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INVESTIGATION OF NITROGENEOUS COMPONENTS IN THERMALLY HYDROCRACKED
HEAVY GAS OIL TREATED WITH VARIOUS CATALYSTS

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OCTOBER 1978

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
Report 77-120 (IR)

ERP/ERL 723/137
77-120 (IR)

1858862-10

INTRODUCTION

This work is carried out as part of the ERL efforts in studying nitrogenous compounds in various feedstocks and synthetic fuels derived from them. The samples studied were those described by Parsons and Ternan (1) in their report on hydrodesulphurization and hydrocracking activity of some supported binary metal oxide catalysts. In this report the technique developed by Wimer (2) and Fritz (3) and modified by Buell (4) for the determination of basic nitrogen compounds is applied.

EXPERIMENTAL

Hydrocracking

The hydrocracking was carried out by the pilot plant of the Bitumen Processing Section of the Energy Research Laboratories, by thermally hydrocracking Athabasca bitumen obtained from the Great Canadian Oil Sands (1). The 345-525°C portion distilled from the hydrocracked product was used as the feed material. Catalysts promoted by Cu, Co, V, Vi, Fe as well as unpromoted catalysts containing 18%, 27%, 30% MoO₃ were used.

Determination of Basicity Values

Essentially the method of Buell (4) was used. The material (about 100 mg) was weighed into a vial (5 ml capacity) with a conical bottom and with magnetic stirrer. The 2.0 ml of a 1:2 mixture of benzene and acetonitrile were added and the mixture was stirred magnetically for about 5 minutes. A combination electrode (glass and silver chloride) and a glass tip from the automatic burette were inserted. The sample was then titrated with a solution of 0.057 N hydrochloric acid in dioxane. Potentiometric readings were obtained from a PH meter (Accumet Model 420, Digital pH/ion meter) and these were recorded.

Determination of Pyrrolic Functions

The samples of appropriate concentrations were dissolved in methylene chloride and examined by infra-red spectrometry with the use of a Beckman model IR-12 spectrometer. The amounts of pyrrolic functions were determined by taking area measurements of the absorbances peaking around 3465 cm^{-1} using appropriate base lines (Figure 1). The absorbance of carbazole was used as a reference.

RESULTS AND DISCUSSION

The basicity values of the catalytically treated samples are shown in Table I.

TABLE I
Basicity Values - meg/gm

Catalyst	Basicity	% N Removed	% of Basic Nitrogen
Alumina alone	0.104	-	38
18% MoO ₃ on Al ₂ O ₃	0.038	45	25
24% MoO ₃ on Al ₂ O ₃	0.057	43	37
30% MoO ₃ on Al ₂ O ₃	0.046	40	28
Cu on 2.2% MoO ₃ on Al ₂ O ₃	0.095	-	35
Co on 2.2% MoO ₃ on Al ₂ O ₃	0.068	24	33
V on 2.2% MoO ₃ on Al ₂ O ₃	0.106	17	47
Ni on 2.2% MoO ₃ on Al ₂ O ₃	0.062	31	33
Fe on 2.2% MoO ₃ on Al ₂ O ₃	0.090	8	36

There was no change from the basicity obtained from pure alumina in the case of the vanadium promoted molybdenum on alumina catalyst. The copper and iron promoted catalysts showed small amounts of decreased basicities. The largest decrease in basicity was shown by the 18% molybdenum oxide on alumina and in this case there was also the largest amount of denitrogenation had taken place. Also the percentage of nitrogen that was basic was the lowest for this sample.

The amounts of pyrrolic compounds in the samples are shown in Table II.

TABLE II
Pyrrolic Functions - Meg/100 gms

Catalyst		% N in Functions
Al ₂ O ₃ alone	9.50	35
18% MoO ₃ on Al ₂ O ₃	5.73	38
24% MoO ₃ on Al ₂ O ₃	6.00	39
30% MoO ₃ on Al ₂ O ₃	7.24	44
Cu on 2.2% MoO ₃ on Al ₂ O ₃	10.05	37
Co on 2.2% MoO ₃ on Al ₂ O ₃	8.76	43
V on 2.2% MoO ₃ on Al ₂ O ₃	9.97	40
Ni on 2.2% MoO ₃ on Al ₂ O ₃	7.89	42
Fe on 2.2% MoO ₃ on Al ₂ O ₃	9.54	38

The largest decrease in pyrrolic groups occurred in the sample treated with the unpromoted molybdenum on alumina catalysts and the lower amounts of molybdenum are more effective as is the case with nitrogen removal. The copper and vanadium promoted catalyst resulted in more pyrrolic groups than in the samples treated with only alumina. Iron appeared to have no effect on pyrrolic groups.

