Magneto-chemical Character studies of Novel Fe catalysts for Coal Liquefaction

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Semi-annual Technical Progress Report (Period April 1, 1999 to October 31, 1999)

The primary objectives of research during this period were :

1. To prepare iron—cobalt-molybdenum trioxide catalysts using co-precipitation method
2. To examine the surface character of these catalysts with CO and Syngas as probe molecules by FTIR spectroscopy.
3. To examine the magnetic properties of these catalysts using NMR and Magnetization techniques.

Sample Preparation

Samples with three different metal loadings A) 25%, B) 15% and C) 5% for two different metal ratios, Fe/Co = 0.3 and 1.5 were prepared at ambient temperature using the co-precipitation 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 0.1 M 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. These precursors are used for both FTIR, Magnetization and NMR studies.

Experimental:

The sample A, B, and C with metal loadings of 5 to 25%, were calcined in an oven for 18 hours at 400°C. For FTIR studies Mattison Research Series FTIR spectrometer was used. It is equipped with an MCT detector operable in the mid IR region (4000-600 cm^{-1}), a diffuse reflectance accessory, an environmental chamber and an automatic temperature controller.

To obtain the spectra of the pure samples, first a background spectrum of KBr was taken at a scan rate of 500, resolution of 4 cm^{-1} and a gain of 4. 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, and 200°C maintaining the same scan rate, resolution and gain. The background spectrum of KBr was subtracted from the sample spectrum and the resulting 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(CO+H₂) 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, and 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.

Results and Discussion:

Magnetization Results

5% ML	Fe/MoO ₃	(precursor)	Paramagnetic	$\chi = 14 \times 10^{-6}$ emu/g.oe	
5% ML	Fe/Co/MoO ₃	(precursor)	Paramagnetic	$\chi = 3.4 \times 10^{-6}$ emu/g.oe	
5% ML	Fe/MoO ₃	(reduced)	Ferromagnetic		$\sigma = 0.52$ emu/g
5% ML	Fe/Co/MoO ₃	(reduced)	Dual Phase	$\chi = 50 \times 10^{-6}$ emu/g.oe,	$\sigma = 0.01$ emu/g
5% ML	Fe/MoO ₃	(+ CO)	Dual Phase	$\chi = 11.9 \times 10^{-6}$ emu/g.oe	$\sigma = 0.068$ emu/g
5% ML	Fe/Co/MoO ₃	(+CO)	Mostly Paramagnetic	$\chi = 3.7 \times 10^{-6}$ emu/g.oe	
5% ML	Fe/MoO ₃	(+CO +H ₂)	Dual Phase	$\chi = 10.9 \times 10^{-6}$ emu/g.oe	$\sigma = 0.013$ emu/g
5% ML	Fe/Co/MoO ₃	(+CO +H ₂)	Mostly Paramagnetic	$\chi = 3.9 \times 10^{-6}$ emu/g.oe	
15% ML	Fe/MoO ₃	(precursor)	Paramagnetic	$\chi = 27 \times 10^{-6}$ emu/g.oe	
15% ML	Fe/Co/MoO ₃	(precursor)	Paramagnetic	$\chi = 1.2 \times 10^{-6}$ emu/g.oe	
15% ML	Fe/MoO ₃	(reduced)	Paramagnetic	$\chi = 16 \times 10^{-6}$ emu/g.oe	
15% ML	Fe/Co/MoO ₃	(reduced)	Ferromagnetic		$\sigma = 0.025$ emu/g
15% ML	Fe/MoO ₃	(+ CO)	Dual Phase	$\chi = 17 \times 10^{-6}$ emu/g.oe	$\sigma = 0.05$ emu/g
15% ML	Fe/Co/MoO ₃	(+CO)	Ferromagnetic		$\sigma = 0.02$ emu/g
15% ML	Fe/MoO ₃	(+CO +H ₂)	Dual Phase	$\chi = 12.8 \times 10^{-6}$ emu/g.oe	$\sigma = 0.023$ emu/g
15% ML	Fe/Co/MoO ₃	(+CO +H ₂)	Ferromagnetic		$\sigma = 0.06$ emu/g

Independent of metal loading the as-prepared samples (precursors) are paramagnetic indicating that Fe-Co-MoO₃ complexation might be occurring in the co-precipitation process.

