

CATALYTIC HYDROTREATMENT OF COAL-DERIVED NAPHTHA USING FIRST ROW TRANSITION METAL SULFIDES

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ABSTRACT

This study is designed to define the possibility of increasing the rate of heteroatom removal from coal-derived naphtha by an order of magnitude greater than the current hydrodesulfurization catalysts. For the unsupported first row transition metal sulfide catalysts, maxima HDS activity is obtained for chromium sulfide and the minimum HDS activity is obtained for manganese sulfide. This is similar to the results presented by Chianelli et al. for hydrodesulfurization of dibenzothiophene. The maximum HDN activity is obtained for chromium sulfide and the minimum HDN activity is obtained for cobalt sulfide. The effect of substituents on the conversion of nitrogen compounds in the naphtha varied. The HDN of alkyl-substituted pyridine and aniline is dominated by an electronic, rather than a steric, effect. The effect of alkyl-substitution on the reactivity of quinoline is relatively small.

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 MoS₂ 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 rate attainable 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 III. # 6 naphtha sample was carried out using the first row unsupported transition metal sulfides at temperatures of 350 and 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 1 unsupported transition sulfide was used.

Individual nitrogen compounds of the hydrotreated III. #6 naphtha were analyzed using a Thermionic Specific Detector (TSD) coupled with an Varian 3700 gas chromatograph containing a carbowax column. Sulfur compounds were analyzed using a Sievers Model 350B Chemiluminescence Sulfur Detector (CSD) coupled with an HP 5890 Series II gas chromatograph containing a SPB-1 column. Identification of the nitrogen and sulfur compounds was accomplished by comparison of the retention time to a standard compound.

RESULTS

The conditions and results for the preparation of the transition metal sulfides are given in Table 1. Transition metal sulfides with intermediate to high surface areas were obtained; these are comparable to the earlier Exxon work. The nitrogen and sulfur content of products and the % HDN and % HDS are shown in Table 2. These catalysts 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 % HDS activity, based on three grams of catalyst, is obtained for chromium sulfide (Figure 1). Increasing the temperature from 350°C to 400°C results an increase of approximately 25 % for sulfur removal. Chianelli et al.(1) reported that chromium sulfide has the highest activity for HDS of dibenzothiophene and manganese sulfide has the lowest activity for the first row transition metals.

The % HDN based on catalyst weight is approximately the same for all of the catalysts, about 40 % (Figure 2). Increasing the temperature from 350 to 400°C results an increase of approximately 10 % for nitrogen removal.

A comparison of the % HDN vs % HDS based on catalyst weight shows that sulfur removal varies while nitrogen removal remains nearly constant (~40%) (Figure 3).

Conversion of Individual Nitrogen Compounds:

The conversion of individual nitrogen compounds was studied at 350°C, 660 psig and a weight hourly space velocity of 1 g/g/hr.

Pyridines

Figure 4 shows the results, as a typical example, for the conversion of compounds in the pyridine class using an iron sulfide catalyst. For this class, pyridine is the easiest compound to convert for all of the catalysts. The rate of conversion of pyridine substituted by a methyl or ethyl group decreases in the order: unsubstituted > 4- > 2- > 3- for all catalysts. Similar results were observed for the commercial Co-Mo-Alumina and Ni-W-Alumina catalysts. Pyridines with substituents of 2 or more carbons are harder to convert than pyridine with a one carbon substituent.

Anilines

The conversion of compounds in the aniline class, using iron sulfide (Figure 5), as a typical example, shows that unsubstituted aniline is the easiest compound to convert; this is analogous to the pyridine class where the unsubstituted compound is easier to convert. For all catalysts, anilines substituted with 2 to 4 carbons are harder to convert than anilines with only a one carbon substituent. These figures also show that the conversion of nitrogen compounds depends on the position the group(s) substituted on the ring. The rate of conversion for the mono-methyl or mono-ethyl substituted anilines are: unsubstituted > 4- \approx 2- > 3-. This is the case for all catalysts. However, the conversion of mono-methyl and mono-ethyl aniline is not as dependent on substituents or their ring position as the pyridines were.