TABLE III

Amounts of Nitrogen Accounted for by Basic and Pyrrolic Groups

Catalyst	
Al ₂ O ₃ alone	73%
18% MoO ₃ on Al ₂ O ₃	63
24% MoO ₃ on Al ₂ O ₃	76
30% MoO ₃ on Al ₂ O ₃	72
Cu on 2.2% MoO ₃ on Al ₂ O ₃	72
Co on 2.2% MoO ₃ on Al ₂ O ₃	76
V on 2.2% MoO ₃ on Al ₂ O ₃	87
Ni on 2.2% MoO ₃ on Al ₂ O ₃	75
Fe on 2.2% MoO ₃ on Al ₂ O ₃	74

If it is assumed that no pyrrolic groups are strongly basic, and from other work it appears that this is the case, then basic and pyrrolic groups account for the major amounts of nitrogen in the samples as shown in Table III. The sample involving the 18% unpromoted molybdenum is the lowest and the catalyst promoted with vanadium is the highest.

REFERENCES

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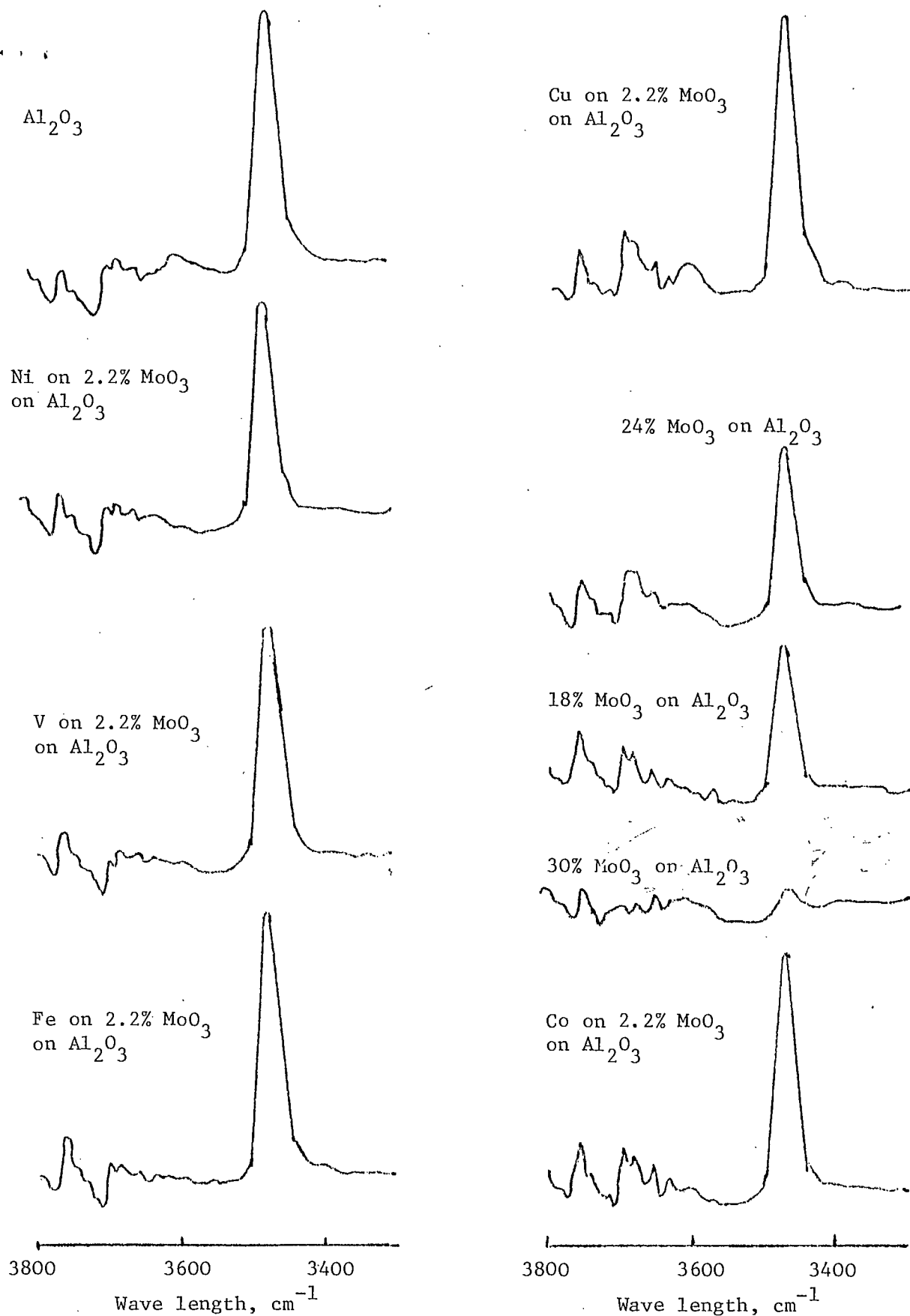


FIGURE 1 Infrared Spectra