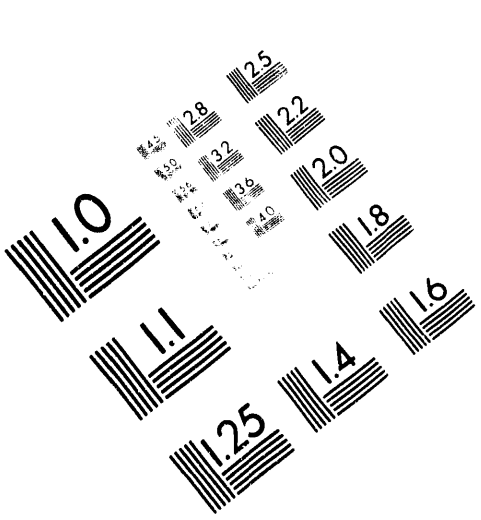

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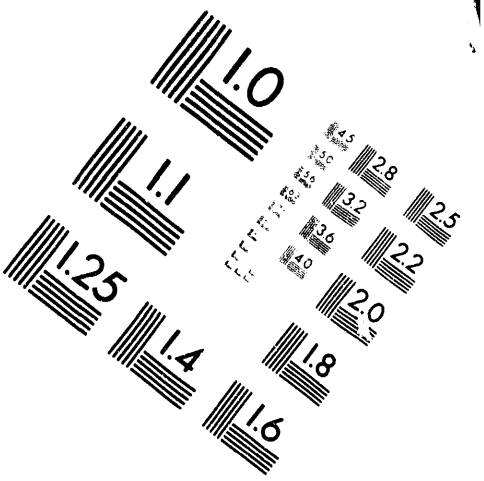

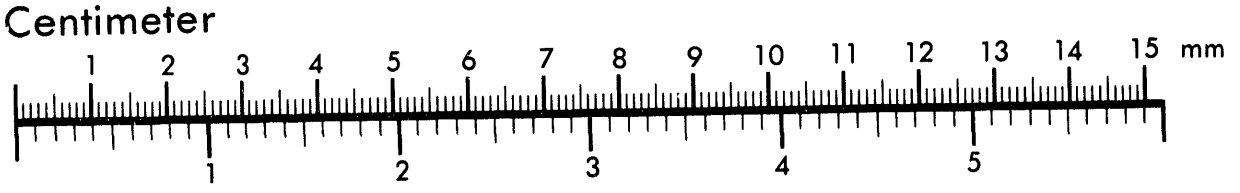

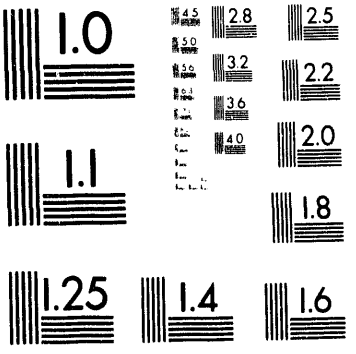

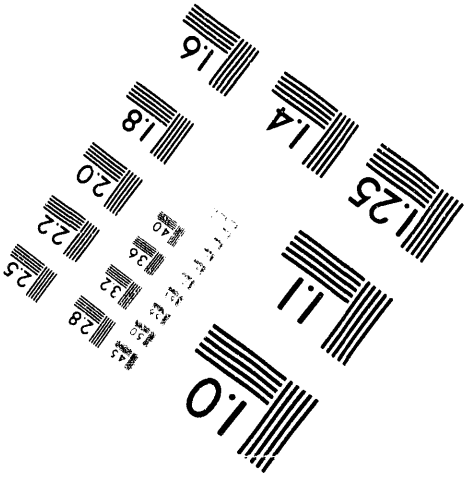

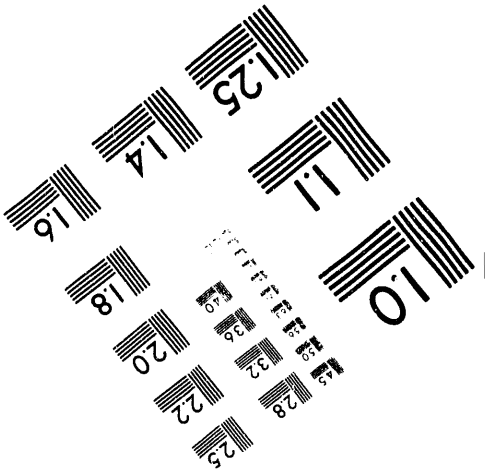

1 of 1

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QUARTERLY TECHNICAL PROGRESS REPORT

