) and sequential precipitation (type B and C) techniques described above. Co-precipitation catalysts are designated as Type A, Type B catalysts are Co atop Cu and Type C catalysts are Cu atop Co

The NMR results are presented in Figure 8 for three sets of alcohol selective catalysts with pure cobalt spectrum as a background reference (broken vertical lines). The reference spectrum consists of five lines [40]: a line at 213 MHz due to fcc phase particles and a line at 221 MHz due to hcp phase crystallites, and three fault lines in pairs due to twinning and stacking at 215.5 and 218.4 MHz and 215.5 and 217.4 MHz. But for minor changes, NMR could not detect any difference in the cobalt spectra for the three types of preparation techniques. This is expected because NMR technique is not sensitive to changes in the surface composition. Interestingly in all the catalysts examined in this series, which are all alcohol selective according to IFP selectivity phase diagram, the hcp

phase crystallite particles are absent. This leads us to believe fcc phase crystallite particles favor alcohol production. Figure 9 shows the effect of metal ratio on the NMR spectrum of cobalt. As observed earlier [23], chromia inhibits intermetallic interaction and all the spectra are similar, independent of metal ratio, and lie fairly close to the pure cobalt spectrum. However at very high Cu/Co ratio we find a couple of weak lines beyond the hcp line which may be due to copper cobalt alloying or formation of solid solution. The absence of significant shifts in NMR lines might suggest that sequence of precipitation does not produce any strong intermetallic interactions. Figure 10 depicts the NMR spectra classified as per the IFP selectivity phase diagram. In the hydrocarbon and alcohol selective catalysts NMR lines are confined to the normally expected cobalt region with minimal scattering indicating that cobalt is essentially structurally unaffected. In the methanol selective regions it seems, as noted earlier, copper cobalt alloying or solid solution formation might be occurring.

The magnetization results showing the effect of sequence of precipitation are presented in Table 1. Comparing the coercive field results for the three preparations of the same metal ratio, co-precipitation samples seem to produce relatively smaller size particles. As the ratio increases, $\text{Cu/Co} > 3$, cobalt seems to go into solid solution with copper and exhibits paramagnetic behavior in all the three preparative protocols. In general A type (co-precipitation) and B type (Co atop Cu) samples, seem to lend themselves for better reduction independent of metal ratio. On the other hand, C type (Cu atop Co) samples seem to be poorly reduced. When the magnetization data is analyzed according to the IFP selectivity phase diagram (Table 2), we find that all catalysts in the methanol region show paramagnetic behavior consistently. This suggests that the

ferromagnetic metal has no role in the production of methanol. In the hydrocarbon selective region as copper content increases considerable amount of cobalt seems to be locked in Cu-Co spinel structures (AB_2O_4). In the alcohol selective region the increase in copper content seems to promote cobalt reduction. Copper and cobalt lying in close proximity appear to retain their normal electronic structural characteristics. Such atomic distributions seem to be favorable for synergetic functioning in the production of alcohols.

Figure 8

NMR Frequencies of Cu/ Co/ Cr Catalysts
Alcohols (intermediate range)