Quinolines

Figure 6 shows results of the conversion of compounds in the quinoline class using iron sulfide as a typical example. The data show that quinoline is harder to convert than the pyridines were. Unsubstituted quinoline, is converted at about the same rate as one carbon alkyl substituted quinoline with the all catalysts.

DISCUSSION

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.

Alkyl-substituted heterocyclic compounds were found in the Illinois #6 naphtha. The position of the substituent influences the rate of HDN. For the first row unsupported transition metal catalysts, HDN reactivities of pyridine, aniline and quinoline varies according to the position of substituent added as follows:

pyridine > 4-R-pyridine > 2-R-pyridine > 3-R-pyridine,
Aniline > 4-R-Aniline \approx 2-R-Aniline > 3-R-Aniline, and
Quinoline \approx 3-Methyl-Quinoline \approx 4-Methyl-quinoline,
where R = methyl or ethyl group. 2-Methylquinoline is present in the naphtha in such small quantities that its conversion could not be followed.

Many publications(2-5) have reported that steric and electronic effects may play an important role for the HDS of a number of sulfur compounds. From the point view of steric hindrance by a substituent group, the order of reaction rates for HDN should be $4 > 3 > 2$. However, from the point view of electronic effect, the rates should be $4 \approx 2 > 3$. HDN of alkyl-substituted anilines and pyridines show the order expected for an electronic effect. The effect of alkyl substituents on the reactivity of quinoline is relatively insignificant. Gates et. al.(5) reported that HDN conversion of 2,6-, 2,7-, and 2,8-dimethylquinoline is approximately the same as that of quinoline.

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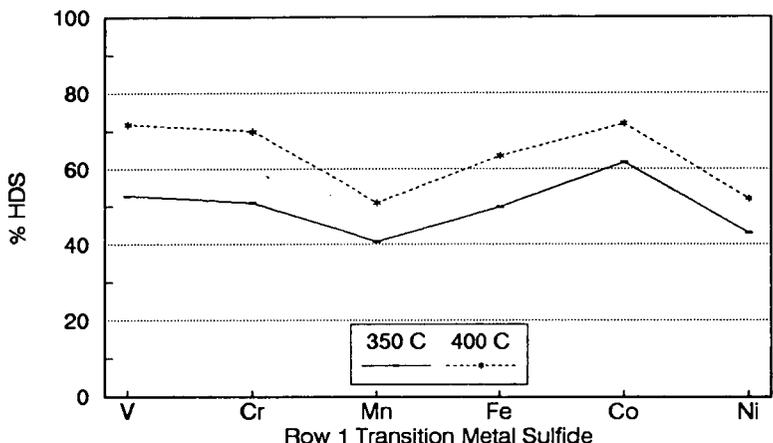
REFERENCES

1. T.A. Pecoraro and R. R. Chianelli, J. Catal., 67, 430(1981).
2. B. C. Gates, J. R. Katzer, and G. C. A. Schuit, "Chemistry of Catalytic Processes," McGraw-Hill, New York, 1979.
3. M. Houalla, D. H. Broderick, A. V. Sapre, N. K. Nag, V. H. J. Beer, B. C. Gates, and H. J. Kwart, J. of Catal., 61, 523(1980).
4. J. H. Singhal, R. L. Espino, and J. E. Sobel, J. Catal., 67, 446(1981).
5. B. C. Gates, J. R. Katzer, J. H. Olson, H. Kwart, and A. B. Stiles, Quarterly Report to DOE, June 21 to September 20, 1978.

