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Date

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Semi-annual Technical Progress Report (Period October 1, 2000 to March 30, 2001)

The primary objectives of research during this period was to compare the results obtained through FTIR spectroscopy on samples prepared by coprecipitation and Pyrolysis methods. The results of this work has been presented at the National Council of Undergraduate Research conference during March 2001.

1. Introduction

Transition metal catalysts have been widely used in the catalytic process. Method of preparation, morphology, and particle size governs the spectroscopic, magnetic, and catalytic properties. Catalytic studies have shown that selectivity is dependant on the above three characteristics. But very little is understood about the mechanism governing the process (1-4). With a view to understand the mechanism involved, we examined a series of Fe/MoO₃ and Fe/CO/MoO₃ catalysts using FTIR spectroscopy prepared by coprecipitation and pyrolysis methods.

2. Experimental Methods

2.1 Sample Preparation:

2.1.1 Coprecipitation Samples:

Samples with three different metal loadings A) 25% B)15% C) 5% for two different metal ratios, Fe/Co= 3.0 and 1.5, were prepared at ambient temperature using the coprecipitation method. The reaction conditions were kept the same for all samples during the preparation. In a typical preparation, a 0.2M ferric and cobalt nitrate solutions in the desired intermetallic ratio were first thoroughly mixed and added to 0.1M molybdate solution made from ammonium paramolybdate at a rate of 3.5-4.0 ml/min via a burette while stirring. The pH of the solution was 5.6-5.7 at the beginning of the precipitation process and dropped to 1.62-1.97 at the end of the precipitation process. After the completion of the precipitation, the mixture was kept standing for 24 hours. The resulting gelatin was stirred again adding 50 ml of water, filtered, and rinsed. The precipitate was dried at 80°C in a vacuum oven overnight and ground to a fine powder for calcination.

2.1.2 Pyrolysis Samples:

In a typical preparation, solid MoO₃ was dissolved in aqueous solution with adding ammonia drop-wise, and then mixed with iron(III) and cobalt(II) nitrate solutions. Citric acid solution was added to the solution at a ratio of one mole of citric acid to one mole of metal ion. The solution was heated at 70-80°C on a hot plate while stirring for rapid dehydration. The dehydrated gel precursor was dried over night at 80°C in an oven. The dried precursor was smashed and ground into a fine powder in a mortar, and

then combusted in an oven for one hour.

2.2 FTIR Spectrometer:

The FTIR spectrometer and DRIFT system consist of a Mattison Research series FTIR spectrometer, equipped with an MCT detector operable in the mid IR region ($4000 - 600 \text{ cm}^{-1}$), a diffuse reflectance, an environmental chamber and an automatic temperature controller.

To obtain the spectra of the pure samples, first background spectrum of KBr was taken at a scan of 500, resolution of 4 cm^{-1} and a gain of 10. Then each catalyst sample was mixed with KBr and loaded into the sample cup of the DRIFT accessory and evacuated for about 2 hours at 80°C to remove moisture and any absorbed gases. IR spectra were taken for each sample at 50°C , 100°C , 200°C maintaining the same scan rate, resolution, and gain. The background spectrum of KBr was subtracted from the sample spectrum and the resultant spectrum was analyzed. To obtain the FTIR spectra of the reduced sample, pure sample was used as a background, and the sample was reduced in a flowing stream of hydrogen for 18 hours at 400°C . Spectra were taken at 50°C , 100°C , and 200°C .

To obtain the carbon monoxide and syngas ($\text{CO} + \text{H}_2$) adsorbed spectra the following procedure was followed. Calcined samples were loaded into the sample cup and evacuated for 2 hours at 80°C . The samples were reduced at 400°C under continuous hydrogen flow at a rate of 20 cc/min . After reducing the sample for 18 hours, hydrogen was outgassed and the temperature was decreased to room temperature. A background scan of the reduced sample was taken at this temperature. CO was admitted at room temperature, while continuing the CO flow, temperature was increased in increments of 50°C till 250°C . CO was desorbed and FTIR spectra were recorded in the reverse order. The same procedure is repeated with syngas.

