



Factors affecting the activity of cobalt molybdate desulfurization catalysts
by Joseph Richard Kioovsky

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Abstract:

The objective of this study was to determine the factors that affect the activity of hydrodesulfurization catalysts. The determination of catalyst activity was made by two distinct methods. One of these methods is defined as the conversion obtained at specified conditions with a standard oil divided by the conversion obtained at the same conditions over new catalyst. The second method is designed, to give an activity measurement that is proportional to the ratio of the reaction rate constant of the desulfurization reaction at specified conditions over used catalyst to the rate over new catalyst. The "bench mark" method was used to obtain the two activities defined above. In this method a standard oil is run, at standard conditions, over the catalyst at the end of each run. The conversion obtained on the bench mark oil is used to calculate the two activity measures.

The conclusions reached were very similar using these two activity measurements. There is theoretical basis for favoring the second method, however. The conclusions reached are listed below and are results of studying Houdry Series "C" catalyst.

1. The space velocity, temperature, pressure and throughput have little influence on catalyst activity over the range studied.
2. Of the feedstock variables, the nitrogen content was the most detrimental to activity.
3. The effects of sulfur content and boiling point seemed to be entangled and no conclusions were drawn as to their individual effects.
4. High values of API gravity are least harmful to catalyst activity.
5. The K factor of the stock had little influence on activity. However, this may be due to the small range of this variable.
6. Equations were obtained (see Conclusions) which appear to make possible the accurate prediction of the effect of any feedstock on catalyst activity.
7. If a stock is run which contains insufficient sulfur to keep the catalyst in the Wulfided form, the subsequent use of a high sulfur stock does not sulfide the catalyst.

FACTORS EFFECTING THE ACTIVITY OF COBALT MOLYBDATE

DESULFURIZATION CATALYSTS

by

JOSEPH RICHARD KIOVSKY

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Approved:

Head, Major Department

Chairman, Examining Committee

Dean, Graduate Division

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ABSTRACT

The objective of this study was to determine the factors that affect the activity of hydrodesulfurization catalysts. The determination of catalyst activity was made by two distinct methods. One of these methods is defined as the conversion obtained at specified conditions with a standard oil divided by the conversion obtained at the same conditions over new catalyst. The second method is designed to give an activity measurement that is proportional to the ratio of the reaction rate constant of the desulfurization reaction at specified conditions over used catalyst to the rate over new catalyst. The "bench mark" method was used to obtain the two activities defined above. In this method a standard oil is run, at standard conditions, over the catalyst at the end of each run. The conversion obtained on the bench mark oil is used to calculate the two activity measures.

The conclusions reached were very similar using these two activity measurements. There is theoretical basis for favoring the second method, however. The conclusions reached are listed below and are results of studying Houdry Series "C" catalyst.

1. The space velocity, temperature, pressure and throughput have little influence on catalyst activity over the range studied.
2. Of the feedstock variables, the nitrogen content was the most detrimental to activity.
3. The effects of sulfur content and boiling point seemed to be entangled and no conclusions were drawn as to their individual effects.
4. High values of API gravity are least harmful to catalyst activity.
5. The K factor of the stock had little influence on activity. However, this may be due to the small range of this variable.
6. Equations were obtained (see Conclusions) which appear to make possible the accurate prediction of the effect of any feedstock on catalyst activity.
7. If a stock is run which contains insufficient sulfur to keep the catalyst in the sulfided form, the subsequent use of a high sulfur stock does not sulfide the catalyst.

INTRODUCTION

Justification for Desulfurization:

Desulfurization has come into importance since it has become necessary to use crude oils that are high in sulfur content. Crude oils from California, Wyoming and many Texas fields may contain as much as 3.0% sulfur.^{57,58} Oils from the Middle East are also high in sulfur content.^{58,7} Furthermore, if shale oils and tar sand oils come into widespread use, it will even further aggravate the sulfur removal problem.³ Also, shale oil is rich in oxygen and nitrogen^{11,19,20} compounds which are removed by methods similar to sulfur removal methods.

There are many reasons for desulfurizing petroleum products. Some of these reasons are listed below:

1. Reduction or elimination of corrosion during refining, handling, or use of most petroleum fractions.²⁴
2. Sulfur removal results in an improvement in the odor of many petroleum products.
3. The color stability and tetra-ethyl lead susceptibility of gasolines are improved.^{27,40}
4. The smoking tendency of kerosene and wick deposits therefrom are improved. Also, its properties as a jet or rocket fuel are improved.³⁴
5. Diesel fuel quality is improved by the elimination of corrosive combustion products.

6. Desulfurization makes possible the use of heavy fuel oils in steel open-hearth furnaces and improves their properties in ship engines and steam plants.³²
7. Low sulfur contents are necessary in heavy tars which are coked to produce raw material for synthetic graphite and electrode manufacture.
8. The catalytic cracking properties of gas oils are improved by desulfurization.^{17,24}
9. Sulfur compounds poison the platinum catalysts used in the reforming process for the production of high-octane gasoline.²⁵

Obviously, then, there is ample motivation for the desulfurization of almost the entire spectrum of petroleum products. This motivation also prompts one to try to understand the operation of the desulfurization process and investigate its operation on a fundamental level.