- A - Coprecipitation
B - Co atop Cu
C - Cu atop Co

EFFECT OF METHOD OF PREPARATION

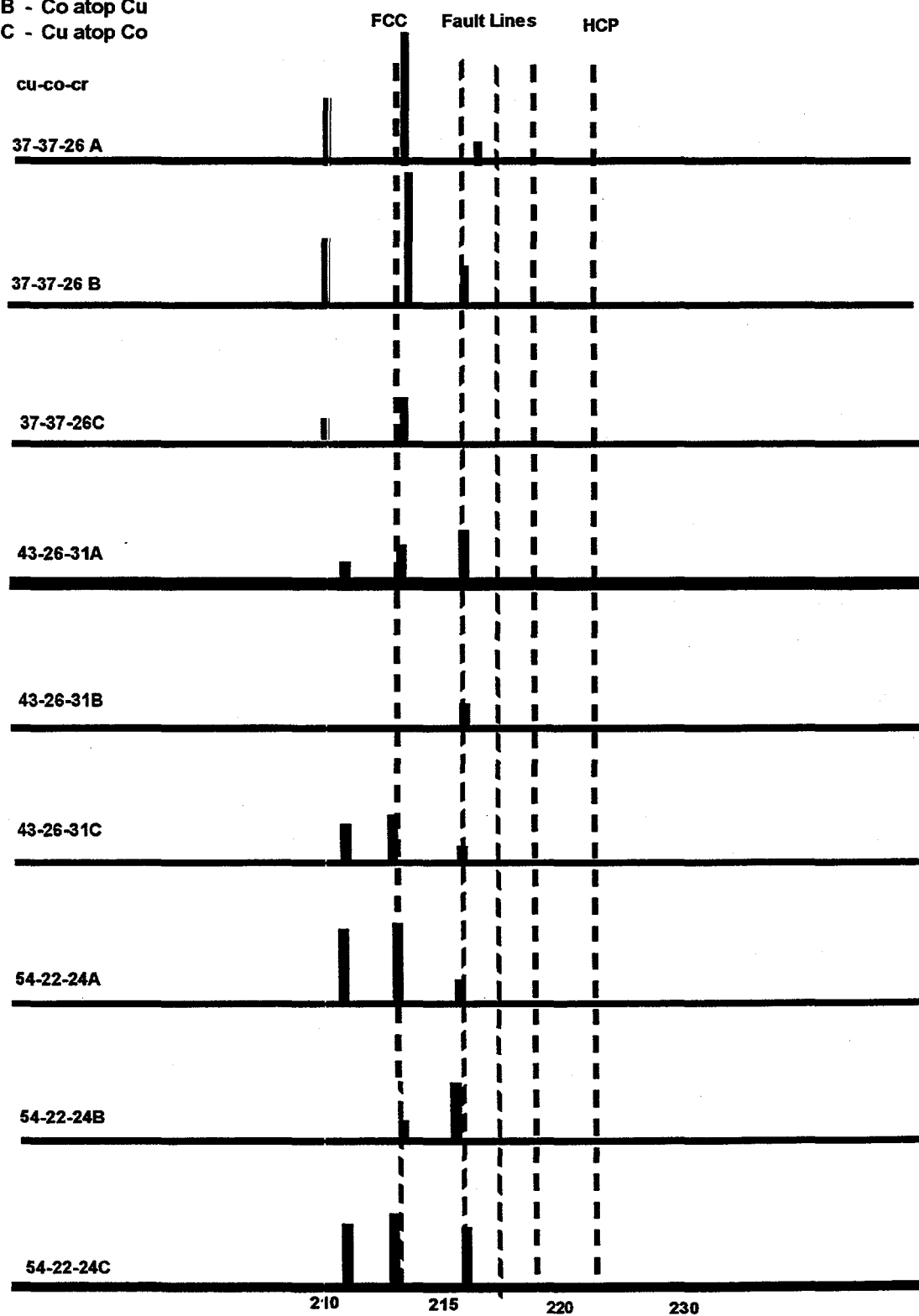