3. Results and Discussion

Description of the FTIR spectrometer along with the procedure to obtain the FTIR spectra on solid samples was described earlier (5). FTIR spectra of precursor, reduced, CO adsorbed, and $\text{CO} + \text{H}_2$ adsorbed samples are shown in Figures 1-3. The vibrational frequencies for representative samples are presented in Table 1. Bands in the regions $600 - 1000 \text{ cm}^{-1}$ were attributed to Mo-O, Mo=O, Fe-O, and Fe-O-Mo vibrations by earlier investigators (6-7). In our previous investigation (8) bands in the regions $1600 - 2000 \text{ cm}^{-1}$ were attributed to Fe-MoO₃ vibrations.

Figure 1 shows vibrational spectra of FeMoO₃ catalysts prepared by both methods. Bands due to Fe-MoO₃ vibrations seem to be more predominant in pyrolysis precursor samples examined. Vibrations due to Fe-MoO₃ in the high frequency region appeared with increasing metal loading in the spectra of the samples prepared by the

pyrolysis method. This indicates as iron content increases Fe-MoO₃ vibrations increase and particle size seems to be smaller, promoting more interactions.

In the reduced samples at low metal loadings more vibrational frequencies in the high frequency region were observed in coprecipitation samples compared to pyrolysis samples. But as the metal content increases, pyrolysis samples seem to produce higher vibrational frequencies. This might suggest that the reduction is poor in pyrolysis samples at low metal loadings.

In CO and syngas adsorbed samples, the Fe-MoO₃ vibrations disappeared completely in coprecipitation samples. In addition, we did not observe any strong bands due to carbonyl and carbonate formations, which are considered a necessary intermediates in direct liquefaction, when samples are exposed to CO and syngas. This may be due to formation of iron carbides since carbide coating might inhibit carbonyl production. In the samples prepared by pyrolysis we observed bands probably due to the formation of carbonyls and carbonates. This suggests that Fe-MoO₃ samples prepared by the coprecipitation method seem to be poor syngas conversion catalysts and pyrolysis samples seem to promote formation of carbonyls and carbonates. This may be due to the difference in particle size associated with the method of preparation. With increasing metal content, vibrational modes due to Fe-CO₃/Fe-MoO₃ and intensity of these bands seem to be increasing.

Figure 3 shows FTIR spectra of Fe-Co-MoO₃ at 25% metal loading prepared by the pyrolysis method. We observed bands due to Fe-MoO₃ and Co-MoO₃ vibrations in the precursor and reduced samples. In CO and CO+H₂ adsorbed samples we did not observe any significant changes due to method of preparation. However, bands due to Fe-CO₃ and Co-CO₃ were observed in all of the samples examined.