FOR PERIOD ENDING

MARCH 31, 1993

RATE ENHANCEMENT FOR CATALYTIC UPGRADING COAL NAPHTHAS

#DE-AC22-90PC91058

P.I.: B. H. Davis

Begin Date: 9/30/91

End Date: 9/29/93

QUARTERLY TECHNICAL PROGRESS REPORT

Rate Enhancement for Catalytic Upgrading Naphthas - Period ending March 31, 1993

Contract No.: DE-AC22-90PC91058

Contractor: University of Kentucky Research Foundation
Kinkead Hall
Lexington, KY 40506-0057

Starting Date: September 30, 1991

Ending Date: September 29, 1993

SUMMARY

The study of the removal of heteroatoms from naphtha using second row unsupported metal sulfide catalysts was completed. For the HDS reaction, the maximum and minimum % sulfur removal, based on three grams of catalyst, is obtained for molybdenum sulfide and niobium sulfide, respectively. Chianelli et al.(1) reported for the second row transition metals that ruthenium sulfide has the highest activity for HDS of dibenzothiophene and zirconium sulfide has the lowest activity.

The maximum activity for HDN, based on three grams of catalyst, is obtained for molybdenum sulfide and the minimum activity is obtained for niobium sulfide, just as was the case for the HDS reaction.

A HDS of dibenzothiophene was carried over the unsupported second row transition metal sulfides following the procedure of Chianelli (1). The results show that the transition metal sulfides prepared at the CAER were similar in activity for HDS of dibenzothiophene as those prepared by Chianelli et al.(1).

INTRODUCTION

Exxon workers(1) showed that some metal sulfides of the second and third row transition metals were more than 10 times as active as MoS_2 for the hydrodesulfurization of dibenzothiophene. Our study is designed to define the possibility of increasing the rate of heteroatom removal by an order of magnitude over the attainable rate with current Co-Mo-alumina or Ni-Mo-alumina catalysts. It is also designed to define whether heteroatom removal has a common rate for all compounds in each heteroatom class or whether some heteroatom compounds are

especially difficult to convert. To characterize a catalyst in terms of its selectivity for individual heteroatom removal reactions for individual compounds in a coal-derived naphtha, methods to determine the amount of each sulfur and nitrogen compounds present in the feed and hydrotreated naphtha is needed. Recently instrumentation with the potential to sample directly from a flame ionization detector to determine the amount of sulfur present in the effluent from a capillary gas chromatograph has become available. Likewise, a nitrogen sensitive GC detector can be utilized for a quantitative determination of individual nitrogen compounds. Thus, the naphtha can be analyzed for composition using a high resolution capillary column gas chromatography.

EXPERIMENTAL:

Hydrotreatment of the Ill. # 6 naphtha sample was carried out using the second row unsupported transition metal sulfides at temperatures of 300 to 400°C. The temperature was varied while holding constant the total pressure (660 psig) and weight hourly space velocity (WHSV = 1 g of feedstock / g of catalyst / hour). For each experiment, 3 grams of the row 2 unsupported transition sulfides was used.

RESULTS

Table 1 shows the conditions and results for the preparation of the row 2 transition metal sulfides. The transition sulfides had intermediate to high surface areas that are comparable to the earlier Exxon work (1).

The nitrogen and sulfur content of products and the % HDN and % HDS are shown in Table 2. These catalysts, except for MoS_x, do not exhibit an especially high

activity for the removal of sulfur and nitrogen, compared to Ni-Mo-alumina and Co-Mo-alumina catalysts.

For the HDS reaction, the maximum and minimum % HDS activity, based on three grams of catalyst, is obtained for molybdenum sulfide and niobium sulfide, respectively (Figure 1). Chianelli et al.(1) reported that ruthenium sulfide has the highest activity for HDS of dibenzothiophene and zirconium sulfide has the lowest activity for the second row transition metals (Figure 2).

The maximum activity for HDN, based on three grams of catalyst, is obtained for molybdenum sulfide and the minimum activity is obtained for niobium sulfide (Figure 3), just as was the case for the HDS reaction.