Figure 9 **NMR Frequencies of Cu/ Co/ Cr Catalysts**
EFFECT OF METAL RATIO

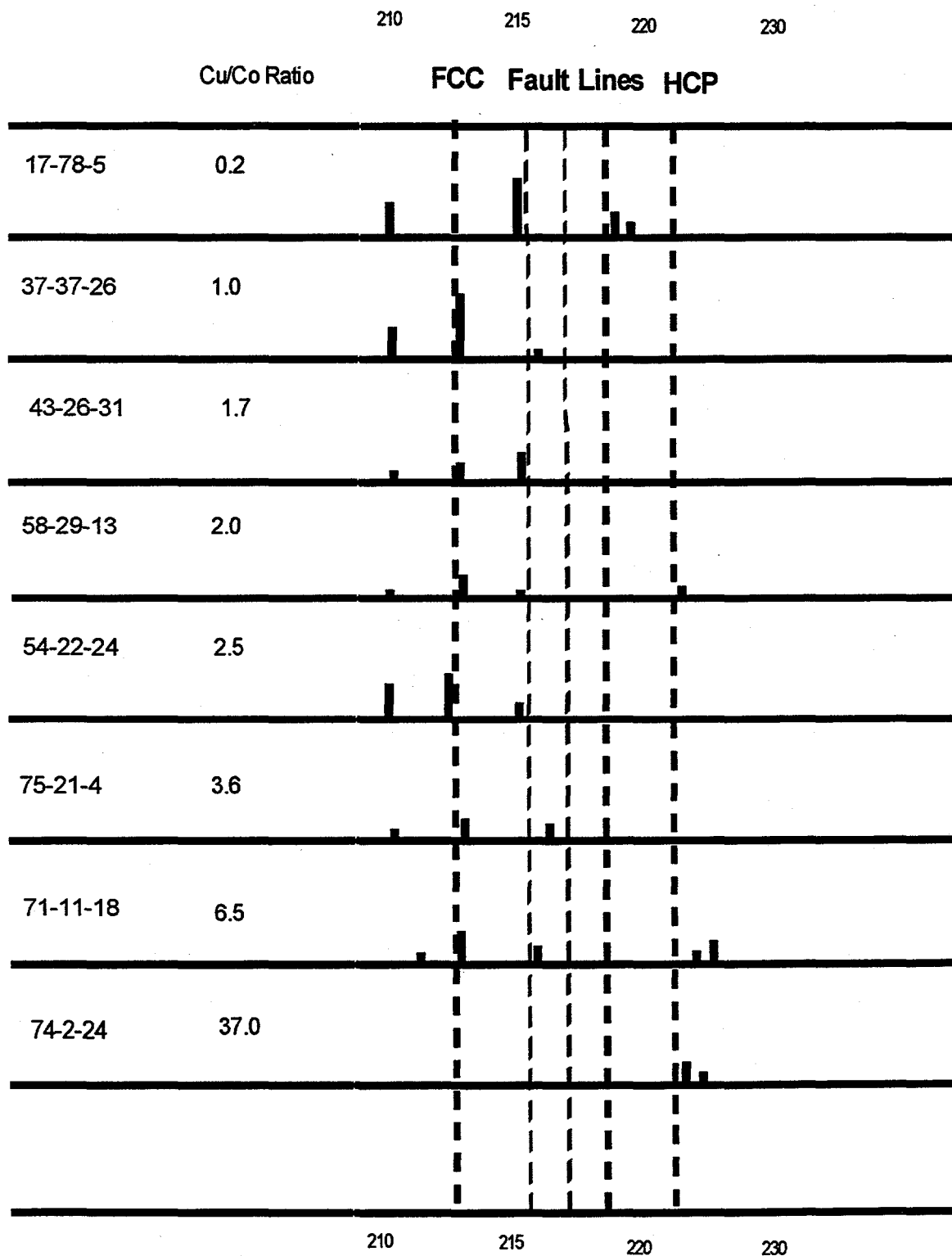
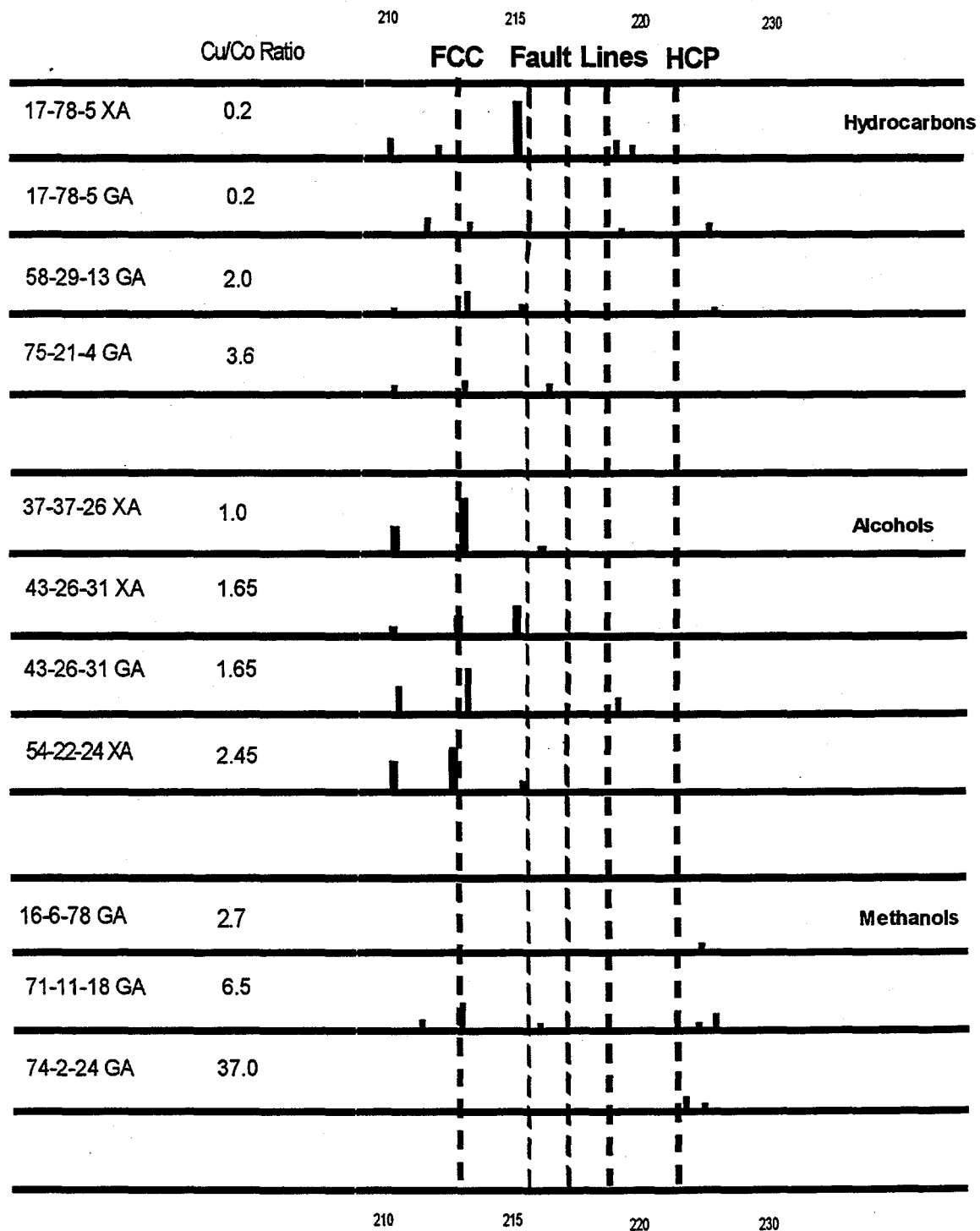