Figure 1: Effect of Method of Preparation

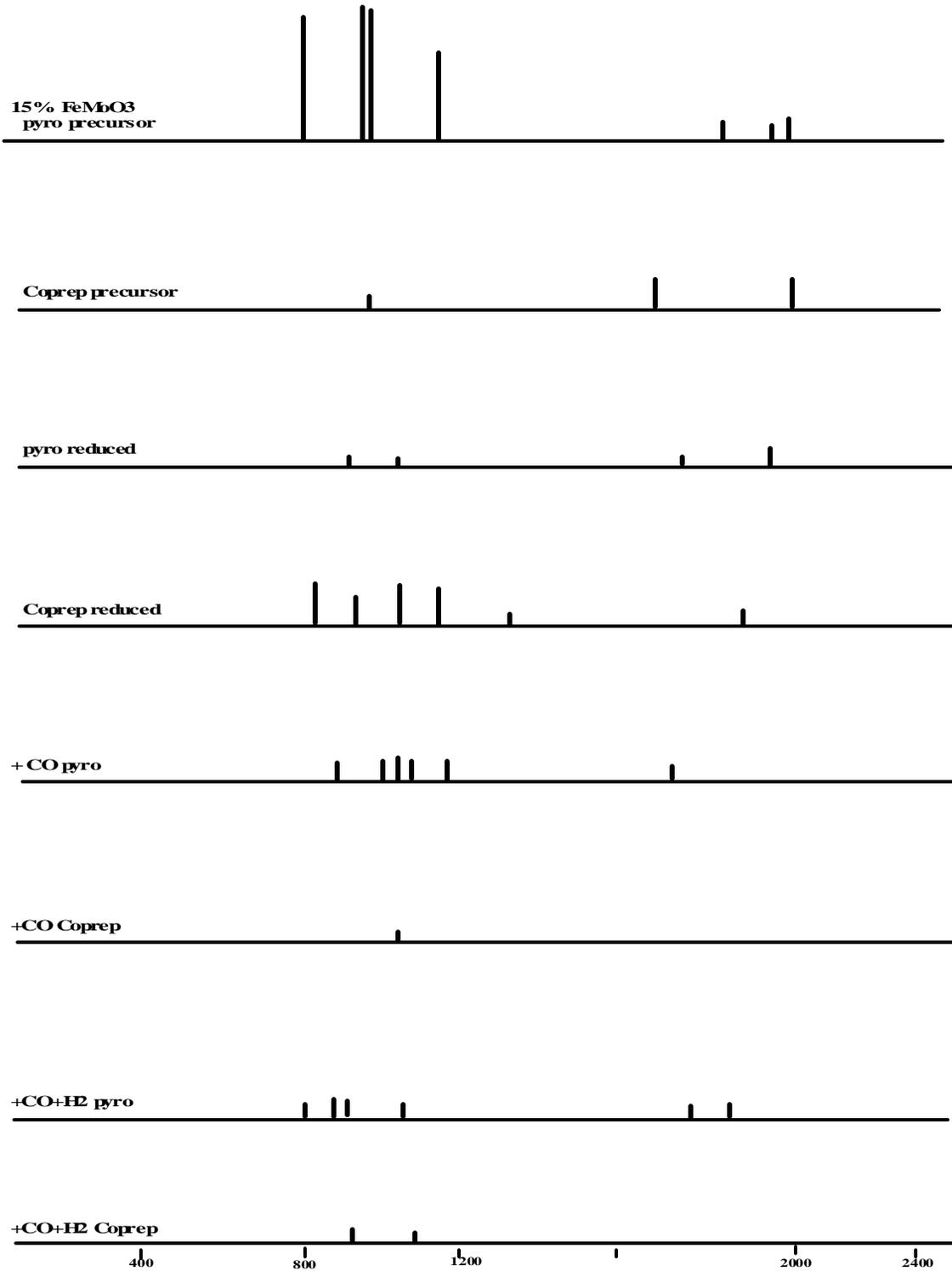


Figure 2 Effect of Metal Loading