At 5 percent metal loading, the presence of cobalt seems to inhibit a reduction to metallic state. We find that the reduction of iron to metallic form is higher in the absence of cobalt. This leads us to believe that Fe-Co complexation with MoO₃ is favored when there is a greater proportion of MoO₃ in the presence of cobalt. However, when metal loading increases to 15 percent, cobalt strongly promotes reduction to metallic form. Exposure to carbon monoxide and syngas seem to enhance reduction to metallic state at 15 percent metal loading more than at 5 percent metal loading if cobalt is present along with iron. This indicates that dissociation of MoO₃ from Fe-Co-MoO₃ complex occurs at higher metal loadings.

NMR Results

NMR data presented in Table 1 and depicted graphically in Figure 1 support the above observations. Most of the cobalt loaded seems to lie in an alloy or complex state with Fe or MoO₃. NMR lines consistently shift to higher frequencies beyond the normal range of cobalt in all samples. However, the subtle changes that might occur due to adsorption of CO or syngas are masked by dominant structures such as the monodentate and bidentate formations which we inferred from the FTIR data.

Table 1: NMR DATA TABLE

SAMPLE		213.0	215.5	217.0	218.4	221.0		
Precursor	5%				219.0	220.8	222.3	223.6
Fe/Co/MoO ₃	15%						222.9	224.7
	25%					220.7	222.1	223.5
Reduced	5%				220.8		222.8	225.6
	15%						221.7	224.1
	25%						221.1	222.0
							223.7	
+CO	5%						221.2	222.5
	15%						221.9	224.3
	25%						221.7	223.6
+Syngas	5%						222.1	224.4
	15%						221.6	223.7
	25%						221.5	223.8

Figure 1: NMR Frequencies of Fe/Co Composites

FTIR Studies:

FTIR spectra of Fe/Mo, Fe/Co/MoO₃ (with Fe/Co =0.3) and Fe/Co/MoO₃ (with Fe/Co= 1.5) of the samples A, B, C with increasing concentration of MoO₃ are presented in Figures 2-5. Vibrational frequency data for pure, reduced, CO adsorbed, and syngas adsorbed samples along with possible vibrational structure assignments are presented in tables 2-4. Earlier investigations (1-2) have attributed bands in the region 600-1000 cm⁻¹ to Mo-O, Mo=O, Fe-O and Fe-O-Mo vibrations. Recent work on Fe-MoO₃ done in this laboratory (3,4) found bands in the region 1500-2000 cm⁻¹ and 2850-2950 cm⁻¹ due to iron molybdate in mono-dentate and bi-dentate structures (5). In the present investigation with Fe/Co/MoO₃, we find again bands due to Mo-O, Mo=O, Fe-O and Fe-O-Mo vibrations along with vibrations due to mono-dentate and bi-dentate structures.

Figures 2 and 3 represent the vibrational frequencies of the pure and reduced samples at 15 and 25% metal loading. Precursors of both Fe/MoO₃ and Fe/Co/MoO₃ catalysts form mono-dentate and bi-dentate structures of iron as well as cobalt with MoO₃. At low concentrations of iron, Co-MoO₃ structures seem to be favored and as the iron content increases both iron and cobalt seem to generate these structures

Figures 2 and 3 show the vibrational frequencies of the reduced samples. We observed additional vibrational bands in the 1500-2000 cm⁻¹ region as metal content increases. Also comparing with the spectra of pure samples, we find fewer number of bands in the low frequency region which are mainly due to Mo-O, Mo=O, Fe-O and Fe-O-Mo vibrations. This might be due to reduction of iron oxide to iron, thus reducing the number of Fe-O-Mo and Fe-O vibrational modes. As such more metal atoms are available to interact with Mo-O, favoring the formation of mono-dentate and bi-dentate structures as evidenced by more bands in the 1500-2000 cm⁻¹ region. This feature is more predominant in sample A where the metal content is the largest.

Shown in Figure 4 and 5 schematically are the vibrational frequencies of CO and CO+H₂ adsorbed species. In Fe/Mo catalysts, exposure to syngas (CO or CO+H₂) seems to dissociate the MoO₃ structures without generating carbonyls of iron. In these catalysts, it is likely that iron carbides might be forming instead of carbonyls, which are essential intermediate products for the formation of longer chain hydrocarbons. In Fe/Co/MoO₃ catalysts, exposure to syngas seems to replace MoO₃ with CO and probably generating cobalt carbonyl structures. It has been observed in our earlier investigations (3,6) of cobalt with chromia as a support has promoted cobalt carbonyl structures. Even though iron with other supports is known to be a hydrocarbon selective catalyst, with MoO₃ as 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. Further support to these findings need to be obtained with direct liquefaction experiments which are currently in progress.

Effect of intermetallic ratio: comparing the pure samples more vibrational structures are excited in Fe/Co=0.3 catalysts than in Fe/Co=1.5 catalysts indicating that cobalt is more active than iron.

