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Co-precipitation is the major method proposed for synthesis of molybdenum oxide supported Fe, Fe/Co, and Fe/Cu catalysts. However, many variables may effect the particle size and surface properties of the synthesized catalysts, such as pH of molybdate solution, precipitation temperature and pH, Fe/Mo atomic ratio, pH of the washing solution, aging of the freshly prepared samples, and the length and temperature of calcination. In this period, we have been working on precipitation between iron(III) nitrate solution and ammonium para-molybdate solution under controlled pH condition, and with different Mo/Fe atomic ratio. The effect of aging time on the property of the samples was also studied.

The samples with the ratio of Fe/MoO₃: 6.5%, 20%, 26%, and 30% were prepared using above mentioned method. The samples with 6.5% and 26% were characterized with thermal analysis, infrared spectroscopy, magnetization, Mossbauer and X-ray diffraction before and after calcination at 400°C. FTIR was examined on precipitate, calcined and reduced samples as well as CO adsorbed and desorbed samples. Magnetization Studies were made on precipitated, calcined, and reduced samples. Their synthesis and characterization are presented in this report.

Sample A, Fe/MoO₃ = 26%, formulated as Fe₂(MoO₄)₃, or Fe₂O₃/3MoO₃

A 0.50M iron(III) nitrate solution was made by dissolving 8.08 g of Fe(NO₃)₃·9H₂O in 40 ml deionized water. A 0.1M ammonium molybdate solution was made by dissolving 5.30 g of (NH₄)₆Mo₇O₂₄·H₂O in 42.9 mL water. The iron(III) nitrate solution was dropwise added into molybdate solution, and a gel-like yellowish green precipitate formed. The final mixture of solution and product had a pH of 1.66, and was stirred over night. After filtration, the precipitate was dried in a vacuum oven at 50°C for one week. The product is dark yellow. The actual yield is a little higher than theoretical yield, indicating that the product is not dry.

Sample B, Fe/MoO₃ = 6.5%, formulated as Fe₂O₃.12MoO₃

A 0.50M iron(III) nitrate solution was made by dissolving 3.23 g of Fe(NO₃)₃·9H₂O in 16 ml deionized water. A 0.1M ammonium molybdate solution was made by dissolving 8.48 g of (NH₄)₆Mo₇O₂₄·H₂O in 68.6 mL water. The iron(III) nitrate solution was dropwise added into molybdate solution, and a light green precipitate formed. The final mixture of solution and product had a pH of 1.56, and was stirred over night. After filtration, the precipitate was dried in a vacuum oven at 50°C for one week. The product is light yellow powder. The percent yield is 90%.

Both samples were calcined at 400°C.

The differential scanning calorimetry data were collected on a Perkin Elmer DSC 7 at a heating rate of 20°C/min to study their thermal properties, and is shown in Fig. 1. The sample B exhibits an endothermic peak ($\Delta H = 200$ J/g) at 158°C with a shoulder at

180°C, and an exothermic peak ($\Delta H = -346 \text{ J/g}$) at around 410°C. The exothermic peak may be related to the phase change of MoO_3 , since sample B consists of a large amount of MoO_3 . Sample A does not show the large exothermic peak as sample B. But a very small exothermic peak can be observed at 420°C which may indicate a small amount of MoO_3 present. The broad endothermic peak in the low temperature region for sample A may be due to the dehydration process. As stated above, the freshly prepared sample A is gelatin-like material and may not be completely dried under 50°C. The nature of these peaks is still not well understood, and further investigation is needed.

Figure 1

The powder X-ray data were collected on a Philips Analytical X-Ray Diffractometer using $\text{CuK}\alpha$ source. XRD patterns for both samples after calcination are shown in Figure 2&3. As can be seen, the final products are well crystalline solids. A search and match procedure was used to identify the phases presented in the prepared samples. The XRD pattern of sample A consists of majority of iron molybdenum oxide and a small amount of molybdenum oxide. The XRD pattern of sample B consists of a majority of molybdenum oxide and a small amount of iron oxide. This result may indicate that under low concentrations of iron, Iron molybdate might not have formed. These are roughly consistent with what was expected from the synthesis. The quantitative analysis of composition on these samples using XRD patterns and other techniques such as SEM is in progress. The particle size was estimated to be 20-50 micrometers using Scherrer's equation from the line broadening in the XRD pattern of sample B.

Magnetization Studies:

The Magnetization character of the two samples 1) $\text{Fe}_2(\text{MoO}_4)_3$ (26% Fe) and 2) $\text{Fe}_2\text{O}_3 \cdot 12\text{MoO}_3$ (6.5% Fe) was examined a) as prepared (precipitated sample) b) heating in air for 18 hours at 400°C and c) after reduction (heating the calcined sample in a flowing stream of hydrogen for 18 hours at 400°C).

The samples remained paramagnetic for all three treatments with no significant differences in the susceptibility values (Table 2). Comparing with the susceptibilities of pure compounds (3) from the CRC data (Table 3) it seems a complex of Fe-Mo-O has formed in both samples which is neither oxidizable nor reducible. The slight increase in the susceptibility values after calcination and subsequent drop after reduction might indicate that molecular oxygen might be physically trapped in the complex structure after calcination which is driven out during reduction.

Mossbauer spectrum analysis of calcined sample 1 shows a single line at 0.18 mm/s away from Fe metal. This means that Fe is in a symmetric environment of oxygen since there is no quadrupole splitting. Absence of Zeeman splitting further confirms that there is no metallic iron. Interpolation from the scatter plot of iron chemical shifts indicates that iron is in a Fe^{2+} state.