Figure 10

NMR Frequencies of Cu/ Co/ Cr Catalysts

SELECTIVITY CHARACTER



A=Coprecipitation
 B= Co atop Cu
 C= Cu atop Cu

Table 1
 Effect of sequence of precipitation

Cu/Co Metal Ratio	Cu/Co/Cr Composition	Ss (emu/g)	Hc (Oe)	Estimated (μ) (emu/g)	Sr (emu/g)	Sr/Ss	
1	37-37-26 A	23.5	484	64	7.8	0.33	
	37-37-26 B	15.5	329	42	4.2	0.03	
	37-37-26 C	409	373	11	1	0.2	
1.7	43-26-31 A	12.2	519	47	3.9	0.32	
	43-26-31 B	15.5	351	60	4.4	0.29	
	43-26-31 C	12.3	433	47	2.9	0.24	
2.5	54-22-24 A	21.1	434	96	4.9	0.23	
	54-22-24 B	14.4	371	65	4	0.28	
	54-22-24 C	1.4	404	6	0.2	0.17	
3.3	44-13-43 A	PARAMAGNETIC BEHAVIOR					
	44-13-43 B	PARAMAGNETIC BEHAVIOR					
	44-13-43 C	PARAMAGNETIC BEHAVIOR					

Table 2
Selectivity Character of Cu-Co-Cr Catalysts

Cu/Co Metal Ratio	Cu/Co/Cr Compositio	Ss (emu/g)	Hc (Oe)	Estimated (emu/g)	Sr (emu/g)	Sr/Ss	
HYDROCARBONS							
0.1	8-71-21	61.6	403	87	14.6	0.23	
0.2	17-78-05	56.5	546	72	34.2	0.38	
2	58-29-13	15.6	302	54	3.1	0.11	
3.5	74-2-21	5.9	469	28	2.2		
ALCOHOLS							
1	37-37-26	23.5	484	64	7.8	0.33	
1.7	43-26-31	12.2	519	47	3.9	0.32	
2.5	54-22-24	21.1	434	96	4.9	0.23	
3.4	44-13-43	PARAMAGNETIC BEHAVIOR					
METHANOLS							
2.7	16-06-78	DID NOT REACH SATURATION					
37	74-02-24	PARAMAGNETIC BEHAVIOR					
1.8	22-12-66	DID NOT REACH SATURATION					
6.5	71-11-18	DID NOT REACH SATURATION					