Three samples of Fe/MO with decreasing iron concentration have been prepared and we are currently investigating their surface characteristics with FTIR spectroscopy.

Future Plans:

Three Fe/Mo catalysts with 5,15 and 25% are prepared using pyrolysis method. Magnetization and FTIR characterization studies on these catalysts will be done during the next six months.

Student Training:

One of the objectives of this project is to provide training for minority undergraduate students. Currently one engineering and one physics major are involved in this project. One engineering student has presented a paper at the National Council of Undergraduate Research conference in April and this paper has been published in their proceedings.

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Figure 2: Effects of Metal Ratio Fe/Mo & Fe/Co/Mo (15%)

Figure 3: Effects of Metal Ratio on Fe/Mo & Fe/Co/Mo (25%)

Figure 4: Effect of Metal Ratio on Fe/Mo & Fe/Co/Mo
with Adsorbed Gases (15%)

Figure 5: Effect of Metal Ratio on Fe/Mo & Fe/Co/Mo
with Adsorbed Gases (25%)

Table 2: Vibrational Frequencies of Fe-Co-MoO and Fe-MoO

5%

Sample		Reduced		Sample + CO ads		Sample + (CO+H ₂)ads		Possible Vibrational Structures
Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Mo	Fe-Co-Mo (Fe/Co =0.3)	Fe-Mo	Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	
2927.1	-	-	-	-	-	-	-	Fe-MoO ₃
2852.3	-	-	-	-	-	-	-	Fe-MoO ₃
1952	1950.3	-	-	-	-	-	-	Fe-MoO ₃
-	1921.6	1937.2	-	-	-	-	1939.6	Co-MoO ₃
-	-	1900.5	1903.4	-	-	-	-	
1886.6	1879.6	1837	-	-	-	-	-	Fe-MoO ₃
1741.5	-	-	-	-	-	-	-	Fe-MoO ₃
1615.3	1621.1	1692	-	-	-	-	-	Fe-MoO ₃
-	-	1514.3	-	-	-	-	1510.4	
1454.8	-	-	-	-	1457.7	-	-	
-	-	-	1386.2	-	-	-	-	Co-MoO ₃
-	-	-	-	-	-	-	1250.9	Co-MoO ₃
-	1140.9	-	-	-	-	-	1145.7	Fe-MoO ₃
-	-	-	1103.9	-	1101.8	-	1102.3	Co-MoO ₃
-	-	-	-	-	-	1054.3	1052.3	MoO ₃ Bulk phase
-	-	-	1005.1	-	1015.1	-	1001.3	MoO ₃ Bulk phase
988.7	993.8	998	-	986.3	-	-	-	Mo=O
-	-	-	-	958.3	-	961.5	-	Fe-O-Mo
-	-	918	930	916.6	937.4	916.5	927.4	
-	874.5	-	-	870.8	-	-	-	Mo-O
-	831.6	832	799.3	813.5	800.8	830.6	807.7	Mo-O
-	748.9	-	-	-	751.9	762	-	Mo-O
697.6	-	-	-	687.6	-	695.4	-	Fe-O

