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

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Semi-annual Technical Progress Report (Period October 1, 98 to March 31, 99)

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.

Sample Preparation

Three samples were prepared at ambient temperature using the co-precipitation method. They were sample A, Fe/Co/MoO₃ 25%, sample B, Fe/Co/MoO₃ 15%, and sample C, Fe/Co/MoO₃ 5%. The reaction conditions were kept the same for all samples during the preparation. In a typical preparation, a 0.2M ferric and cobalt nitrate solution 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.

FTIR Studies

Experimental:

The sample A, B, and C with metal loadings of 5 to 25%, while maintaining Fe/Co ratio at 0.3, 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:

FTIR spectra of the samples A, B, C with increasing concentration of MoO_3 are presented in Figures 1-4. Vibrational frequency data for different environments (pure sample, reduced, CO adsorbed, $\text{CO}+\text{H}_2$ adsorbed) along with possible vibrational structure assignments was presented in tables 1, 2, and 3. Also included in the table are the vibrational frequencies obtained earlier with Fe-Mo catalysts. We are currently analyzing the possible mechanisms regarding the role of cobalt in the catalyst composite. Earlier investigations (1-2) have attributed bands in the region $600\text{-}1000\text{ cm}^{-1}$ to Mo-O, Mo=O, Fe-O and Fe-O-Mo vibrations. Recent work on Fe- MoO_3 done in this laboratory (3,4), found bands in the region $1500\text{-}2000\text{ cm}^{-1}$ and $2850\text{-}2950\text{ cm}^{-1}$ due to iron molybdate in mono-dentate and bi-dentate structures. In our present investigation with Fe/Co/ MoO_3 , 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.

Figure 1 presents the vibrational frequencies of the pure samples with decreasing metal concentration. We did not observe any significant changes in the observed spectra due to change in temperature. However with increasing metal content, there is an increase in the vibrations due to mono and bi-dentate structures. This suggests that as number of metal atoms on the surface increases, mono-dentate and bi-dentate structure formations are promoted.

Figure 2 shows the vibrational frequencies of the reduced samples. We observed, additional vibrational bands in the $1500\text{-}2000\text{ cm}^{-1}$ 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 $1500\text{-}2000\text{ cm}^{-1}$ region. This feature is more predominant in sample A where the metal content is the largest.

Figure 3 presents schematically the vibrational frequencies of CO adsorbed species. In samples A and B vibrational modes due to bi-dentate structures seems to be promoted, while in sample C, these are suppressed. A strong band around 1000 cm^{-1} due to MoO_3 bulk phase was present both in reduced and CO adsorbed samples while absent in pure

samples. It seems CO interaction with the catalyst leads to the dissociation of MoO_3 from metal molybdate structures. The high frequency bands ($1800\text{-}2000\text{ cm}^{-1}$) present in both pure and reduced samples were distinctly absent in CO adsorbed samples. The high frequency band could be due to carbonyl structures observed in our earlier work (6) on Cu/Co/Cr catalysts. The absence of the high frequency bands and the appearance of vibrations due to bulk phase MoO_3 further confirms the dissociation of MoO_3 .

Figure 4 depicts the vibrational frequencies of syngas absorbed samples. It appears that in the presence of H_2 , metal- molybdate formations are promoted as evidenced by the frequencies in the $1500\text{-}2000\text{ cm}^{-1}$ region. As more metal atoms are available for interaction with molybdate with increasing metal content, new vibrational modes appears to occur.

Figure 5 is a comparison chart of the frequencies observed in pure, reduced, CO adsorbed and syngas adsorbed catalyst at 15% metal loading. It seems the effect of hydrogen exposure on the catalyst is to generate more metal atoms and thus promoting the formations of metal molybdate structures. Further it confirms that CO interaction with the catalyst leads to the dissociation of MoO_3 from metal molybdate structures.