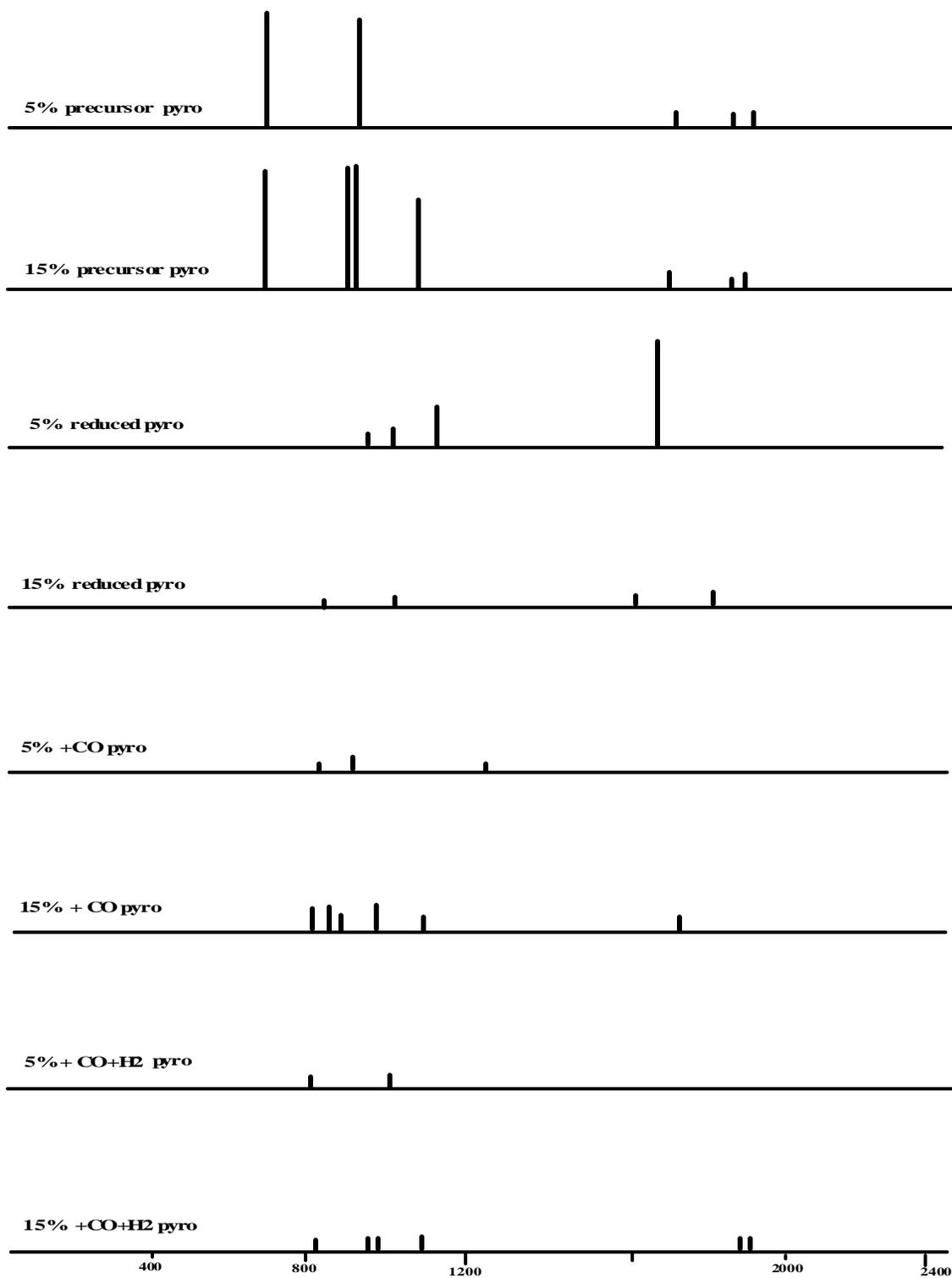


Figure 3 Effect of Method of Preparation (Fe-CoMoO₃, ML25%)