Table 2

	Sample	%Fe	χ (10^{-6} emu/g.Oe)		
			Precipitated	Calcined	Reduced
1	$\text{Fe}_2(\text{MoO}_4)_3$	26	27	37	33
2	$\text{Fe}_2\text{O}_3 \cdot 12\text{MoO}_3$	6.5	14.2	19.6	13.8

Table 3: χ Values of Pure Compounds

Sample	χ (10^{-6} emu/g.Oe)
Pure FeO	7200
Pure (Fe_2O_3)	3586
Pure (MoO_3)	3
Pure Mo	89
MoO_2	41
Mo_3O_8	42
Mo_2O_3	Diamagnetic - 42
O_2	3449

FTIR Studies:

FTIR studies on the two Fe-Mo samples (6.5% and 26% Fe) were investigated on Mattison Research series FTIR spectrometer using Diffuse reflectance FTIR spectroscopy. Each sample spectra were taken under the following conditions. Fresh sample (as prepared) before calcination. sample calcined at 400°C and reduced sample.

The samples were reduced at 400°C with continuous hydrogen flow at 20 cc/min. After reducing the samples for 18 hrs CO was admitted at room temperature and while continuing the CO flow temperature was increased in increments of 50°C till 250°C. Spectra were taken at each temperature. CO was desorbed at 250°C and spectra were recorded in the reverse order. For each spectra the resolution, gain and scan rate are kept at 4cm⁻¹, 10 and 500 respectively. To assist in analyzing the observed frequencies sample spectra of Molybdenum (IV) oxide (MoO₃) and Ammonium para molybdate (NH₄)₆Mo₇O₂₄ were also taken.

The observed vibrational frequencies on both samples are diagrammatically represented in Figure 4 and the data along with possible assignments are presented in Table 1. In all the samples investigated, we did not observe any significant changes in the observed vibrational frequencies due to change in temperature. IR studies on Iron Moly catalysts(1-2) indicate the presence of bands in the region 1000 – 700 cm⁻¹ region due to Mo-O stretching vibrations. In our studies we observed bands in the same region which could be attributed to Mo-O vibrations as indicated in Table 1. One striking feature observed in all the spectra is the absence of the band at 1040 cm⁻¹ in both calcined and reduced samples. This shows the possibility of formation of a hydrated MoO₃ phase in the initial stages of the precipitation. We also noticed that in none of the samples studied we observed any vibrational frequencies attributable to FeO. This might suggest that some complex of Fe-Mo-O, might have formed. In the CO adsorbed and desorbed spectra except for two bands which may be due to Mo-O vibrations all other frequencies were absent. Our studies indicate that neither iron nor molybdenum are in the pure metallic form and the complex FeO-MoO might function as a catalyst instead of Fe metal

Future Plans:

The present investigation show some interesting results and we presented some preliminary analysis of the data obtained. More detailed work on more samples is yet to be done. We also plan to send the samples used in the present investigation to Dr. Fran Waller our Industrial collaborator for catalytic studies. In the future we plan to investigate FTIR, XRD and Magnetic characterization studies on Fe/Co/MoO and Fe/Cu/MoO using Co-Precipitation technique. The equipment ordered for Pyrolysis studies has arrived and we will set up the system ready for study of these samples using Pyrolysis technique.

Student Training:

One of the objectives of this project is to provide training for minority undergraduate students at a school with predominant minority enrollment. Out of the 4 students involved in these projects, two are engineering majors and two are physics majors. Students are currently being trained in preparing the Fe-Mo catalysts. They already have enough experience with the general techniques of preparing the catalysts by co-precipitation methods.

Figure 4: Vibrational Frequencies of FeMo

Table 1

MoO ₃	(NH ₄) ₆ Mo ₇ O ₂₄	Fe ₂ O ₃ 12MoO ₃ (6.5%)					Fe ₂ (MoO ₄) ₃ (28%)					Assignments
		Precipitate	Calcined	Reduced	wCO	Desorbed	Precipitate	Calcined	Reduced	wCO	Desorbed	
-	-	2075	-	-			-	-	-			-
1953	-	-	-	-			-	-	-			MoO ₃
1923	-	-	1952	-			-	1929	-			MoO ₃
1889	-	1835	-	1826			-	-	1855			MoO ₃
-	-	-	-	-			1760	1755	1707			-
1644	1644	1638	1619	-			1611	1619	-			Para molybdate
-	-	-	-	1531			-	-	1510			-
-	1453	1441	-	-			1409	-	-			-
-	-	-	-	1335			-	1324	1380			-
-	-	-	-	-			-	-	-			-
1128	-	-	1125	-			-	1150	-			-
1081	-	1040	-	-			1042	-	-			hydrated MoO ₃
978	944	941	994	905	1002		947	957	950	971	989	Fe-O-Mo
-	845	857	850	857			826	876	836	905	895	Mo-O
-	795	-	-	799			-	791	-			Mo-O Octahedral
-	736	-	-	754	767	771	-	-	-			Mo-O Octahedral
-	-	697	692	-			698	-	-			Fe-O Octahedral

1 Belhekar, A.A., Ayyappan, S., and Ramaswamy, A.V., J. Chem. Tech. Biotechnol., **59**, 395 (1994).

2 Sun-Kou, M.R., Mendioroz, A., Fierro, J.L.G., and Palacios, J.M. Journal of Materials Science, **30**, 496 (1995).

3 Handbook of Chemistry and Physics, 70th Edition, CRC Press 1989-1990.