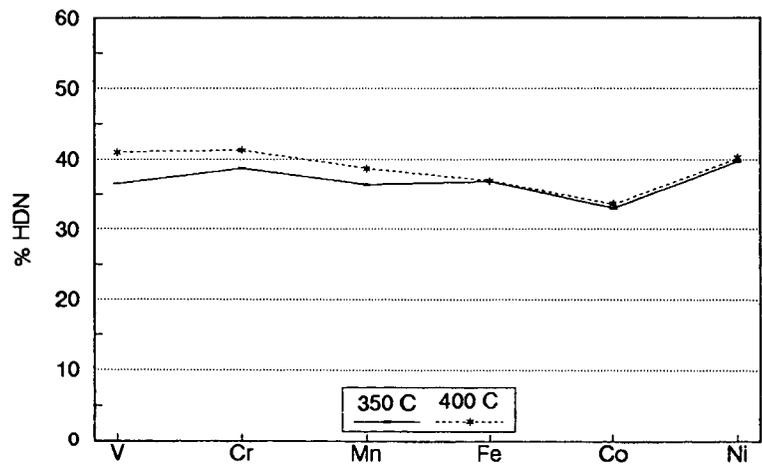
Table 1							
Row 1 Transition Sulfide Preparation Conditions and Results							
	Ti	V	Cr	Mn	Fe	Co	Ni
Metal	20g	20g	25g	25g	25g	30g	25g
Chloride	TiCl ₄	VCl ₄	CrCl ₃	MnCl ₃	FeCl ₃	CoCl ₂	NiCl ₂
Li ₂ S	9.70g	9.53g	10.88g	10.68g	10.83g	5.79g	8.86g
EA, mL	None	None	None	800	800	800	800
THF, mL	800	800	800	None	None	None	None
S _a , m ² /g	4.4	25.82	13.02	1.7	10.18	9.34	1.99

EA = Ethyl Acetate
 THF = Tetrahydrofuran
 S_a = Surface Area

Table 2						
Nitrogen and Sulfur Content of Products from the Hydrotreatment of Illinois #6 Naphtha						
Temp. °C	Pressure, psig	Catalyst	Nitrogen, Wt. ppm	Sulfur, Wt. ppm	Nitrogen % HDN	Sulfur % HDS
350	660	VS _x	1030	370	36.6	52.8
350	660	CrS _x	996	385	38.7	50.9
350	660	MnS _x	1058	465	36.4	40.7
350	660	FeS _x	1049	393	36.9	49.9
350	660	CoS _x	1113	301	33.1	61.6
350	660	Ni ₂ N	977	446	39.8	43.1
400	660	VS _x	958	223	41.0	71.6
400	660	CrS _x	953	237	41.3	69.8
400	660	MnS _x	995	385	38.7	50.9
400	660	FeS _x	1047	288	37.0	63.3
400	660	CoS _x	1103	220	33.7	71.9
400	660	Ni ₂ N	970	376	40.3	52.0