Table 3: Vibrational Frequencies of Fe-Co-MoO and Fe MoO
15%

Sample			Reduced			Sample + CO ads			Sample + (CO+H ₂)ads			Possible vibrational structures
Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	
1948.7	1922.8	1936.4	-	-	-	-	-	-	-	1939.4	1944.9	Fe-MoO ₃
-	-	-	-	1901.3	1900.5	-	-	1910.3	-	-	-	Fe-MoO ₃
-	1879.2	-	-	-	-	-	-	-	-	-	-	Co-MoO ₃
-	-	-	1845.92	1811.9	1841.7	-	-	1855.9	-	-	1855.6	
1769	-	1726.7	-	1723.5	1704.8	-	-	-	-	1717.3	-	
-	-	-	1699.3	1686.6	-	-	-	1677.6	-	1663.8	1690.3	Co-MoO ₃
1615.1	1615.3	1608	-	-	-	-	-	-	-	-	-	Fe-MoO ₃
-	-	-	-	1582.6	-	-	1583	-	-	1584.3	-	Co-MoO ₃
-	-	-	1504	1523.9	1511.4	-	-	1514.7	-	-	1528.6	
-	-	-	-	1485.9	-	-	1486	-	-	1479.8	1493.4	Co-MoO ₃
-	1408.4	1426.8	-	-	-	-	1420.3	-	-	1449.1	1443.4	Co-MoO ₃
-	-	-	-	1385	1394.6	-	-	-	-	-	-	
-	-	-	-	1325.7	-	-	-	-	-	1301.3	1327.2	Co-MoO ₃
-	-	-	1264.6	-	-	-	1268.8	1270	-	1267.9		
-	-	-	-	-	-	-	-	-	-	1234.4		Co-MoO ₃
-	1126.5	1126.9	-	1101.9	1114.8	-	1112.5	1101.7	-	1109	1104.9	Co-MoO ₃
-	-	-	-	-	-	1044	1035	-	-	1059.8	-	MoO ₃ Bulk phase
-	-	-	1001.82	1006.5	1004.5	-	1006.6	1005.4	-	1006.2	1005.3	MoO ₃ Bulk phase
993.9	990.8	992.7	-	-	-	988.9	-	-	-	-	-	Mo=O
957.4	963.3	-	-	-	-	-	977.6	966.6	966	-	968.2	Fe-O-Mo
-	-	-	-	940.3	938.9	-	932.5	-	923.7	927.4	936.5	
841.6	832.1	-	831.7	-	-	-	-	-	834	-	-	Mo-O
-	-	819.8	-	-	822.5	-	-	-	812.8	807	-	MoO ₃ Bulk phase
-	730.5	-	-	-	-	791.1	-	-	766.8	-	-	Mo-O
-	-	-	731.3	-	-	-	-	-	737.2	-	-	
-	-	-	-	-	-	-	-	-	-	680.9	-	Fe-O

Table 4: Vibrational Frequencies of Fe-Co-MoO and Fe-MoO
25%

Sample			Reduced			Sample + CO			Sample + (CO+H ₂)			Possible vibrational structures
Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	Fe-Mo	Fe-Co-Mo (Fe/Co = 0.3)	Fe-Co-Mo (Fe/Co = 1.5)	
2929.1	-	-	-	-	-	-	-	-	-	-	-	Fe-MoO ₃
-	1950.9	-	-	-	-	-	-	-	-	-	-	-
1927	1922.2	1937.5	-	1938.9	-	-	-	-	-	-	-	Co-MoO ₃
-	-	-	-	1901.9	-	-	-	-	-	-	-	Fe-MoO ₃
-	1881.3	-	1847.8	1837.9	1853.1	-	-	-	-	-	1849.5	Fe-MoO ₃
1757.9	1754.1	1764.3	1712.2	1783.8	-	-	1722.9	-	-	1720.1	1740.5	Fe-MoO ₃
-	-	-	-	1683.2	1674.9	-	1656.5	1662.2	-	1663.1	1650.5	Co-MoO ₃
1611.7	1612.5	1611.9	-	-	-	-	1623	1627	-	-	-	Co-MoO ₃
-	1508.8	-	-	1531.8	-	-	1580.5	1588.6	-	1508.9	-	Co-MoO ₃
-	-	-	1487.6	-	1482.1	-	1480.1	1460.6	-	-	1465.7	-
-	1406.8	1416.3	-	-	-	-	1416.1	1414.5	-	1419.5	1429.7	Co-MoO ₃
-	1333.8	-	-	1385.7	-	-	-	-	-	1336.7	-	Co-MoO ₃
-	-	-	1261.2	-	-	-	1267.5	1275.8	-	-	1266.2	Co-MoO ₃
-	-	-	-	-	-	-	1218.1	-	-	-	-	-
1149.6	1161.1	-	1146.8	-	-	-	1167.4	-	-	-	1150.4	Fe-MoO ₃
-	1132.6	1115	-	-	-	-	1117.2	1105.2	-	1112.8	1103.7	Co-MoO ₃
-	-	-	-	-	-	1038.5	1048.3	-	-	1040.5	-	MoO ₃ Bulk Phase
-	-	-	-	1006	1001.9	-	1006.1	1004.7	-	1005.5	1005.5	MoO ₃ Bulk Phase
993.8	992.7	-	-	-	-	-	-	-	995.8	-	-	Mo=O
-	957.2	961.5	-	-	960.3	974	972.5	968.9	970.6	-	971.3	Fe-O-Mo
-	-	-	933.2	939.6	940.1	-	932.8	930.8	934.1	950.5	923.2	Mo-O
-	881.7	895.2	-	-	895.2	883.9	-	-	-	-	-	Mo-O
861.7	837.7	-	857.4	-	-	830.7	835.8	-	-	834.9	-	Mo-O
-	-	-	-	-	-	-	-	-	812.7	-	-	Mo-O
786.9	781.5	-	-	-	-	-	-	-	780	-	-	Fe-O
-	686.4	-	-	-	-	-	683.9	-	-	687.7	-	Fe-O