2. FTIR Studies:

Three catalysts with Cu/Co ratios 0.2, 1, and 37, representing the hydrocarbon, alcohol, and methanol selective regions were chosen to examine the effect of sequence of precipitation. Samples were prepared carefully using the co-precipitation (type A) and sequential precipitation (type B and C) techniques described earlier. Each of the calcined sample is loaded in to the sample cup of the Diffuse Reflectance Accessory (DRA), and evacuated for one hour at 80°C to remove moisture and adsorbed gases. These were reduced in-situ under hydrogen flow for 18 hrs at 350°C. Hydrogen was outgassed while decreasing the temperature to room temperature. Carbon monoxide was admitted at room temperature, and while continuing the CO flow, temperature was increased gradually insteps of 50°C and FTIR spectra were recorded at each temperature upto 250°C. No significant changes were observed in the C-O Vibrational frequencies of the spectra taken at different temperatures. FTIR spectra of the three sets of catalysts were graphically represented in Figures 11-13 and the vibrational frequencies are presented in Table 3.

The observed bands can be broadly classified in to five distinct groups [41]. The bands in the region 800 – 900 cm^{-1} are due to CO adsorption on chromia , bands in the region 1020-1090 and 1420-1450 cm^{-1} are due to non coordinated carbonates, bands in the region 1040-1080, 1300-1370, and 1470-1530 cm^{-1} are due to Monodentate carbonates, bands in the region 980-1030, 1220-1270, 1530-1670 cm^{-1} are due to Bidentate carbonates and finally those in the region 1800-2000 cm^{-1} are due to carbonyls formed by CO adsorption on cobalt [47].

In the Hydrocarbon selective catalyst (Cu/Co=0.2), vibrational frequencies due to carbonyl structures seem to be promoted in the co-precipitation catalysts, while distinctly absent in the B and C catalysts. In alcohol and methanol selective catalysts, these carbonyls structures

were excited in type B catalysts and were absent in type A and C catalysts. As indicated earlier the carbonyl bands are likely associated with CO adsorbed on positively charged centers of Co^{2+} ions. The absence of carbonyl bands in type C catalysts in all the three ratios may be attributed to the non-availability of Co^{2+} ions on the surface. Also in the type A catalysts (Cu/Co ratios 1.0, 37.0), alcohol and methanol selective catalysts, the surface cobalt atoms available for interaction with CO may be less due to the percent of cobalt present in the catalyst being low. The basis for the absence of the carbonyl bands in the type B hydrocarbon selective catalyst remains unclear.

Another feature that can be noticed is the absence of bands in the region $1420\text{-}1530\text{ cm}^{-1}$ in type B hydrocarbon selective catalysts and in all type C catalysts. It has been observed earlier by Nakamoto [48] that frequency values of the coordinated COO^- group depend on the metal character. If the degree of ionization is higher, these stretching vibrations may be absent [41].

Figure 11: Effect of Sequence of Precipitation Cu-Co-Cr (17-78-5)
(Hydrocarbon selective)

Cu/Co/Cr

II_s/III

III

II_a

IVA

IVB

 $(CO_3)^{2-}$ **With Carbon Monoxide**

(A) Co-precipitation



(B) Co atop Cu



(C) Cu atop Co

**Desorbed**

(A) Co-precipitation



(B) Co atop Cu



(C) Cu atop Co



800

1000


1200

1400


1600


1800

2000


 Chromia


 Non coordinated
carbonate


 Mono dentate
carbonate


 Bidentate
carbonate



 (Carbonyls)

Figure 12: Effect of Sequence of Precipitation Cu-Co-Cr (37-37-2)
(Alcohol selective)

