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

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The primary objectives of research during this period were :

1. To prepare ferric molybdate –molybdenum trioxide catalysts with different Fe/Mo ratio using co-precipitation method and Pyrolisis.
2.
3. To examine the magnetic character of the catalysts at different stages (i.e, prior to and after exposing to CO only and CO + H_2).
4. To examine the catalytic character of these catalysts.

Sample Preparation:

Three samples with Fe/Mo ratios 25%, 15% and 5% were prepared using co-precipitation method report earlier (1). The same precursors that were used for FTIR magnetization and catalytic studies.

Magnetization studies:

Iron Molybdenum catalysts with two different intermetallic ratios (Fe/Mo = 5% and Fe/Mo = 15%) were examined. Their magnetic and Mossbauer characteristics were determined as:

i) Precursor (as prepared) ii) after reduction (passing hydrogen over the sample for 18 hours at a temperature of 400°C) iii) after exposing the sample to carbon monoxide and iv) after exposing the sample to syngas (a mixture of CO + H_2, CO/H_2 = 1). The experimental results are presented below.

Catalyst composite	Magnetization Magnetic moment σ(emu/g)	susceptibility χx10^6	Oxidation state	Mossbauer Chemical shift δ mm/s	Quadrupole splitting ΔE mm/s
Fe/Mo 5% (Precursor)**P**	--	14	Fe^{3+}	0.67	--
Fe/Mo 5% (reduced)**F**	0.52	--	Fe^{3+}	0.59	--
Fe/Mo 5% (+CO) **DP**	0.068	11.9	Fe^{3+} Fe^{2+}	0.685 1.16	0.79 1.74
Fe/Mo5% (+CO+H_2) **DP**	0.013	10.9	Fe^{3+} Fe^{2+}		
Fe/Mo(15%) (Precursor) **P**	--	27	Fe^{3+}	0.68	--
Fe/Mo(15%) (reduced) P	--	16	Fe^{3+} Fe^{2+}	0.684 1.125	0.828 1.710
Fe/Mo(15%) (+CO) **DP**	0.05	17	Fe^{3+} Fe^{2+}	0.685 1.16	0.75 1.70
Fe/Mo(15%) (+CO+H_2) **DP**	0.023	12.8	Fe^{3+} Fe^{2+}	0.74 1.22	0.82 1.78

P: paramagnetic, **F**: Ferromagnetic, **DP**: Dual Phase- Paramagnetic with small ferromagnetic component

The abssence of Quadrupole splitting ΔE in the Mossubauer spectra of the precursors for both 5% and 15% iron concentration, indicates that the electron configuration of iron is (Fe^{3+}) $3d^5$ and is in a $6S_{5/2}$ ionic state. The half filled 3d shell forms a spherically symmetric charge distribution, and does not therefore contribute to the electric field gradient (q). Both $q_{valence}$ and q_{latice} are zero. There exist no ionic charges in the as prepared Fe-Mo composite. It is reported that (2) Fe^{3+} in oxidic matrices shows chemical shifts (isomeric shift d) in the range 0.47 –0.6 mm/s. The observed shift in the two Fe-Mo composites is about 0.68, indicating that the precursor, as expected is in a Fe-MoO_3 matrix. When exposed to carbon monoxide, substantial quadrupole splitting occurs (ΔE = 0.79 and 0.75 mm/s) indicating that appreciable ionic charge production occurs in the lattice. In addition CO adsorption leads to the production of Fe^{2+} species with an outer electron configuration $3d^{6-x}$, $4s^x$, x ~ 10% as per the Walker, Werthiem Jaccarino graph (3). Almost identical situation is observed for both 5% and 15% iron samples. Adding hydrogen along with CO (syngas adsorption) increases quadrupole splitting in the 15% sample and decreases in the 5% sample. That means lattice ion concentration is promoted by increasing the iron content in the composite. Syngas adsorption also generates Fe^{2+} species but with almost no 4s population, reaching a complete $3d_6$ configuration. Both CO and CO+H_2 addition seem to result in charge transfer to the metal atom as well as to the lattice.

The magnetization data clearly shows that Fe-Mo composite is essentially paramagnetic and exposure to CO or CO+H_2 leads to the generation of a small amount of ferromagnetic species in the composite. Addition of H_2 results in a reduction of the catalyst composite and generation of ferromagnetic species. No magnetic hyperfine structure characteristic of metallic iron is observed in any of the samples, and hence the internal magnetic field is insignificant.