Since MoS_x shows the maximum activity for the HDS and HDN of Illinois #6 naphtha, Mo_2N catalyst was also synthesized and tested. The Mo_2N was synthesized at atmospheric pressure by temperature-programmed reduction of MoO_3, in ammonia gas (2). The oxide were packed in a quartz tube between pads of quartz wool. The loaded reactor was rapidly increase to ca. 355°C, increased at a rate of 0.6 C/min to 465 C, increased at another rate of 1.8 C/min to 705 C, and held at 705 C in NH_3 for 30 minutes. After the synthesis was over, the reactor was cooled to room temperature under the flow of NH_3 and the sample was "passivated" by air for more than 18 hours. The BET surface area of the Mo_2N catalyst obtained using this method is 153 m^2/g. For the %HDS and %HDN of Illinois #6 naphtha, Mo_2N had higher activity than the row 2 transition metal sulfides, except MoSx, for the removal of sulfur and nitrogen (Figures 1 and 3).

A comparison of the % HDN vs % HDS based on catalyst weight shows that sulfur removal is easier than nitrogen removal (Figure 4).

DISCUSSION

The general shape for the HDS activities with the position of the metal in the periodic table position of second row transition metals using dibenzothiophene (Figure 2) or Illinois #6 naphtha (Figure 1) as feedstock is similar; however, the positions for the maximum and minimum activities are different. This difference may be due to the difference in feedstock and reactor type between our's (coal-derived naphtha and plug flow reactor) and Chianelli's (Dibenzothiophene and batch reactor) studies.

(1) HDS of DBT Using Autoclave Batch Reactor:

The HDS of DBT was carried out over the second row of the transition metal sulfides following the procedure of Pecoraro and Chianelli (1). A reaction system using a 1-liter autoclave was set up to measure rate constants for HDS of DBT over unsupported 2nd row transition meal sulfide catalysts. A schematic diagram of the reaction system is shown in Figure 5. The autoclave is operated in the batch mode with respect to the liquid solution while a small controlled flow rate of hydrogen (0.2 scfh) is continuously added flows into the autoclave through a gas sparger (orifice diameter = 0.5 microns) immersed in the liquid solution. The catalyst is suspended and mixed with the liquid solution by a Magnedrive stirrer operated at 1000 rpm. The product gases flow out of the autoclave and into a condenser (maintained at room temperature) to collect the condensable portion of the gases. A back pressure regulator downstream of the condenser maintains a constant pressure of 450 psig in the autoclave. The liquid solution in the autoclave is sampled during the course of the

reaction via a dip tube filter (orifice size = 0.5 microns) to ensure that the catalyst particles remain in the autoclave. The volume of the sample loop is approximately 2 ml. A description of the procedure follows.

A solution of 4.6 wt. % DBT in decalin is prepared and filtered while hot as given in Pecoraro and Chianelli (1). A known amount of catalyst (about 1.5 g) and 500 ml of the DBT solution is charged into the autoclave. A constant flowrate of hydrogen (0.2 scfh) and a pressure of 450 psig is established in the autoclave. The reactor is then heated to the desired reaction temperature of 350°C. The heat up period typically takes 2 hours and 15 minutes. Samples of the DBT solution are taken before the heat up period, just as the reactor temperature reaches 350°C and during the course of the reaction.

Three products are observed for the HDS of DBT over the transition metal sulfides. The major product for all the catalysts is biphenyl, cyclohexyl benzene and a compound that appears to be hydrogenated DBT (retention time close to DBT and contains sulfur) are present in small amounts.

Figures 6 to 9 show the composition of the liquid solution as a function of time over the transition metal sulfides studied. The mole percentages shown on the y-axis are normalized to a 100% DBT when the temperature reaches 350°C. These figures clearly show biphenyl as the major product of the reaction. While the reaction time is only 8 hours for RuSx, the most active catalyst, the reaction time is 27 hours for the other, less active catalysts.

The mole percent of DBT shows a linear decline with reaction time indicating a zero-order reaction. This is similar to that observed by Pecoraro and Chianelli (1).

Hence, zero-order rate constants are obtained for DBT conversion (figures 10 to 13). The rate constants so obtained are expressed in terms of molecules of DBT converted per gram of catalyst per second (following Pecoraro and Chianelli (1)) and plotted as a function of the position of the transition metal in the periodic table in Figure 14. The data in figure 14 clearly show that the trend in activity for DBT HDS for the transition metal sulfides follow the trend as shown in Pecoraro and Chianelli (1) for DBT HDS activity at 400°C. Further, the rate constants for ruthenium and molybdenum sulfides compare very well with those calculated by Pecoraro and Chianelli (1) at 350°C (Table 3). Pecoraro and Chianelli (1) did not obtain rate constants for the other catalysts at 350°C and hence rate constants for these catalysts cannot be compared. However, they mention that the trend in activity of these catalysts at 350°C is similar to the trend in activity at 400°C as shown by these experiments.