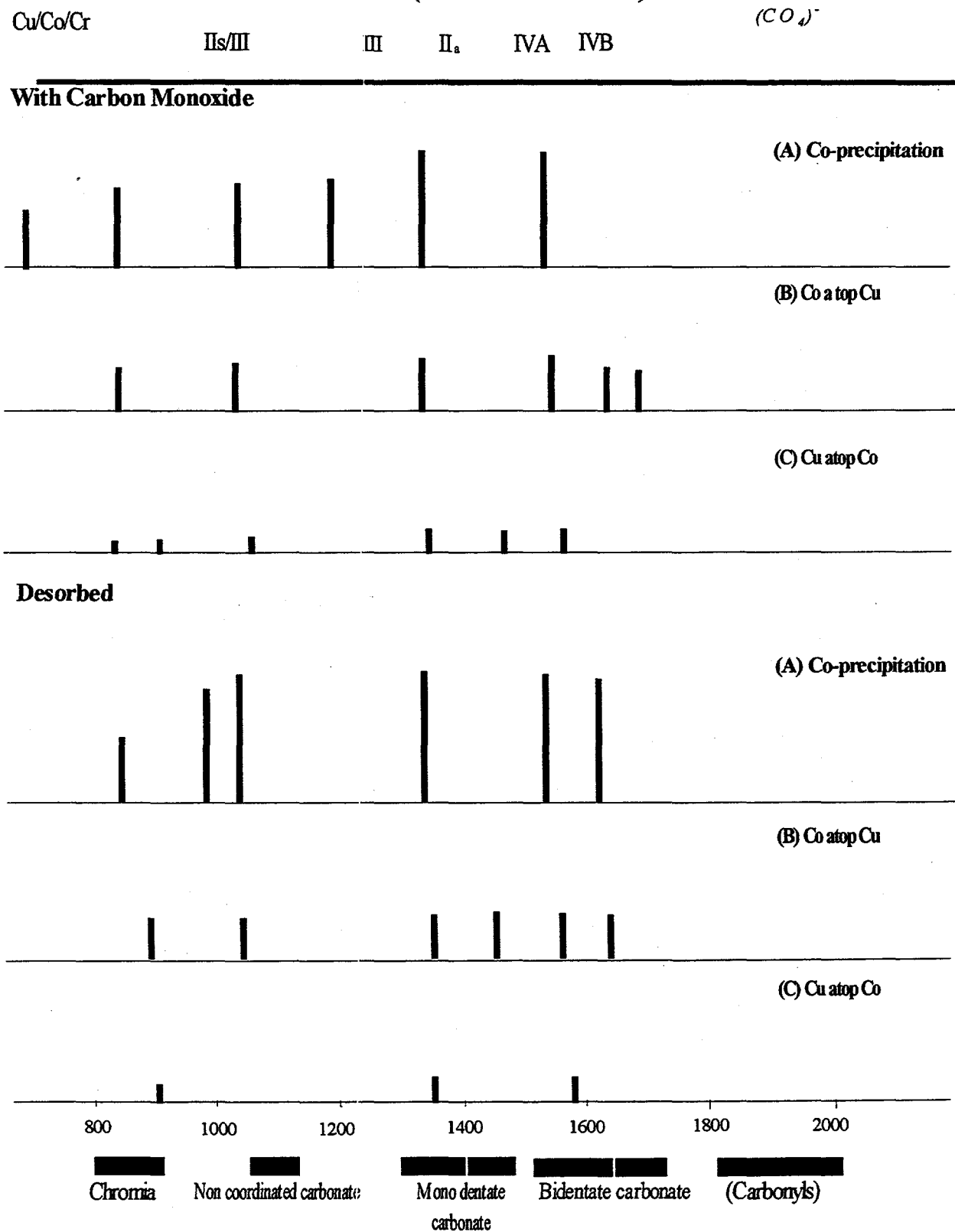


Table 3
Vibrational Frequencies of Cu-Co-Cr Catalysts
(Effect of Sequence of Precipitation)
With Carbon Monoxide

17-78-5A	17-78-5B	17-78-5C	37-37-26A	37-37-26B	37-37-26C	74-2-24A	74-2-24B	74-2-24C
1954	-	-	-	-	-	1931	-	-
-	-	-	-	-	-	-	1883	-
1735	-	-	-	1693	-	-	-	-
-	1600	1653	-	1635	-	1672	1625	1667
1585	-	1575	1523	1542	1566	1563	-	-
1474	-	1468	-	-	1474	-	1435	1453
1380	-	-	1326	1337	1348	1354	-	-
1276	-	-	-	-	-	-	-	-
-	-	-	1185	-	-	-	1177	-
1073	1074	-	1022	1028	1053	1018	1017	-
-	953	-	-	-	919	923	-	944
-	-	-	837	842	833	-	854	-
-	721	-	-	-	-	-	-	775
-	-	-	691	-	-	-	-	727
					Bands were very weak			Bands were very weak