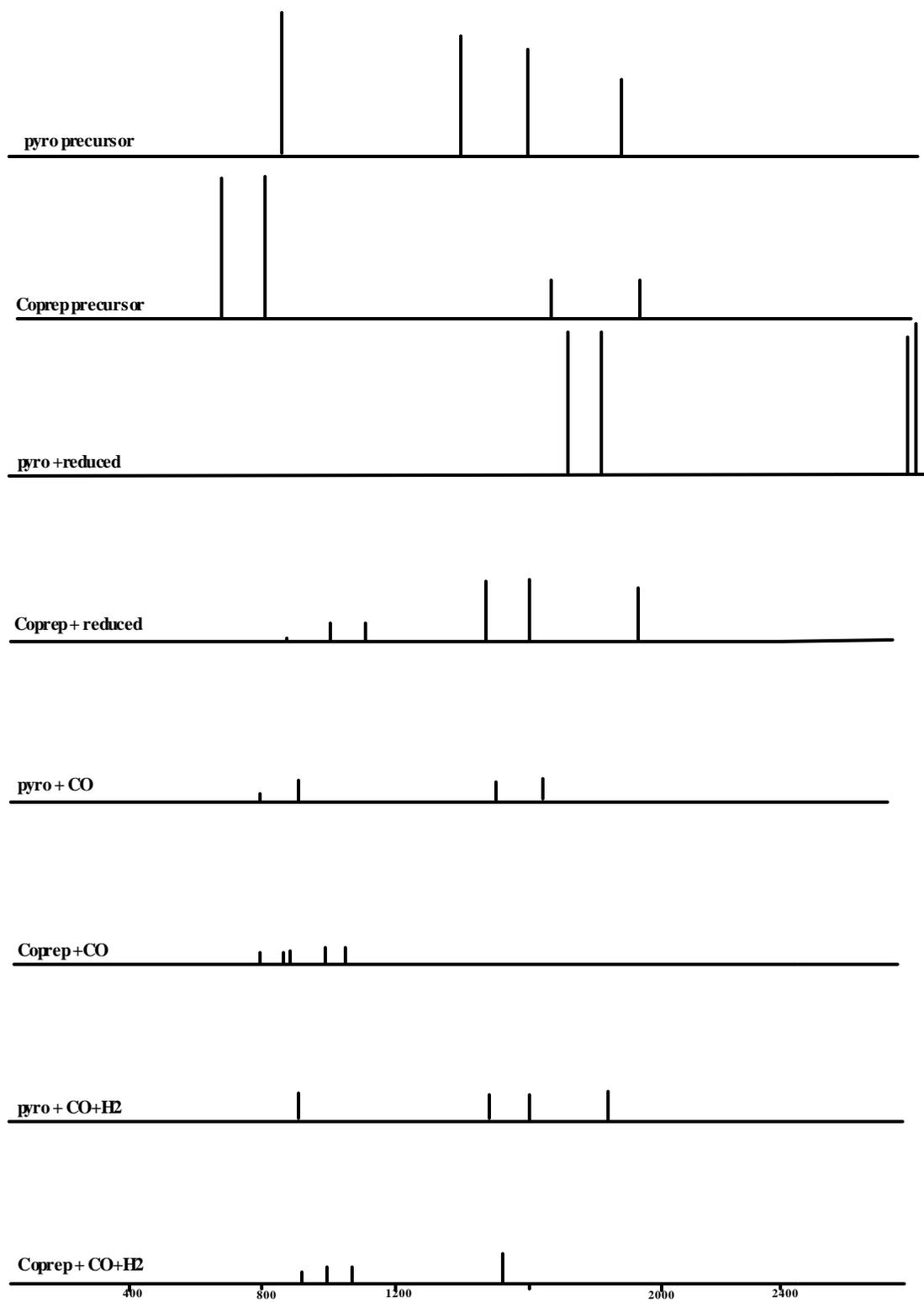


Table 1 Vibrational Frequencies of Fe-MoO₃ and Fe-Co-MoO₃

Fe/MoO ₃ 25% Coprecipitation				Fe/MoO ₃ 5% Coprecipitation				Fe/MoO ₃ 15% Coprecipitation			
precursor	reduced	CO	CO+H ₂	precursor	reduced	CO	CO+H ₂	precursor	reduced	CO	CO+H ₂
1933	1857	1801	1713	1613	1938	1661	833	1952	1846	3747	1084
1747	1494	1702	1096	1129	1904	1596	772	1616	1265	1038	921
1605	1271	1278	1002	990	1835	1095		990	1155		
1326	854	1096	982		1689	965			1001		
1154		981	937		1509	832			930		
994		937	839		1002				814		
956		838	813								
907											
787											