Fig.1 Effect of Metal Ratios Fe/Co/MoO₃ (Pure)

Fig. 2 Effect of Metal Ratios Fe/Co/MoO₃ (Reduced)

Fig. 3 Effect of Metal Ratios Fe/Co/MoO₃ (With CO)

Fig. 4 Effect of Metal Ratios Fe/Co/MoO₃ (With CO+H₂)

Fig.5 Comparison of Vibrational frequencies

Table 1 Vibrational Frequencies of Fe-Co-MoO and Fe-MoO
5%

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

Table 2 Vibrational Frequencies of Fe-Co-MoO and Fe MoO
15%

Sample		Reduced		Sample + CO ads		Sample + (CO+H ₂)ads		Possible vibrational structures
Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	Fe-Mo	
1922.8	1948.7	-	-	-	-	1939.4	-	Fe-MoO ₃
-	-	1901.3	-	-	-	-	-	Fe-MoO ₃
1879.2	-	-	-	-	-	-	-	Co-MoO ₃
-	-	1811.9	1845.92	-	-	-	-	
-	1769	1723.5	-	-	-	1717.3	-	
-	-	1686.6	1699.3	-	-	1663.8	-	Co-MoO ₃
1615.3	1615.1	-	-	-	-	-	-	Fe-MoO ₃
-	-	1582.6	-	1583	-	1584.3	-	Co-MoO ₃
-	-	1523.9	1504	-	-	-	-	
-	-	1485.9	-	1486	-	1479.8	-	Co-MoO ₃
1408.4	-	-	-	1420.3	-	1449.1	-	Co-MoO ₃
-	-	1385	-	-	-	-	-	
-	-	1325.7	-	-	-	1301.3	-	Co-MoO ₃
-	-	-	1264.6	1268.8	-	1267.9	-	
-	-	-	-	-	-	1234.4	-	Co-MoO ₃
1126.5	-	1101.9	-	1112.5	-	1109	-	Co-MoO ₃
-	-	-	-	1035	1044	1059.8	-	MoO ₃ Bulk phase
-	-	1006.5	1001.82	1006.6	-	1006.2	-	MoO ₃ Bulk phase
990.8	993.9	-	-	-	988.9	-	-	Mo=O
963.3	957.4	-	-	977.6	-	-	966	Fe-O-Mo
-	-	940.3	-	932.5	-	927.4	923.7	
832.1	841.6	-	831.7	-	-	-	834	Mo-O
-	-	-	-	-	-	807	812.8	MoO ₃ Bulk phase
730.5	-	-	-	-	791.1	-	766.8	Mo-O
-	-	-	731.3	-	-	-	737.2	
-	-	-	-	-	-	680.9	-	Fe-O

Table 3 Vibrational Frequencies of Fe-Co-MoO and Fe-MoO
25%

Sample		Reduced		Sample + CO		Sample + (CO+H ₂)		Possible vibrational structures
Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	Fe-Mo	Fe-Co-Mo	Fe-Mo	
-	2929.1	-	-	-	-	-	-	Fe-MoO ₃
1950.9	-	-	-	-	-	-	-	
1922.2	1927	1938.9	-	-	-	-	-	Co-MoO ₃
-	-	1901.9	-	-	-	-	-	Fe-MoO ₃
1881.3	-	1837.9	1847.8	-	-	-	-	Fe-MoO ₃
1754.1	1757.9	1783.8	1712.2	1722.9	-	1720.1	-	Fe-MoO ₃
-	-	1683.2	-	1656.5	-	1663.1	-	Co-MoO ₃
1612.5	1611.7	-	-	1623	-	-	-	Co-MoO ₃
1508.8	-	1531.8	-	1580.5	-	1508.9	-	Co-MoO ₃
-	-	-	1487.6	1480.1	-	-	-	
1406.8	-	-	-	1416.1	-	1419.5	-	Co-MoO ₃
1333.8	-	1385.7	-	-	-	1336.7	-	Co-MoO ₃
-	-	-	1261.2	1267.5	-	-	-	Co-MoO ₃
-	-	-	-	1218.1	-	-	-	
1161.1	1149.6	-	1146.8	1167.4	-	-	-	Fe-MoO ₃
1132.6	-	-	-	1117.2	-	1112.8	-	Co-MoO ₃
-	-	-	-	1048.3	1038.5	1040.5	-	MoO ₃ Bulk Phase
-	-	1006	-	1006.1	-	1005.5	-	MoO ₃ Bulk Phase
992.7	993.8	-	-	-	-	-	995.8	Mo=O
-	-	-	-	972.5	974	-	970.6	Fe-O-Mo
957.2	-	939.6	933.2	932.8	-	950.5	934.1	Mo-O
881.7	-	-	-	-	883.9	-	-	Mo-O
837.7	861.7	-	857.4	835.8	830.7	834.9	-	Mo-O
-	-	-	-	-	-	-	812.7	Mo-O
781.5	-	-	-	-	-	-	780	Fe-O
686.4	786.9	-	-	683.9	-	687.7	-	Fe-O

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