Catalytic studies:

Two samples with Fe/Mo ratios 25% and 15 % were sieved to 60/100 mesh. Then a 1.0 gram sample was loaded and reduced in the reactor using 4% H_2 in He. The exact protocol employed with these samples was similar to the previous work done on Cu-Co-Cr samples (4).

Each catalyst was then tested for catalytic activity at 280°C and 900 psi total pressure with an inlet gas composition of $H_2/CO/N_2$ equal to 40/40/20. Nitrogen was the internal standard for calculation of carbon mass balances. Each catalyst was tested for 2 days at steady state. Total time on-line with catalyst reduction was 4 days.

Sample	CO Conv(%)	Product			
		Total hydro Carbon (%)[2]	CO_2(%)	CH_3OH(%)	Unknown(%)[3]
Fe/Mo[1a] (25%)	3.5	54.2	22.7	2.0	20.6
Fe/Mo[1b] (15%)	0.4	61.2	23.1	1.7	15.0

1a. The carbon mass balance is 100%; 1b. The carbon mass balance was 103%
2. Selectivity was expressed in mol %
3. The unknowns were one or two compounds larger than decane based GC calibrations and separation characteristics of the GC columns; most probably hydrocarbons

Sample	Product				
	Methane	Ethane	Ethylene	Propane[4]	Butane
Fe/Mo[1a] (25%)	38.8	8.3	0.8	5.1	1.2
Fe/Mo[1b] (15%)	42.9	9.4	0.7	5.8	1.4

4. The major C_3 was propane. There was a small amount of propylene.

Discussion:

The results of the FTIR studies were reported earlier (1). The results indicate the absence of vibrational frequencies in the region 2000 – 1200 cm^{-1} when the catalyst is exposed to carbon monoxide or CO + H_2 (Syngas). Ferric-molybdenum systems are good oxidative dehydrogenation catalysts. That means they have the ability to form strong surface hydrogen. Since hydrogen is not IR active, the bands in the region 2000 – 1200 cm^{-1} that were present both in the pre-cursor and the reduced sample might have been suppressed in the presence of CO and CO + H_2. The catalytic data shows a drop in higher hydrocarbon production, the product being mostly methane: 38.8% (C_1), 9.1% (C_2), 5.1% (C_3) and 1.2% (C_4). It seems that hydrocarbons are more saturated than unsaturated. This appears to be consistent with very high activity for H_2 dissociation and hydrogenation. The magnetization data supports these findings indicating the presence of Fe^{2+} ions in CO and CO+H_2 exposed catalysts. Since more hydrogen is available which in turn might be reducing the catalyst and perhaps responsible for the presence of the ferromagnetic component in these catalysts.

Pyrolysis:

Synthesis of ferric molybdate-molybdenum trioxide catalysts by pyrolysis of organic precursors. -- Highly dispersed ferric molybdate-molybdenum trioxide catalysts that are proposed to be used as a catalyst for coal liquefaction have been synthesized by pyrolysis of organic precursors. The synthesis consists of 1) dissolution of molybdenum trioxide in aqueous solution by drop-wise addition of the concentrated ammonium hydroxide solution, 2) mixing with ferric nitrate and citric acid solution, 3) rapid dehydration of the solution at temperature below 90^{o}C to form the organic precursors, and 4) calcination of the precursors in air to form oxides catalysts. Three catalysts with desired chemical composition of $Fe_2(MoO_4)_3$, $Fe_2(MoO_4)_3/2MoO_3$, $Fe_2(MoO_4)_3$ /$12MoO_3$ have been prepared using this method.

The XRD analysis on the sample $Fe_2(MoO_4)_3$ indicate that the particle size was in the micron range. A possible reason for larger particle size might be due to long calcination time. To understand the thermal decomposition process and optimize pyrolysis conditions, the organic precursor samples with various chemical composition have been studied with TGA, DTA, and DSC in the temperature region between 50^{o}C to 800^{o}C. The preliminary thermal analysis under Ar gas reveals the occurrence of an exothermic reaction at about 200^{o} C and an endothermic reaction about 670^{o}C. Both reaction temperatures increase with increasing molybdenum content. The thermal analysis under air and oxygen is in progress. The identification of phases in the catalysts and the particle size are also in progress.

Future Plans:

Magnetization and FTIR characterization studies on catalysts prepared using pyrolysis will be done during the next six months. Three Fe/Co/MoO samples in the range $0.3 <$ Fe/Co < 3.0 will be prepared using Co-Precipitation technique and will be used for FTIR and magnetization studies.

Student Training:

One of the objectives of this project is to provide training for minority undergraduate students. Out of the 4 students involved in these projects, two are engineering majors and two are physics majors.