Row 1 Transition Metal Sulfide
 Figure 1. HDS of Illinois #6 Naphtha



Row 1 Transition Metal Sulfide
 Figure 2. HDN of Illinois #6 Naphtha

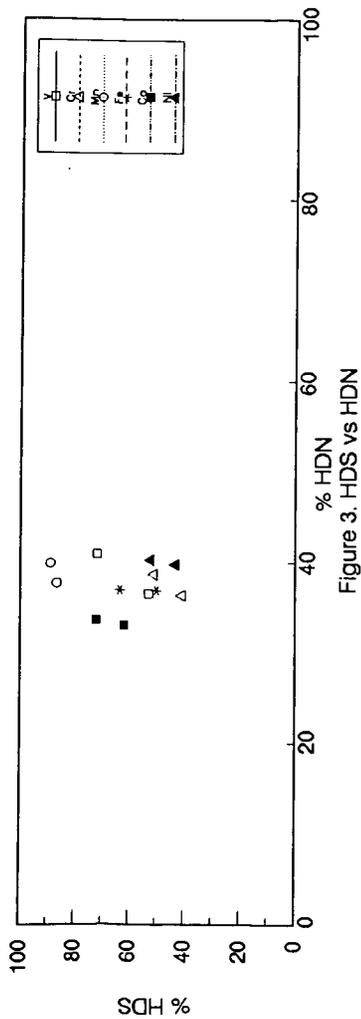


Figure 3. HDS vs HDN

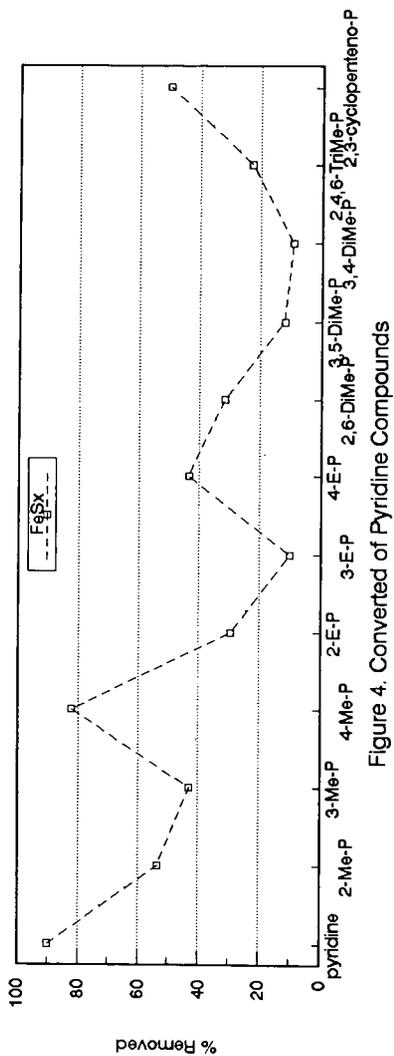


Figure 4. Converted of Pyridine Compounds

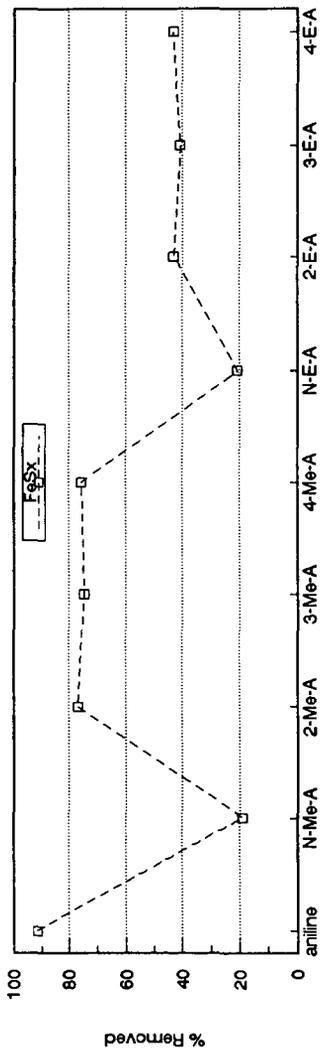


Figure 5. Conversion of Aniline Compounds

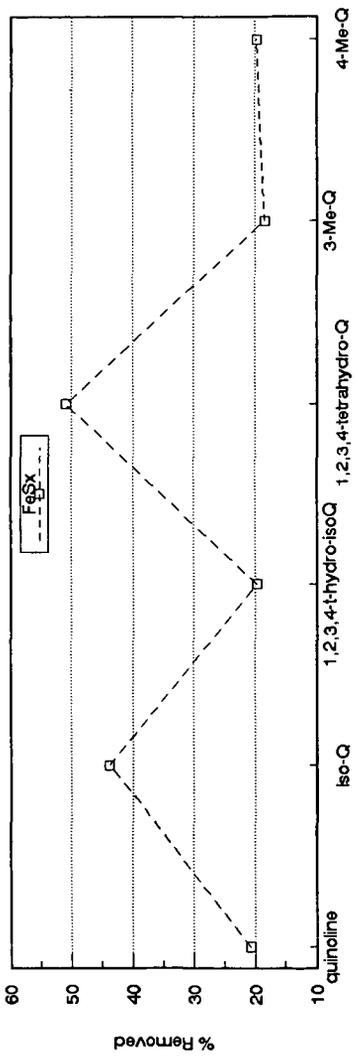


Figure 6. Conversion of Quinoline Compounds