The conclusion drawn from these experiments is that the transition metal sulfide catalysts prepared in our laboratory are similar in activity for HDS of DBT to those prepared by Pecoraro and Chianelli (1).

(2) Effect of Feedstock:

When a heterogeneous catalytic reaction occurs, several processes must take place.

1. Molecular diffusion from the exterior surface of the catalyst particle into the interior pore structure.
2. Chemisorption of the reactants on the catalyst surface.
3. Reaction on the surface.
4. Desorption of adsorbed species from the surface of catalyst.

5. Transfer of products from the interior catalyst to the external surface of the catalysts by diffusion.

In general, hydrotreatment of the heavy fractions of coal derived materials is complicated by the molecular weight, and the corresponding large size, of the molecules converted. The large size introduces severe diffusional problems during processing. However, this is not a problem in the hydrotreatment of coal derived naphtha, since the dominant fraction of the material contains only one ring of five or six carbons; two ring components are the largest molecules that will be encountered and these represent only approximately 10 % of the nitrogen compounds and approximately 24 % of the sulfur compounds. Thus, diffusion limitations due to size exclusion should not be a problem in this study. The remaining three steps, chemisorption of reactant, reaction on the surface, and desorbed products, may play an major role for the naphtha hydrotreatment. Since the naphtha contains hundreds of different compounds, the adsorption competition between compounds would be an important factor for the conversion of heteroatoms. This might be a reason why the maximum conversion is located in different periodic position of second row transition metal between HDS of dibenzothiophene and Illinois #6 naphtha. In order to exam the effect of adsorption competition, variety of feedstocks (DBT in decalin, DBT in naphtha, and DBT in 50 % of decalin and 50 % of naphtha) will be tested over 2nd row transition metal sulfides using batch and plug flow reactors, respectively.

(3) Effect of Reactor type:

The different type of reactors used between our test (plug flow reactor) and Chianelli's test (CSTR) might be another reason why the maximum conversion is

located in different periodic position of second row transition metal sulfide. In order to clarify this point, the same feedstock used in Chianelli's test will be used in our plug flow reactor to obtain the HDS of DBT rates over unsupported 2nd row transition metal sulfides.

REFERENCES

1. T. A. Pecoraro and R. R. Chianelli, *J. Catal.*, **67**, 430 (1981).
2. L. Volpe and M. Boudart, *J. Solid State Chem.*, **59**, 332 (1985).

Table 1

Row 2 Transition Sulfide Preparation Conditions and Results

	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Metal	30g	30g	20g		20g		
Chloride	$ZrCl_4$	$NbCl_5$	$MoCl_5$		$RuCl_3$		
Li_2S	11.83g	12.75g	8.38g		6.64g		
EA, mL	None	None	None		800		
THF, mL	800	800	800		None		
S_g, m^2/g	2.84	50.17	33.84		26.65		

EA = Ethyl Acetate
THF = Tetrahydrofuran
S_g = Surface Area

Table 2

HDS and HDN of Illinois #6 Naphtha using Row 2 Transition Metal Sulfides

Temp. °C	Pressure, psig	Catalyst	Nitrogen, % HDN	Sulfur, % HDN
300	660	ZrS_x	22.0	27.2
300	660	NbS_x	21.4	26.2
300	660	MoS_x	51.1	80.8
300	660	RuS_x	28.8	44.6
300	660	PdS_x	33.4	40.4
300	660	$Mo2_N$	48.1	55.1
350	660	ZrS_x	28.2	40.6
350	660	NbS_x	25.1	34.7
350	660	MoS_x	81.5	93.9
350	660	RuS_x	34.3	58.9
350	660	PdS_x	37.2	56.6
350	660	$Mo2_N$	57.2	79.9
400	660	ZrS_x	33.9	62.0
400	660	NbS_x	26.6	50.7
400	660	MoS_x	93.6	98.6
400	660	RuS_x	37.6	67.2
400	660	PdS_x	39.9	64.2
400	660	$Mo2_N$	63.8	85.7

Table 3

Rate Constants (zero-order) for the HDS of DBT over 2nd Row Transition Metal Sulfides

	Rate Constant (molecules DBT/g cat-sec)	
Catalyst	CAER	Percoraro & Chianelli
RuS_2	1.2×10^{18}	1.55×10^{18}
MoS_2	1.1×10^{17}	1.00×10^{17}
PdS	6.3×10^{16}	---
NbS	1.2×10^{16}	---

DATE
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