Desorbed

-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	1783
1602	1605	1663	1624	1649	-	-	1602	-
-	-	1522	1542	1561	1572	1587	-	1592
1450	-	-	-	1451	-	-	1408	-
-	-	1381	1349	1350	1351	1326	-	-
-	-	-	-	-	-	-	1216	-
1178	-	-	-	-	-	-	-	1278
-	-	-	1034	1041	-	-	1027	1117
989	-	-	980	-	907	936	-	925
-	-	-	844	896	-	-	868	-
-	-	-	-	-	-	-	-	773
-	-	-	-	-	-	-	-	726
					Bands were very weak	Bands were very weak		Bands were very weak

3. Catalytic Results:

Three sets of samples were chosen as per the IFP selectivity phase diagram to yield hydrocarbons $\text{Cu/Co} = 0.2$, alcohols $\text{Cu/Co} = 1.0$, and methanols $\text{Cu/Co} = 37$. With each metal ratio three samples, co-precipitation (A), Co atop Cu (B) and Cu atop Co (C) were prepared following the respective protocols discussed earlier. The samples were sent to Dr. F.J. Waller of Air Products Inc., the Industrial partner, for catalytic measurements. The catalytic results are presented in Table 4. The gratifying feature is, our samples, though not very efficient, follow the product selectivity patterns of IFP [38, 39]. The disturbing feature is that CO_2 formation is relatively high (about 40%) and mixed alcohol ($\text{C}_2\text{-C}_6$) yield was maxed only around 10%. Type C preparation catalysts seem to give maximum (85%) yield of hydrocarbons among the three. Interestingly the type B catalyst, though falls in the hydrocarbon region of the selectivity phase diagram yielded 18% $\text{C}_2\text{-C}_6$ alcohols, highest alcohol yield of all the catalysts prepared. Again the type B catalyst had the maximum methanol yield for $\text{Cu/Co} = 37$. The catalytic results seem to indicate that type B preparation catalysts, Co atop Cu in general performed better with maximum product yield in the specific selectivity regions and the co-precipitation catalysts, type A, performed poorly with very high CO_2 conversion.

Table 5 shows the catalytic results on co-precipitated alcohol selective catalysts, $1 \leq \text{Cu/Co} \leq 3.4$. All the catalysts show poor CO conversion and an average alcohol production of about 10%. But for the catalyst $\text{Cu/Co} = 3.4$ which falls in the IFP alcohol selective region, there are no significant differences in the performance. The $\text{Cu/Co} = 3.4$ catalyst exhibit a unique behavior with more than 60% methanol production. It is also interesting to note that this catalyst exhibits paramagnetic behavior indicating that cobalt

may be in solid solution with copper. We also find that one can not expect specific selectivity by following rigorously either the ratio rule or the IFP phase diagram.

Table 4 Catalytic Data
Effect of Sequence of Precipitation

Sample	Cu/Co %	CO ₂ %	Methanols %	Mixed %	Alcohol %	Hydrocarbons %	Unknown %
17-78-5A		41	1	6	50	2	
17-78-5B	0.1	36	3	18	37	6	
17-78-5C		9	1	1	85	5	
37-37-26A		55	5	10	25	5	
37-37-26B	1	20	3	11	62	5	
37-37-26C		61	3	6	30	<1	
74-2-24A		51	34	2	13	<1	
74-2-24B	37	28	60	4	7	1	
74-2-24C		34	52	3	10	1	

Table 5
Conversion and Molar Selectivity of Alcohol Selective Catalysts

Sample ID	Cu/Co Metal ratio	CO conv. %	CO ₂ %	Methanols %	Mixed %	Alcohols %	Hydrocarbons %	Unknown %
37-37-26	1	5	55	5	10	25	5	
43-26-31	1.7	3	56	3	7	32	2	
54-22-24	2.5	10	57	5	11	23	4	
44-13-43	3.4	8	27	62	2	8	1	