Fe/MoO ₃ 15% Pyrolysis				Fe/MoO ₃ 5% Pyrolysis			
precursor	reduced	CO	CO+H ₂	precursor	reduced	CO	CO+H ₂
1949	1849	1711	1866	1954	1682	1236	1017
1924	1671	1106	1802	1884	1106	937	847
1752	1003	1010	1105	1759	1004	842	
1123	861	979	979		932		
957		936	938				
903		844	845				
791							

Fe/Co/MoO ₃ 25% Coprecipitation				Fe/Co/MoO ₃ 25% Pyrolysis			
precursor	reduced	CO	CO+H ₂	precursor	reduced	CO	CO+H ₂
1924	1902	1106	1505	1901	3888	1694	1845
1617	1683	1005	1103	1610	3722	1514	1665
882	1532	963	1007	1410	1853	975	1536
683	1104	933	934	882	1699	834	975
		836					

4. Conclusion

FTIR studies on FeMoO₃ catalysts indicate that samples prepared by the pyrolysis method produce smaller size particles and promote more interactions with the metal catalysts. In samples prepared by coprecipitation, it is likely that iron carbides might be forming, inhibiting carbonyl and carbonate formations. In Fe-Co-MoO₃ catalysts exposure to syngas seems to replace MoO₃ with CO, generating cobalt carbonyl structures. Even though iron with other supports is known to be a hydrocarbon selective catalyst, with MoO₃ as a support, seems to be a poor syngas conversion catalyst, while cobalt with MoO₃ as a support generate carbonyl-like structures. These findings suggest that Fe-CO-MoO₃ is a better syngas conversion catalyst and pyrolysis method seems to promote these formations better than coprecipitation method. Our direct liquefaction experimental results support these findings.

5. Future Plans :

Future work include completion of the FTIR and NMR work on the remaining Fe/Co/MoO₃ samples prepared by pyrolysis.

6. Student Training :

One of the objectives of this project is to provide training for minority undergraduate students. Currently one new student is being trained to prepare the samples using pyrolysis method and for collection of data using FTIR and magnetization techniques. The results of this work were presented by the new student at the National Council of Undergraduate Research held at Lexington, Kentucky during March 2001 and will be published in the proceedings.

7. References

1. Bauer, J., Brian, B.W, Butler, S.A., Dyer, P.N., Parsons, R.L., and Pierantozzi, "Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals," Herman, R.G., Ed., Plenum Press, p-129 (1984).
2. Hall, C.C., Gall, D., and Smith, S.L., *J.Inst.Pet.*, 38, 845 (1952).
3. Farlet, R., and Ray, D.J., *J. Inst. Pet.*, 50, 27 (1964).
4. Satterfield, C.N., and Huff, G.A., *J. Catal.*, 73, 187 (1982); 85, 370 (1984).
5. Collier, C., Tsega, A., Akundi, M. A., and Murty A. N., *Proceedings of 11th National Conference on Undergraduate Research V*, 1544 (1997).
6. Belhekar, A.A., Ayyappan, S., and Ramaswamy, A.V., *J. Chem. Tech. Biotechnol.*, 59, 395 (1994).
7. Sun-Kou, M.R., Mendioroz, A., Fierro, J.L.G., and Palacios, J.M. *Journal of Materials Science*, 30, 496 (1995).
8. Collier, C., Tsega, A., Akundi, M. A., and Murty A. N., *Proceedings of 13th National Conference on Undergraduate Research V*, 1416 (1999).
9. Murty, A. N., Donatto, U. A., Washington, J. W., Hoard, T. L., Akundi, M. A., and Harris, C., *IEEE Transactions on Magnetics*, 30, 4772 (1994)