Types of Sulfur Compounds in Petroleum:

The presence of elemental sulfur in some crude oils has actually been proven by Eccleston, Morrison and Smith.²¹ However, elemental sulfur accounts only for a small part of the sulfur in most oils.

The work of Hale, Thompson, Barker, Smith and Ball¹⁵ on naphthas from seventeen crude oils shows the sulfur to be present mainly as S, H₂S, disulfides, mercaptans, aliphatic and cyclic sulfides, thiophenes and aromatic sulfides. The most extensive investigation has been that

of the American Petroleum Institute's Project 48 on Wasson, Texas crude oil.⁶¹ With respect to the portion of this crude boiling up to 453°F (approximately the mid-boiling point of kerosene) the following conclusions can be made.

1. Forty compounds were identified boiling below 346°F, including alkane thiols, aliphatic sulfides and alicyclic sulfides.
2. Of these compounds, secondary thiols are the most abundant. However, their concentration becomes negligible in fractions containing above 12 to 13 carbon atoms per molecule.
3. Primary thiols disappear in fractions with more than 5 to 6 carbon atoms per molecule.
4. Tertiary thiols were not present in this fraction.
5. In general, the content of aliphatic sulfides decreases and that of alicyclic sulfides increases with increasing molecular weight.

The Wasson crude was also topped at 328°F and de-asphaltened (n-pentane insolubles removed). The remaining 76.1 percent of the crude contained sulfur compounds of which 65 percent were benzothiophenes, dibenzothiophenes, or four-ring thiophenes. The remainder of the sulfur compounds were predominately sulfides with some simple (one-ring) thiophenes.

McCoy and Weiss⁴³ state that there are very few compounds in petroleum in which the sulfur atom is connected to more than one benzene ring such as in diphenyl sulfide.

In gas oils (fraction boiling between approximately 650 to 1000°F) the preponderant sulfur compounds are benzothiophenes.²⁶ Gas oils from Texas, Venezuela, and the Middle East showed 60 to 70 percent of the sulfur to be in the form of benzo- and dibenzothiophenes.

The results of this and other work^{4,6,9,54,60} support the observation that the aromaticity of the sulfur compounds increases with increasing molecular weight.

The Hydrodesulfurization Reaction:

The predominant method used for the commercial removal of sulfur from oils is hydrodesulfurization. This process involves the reaction of sulfur compounds with hydrogen over a mild hydrogenation catalyst to produce hydrocarbons and H₂S.

In general, these reactions are carried out at 600 to 800°F and at pressures of 250 to 1000 psig.

The typical reactions that the several types of sulfur compounds found in petroleum undergo at high temperatures and pressures over mild hydrogenation catalysts are shown below.⁴⁴

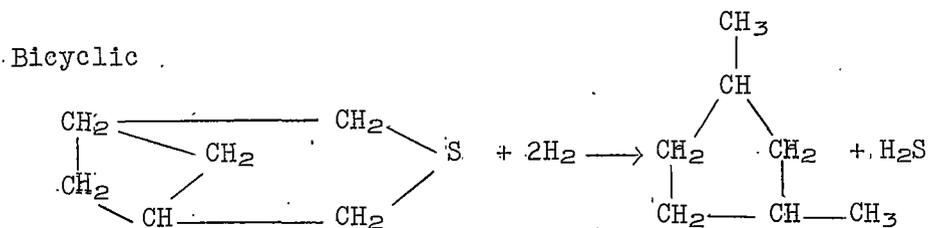
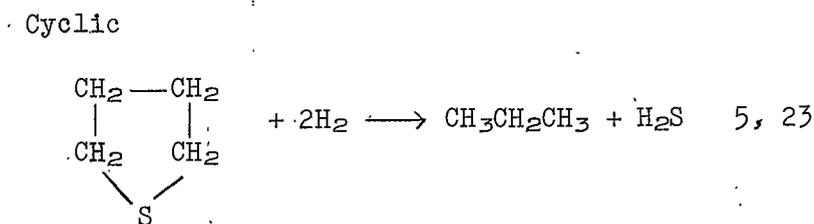
TABLE I

HYDRODESULFURIZATION REACTIONS

I. Thiols: References
 $*RSH + H_2 \longrightarrow RH + H_2S$ 8, 13, 18, 30, 36

II. Disulfides:
 $RSSR + H_2 \longrightarrow 2RH + 2H_2S$ 30, 62

III. Sulfides:
 Aliphatic
 $R-S-R' + 2H_2 \longrightarrow RH + R'H + H_2S$ 18, 30



IV. Thiophenes:

$$\begin{array}{c}
 \text{CH} - \text{CH} \\
 || \quad || \\
 \text{CH} \quad \text{CH} \\
 \diagdown \quad / \\
 \text{S}
 \end{array}
 + 4H_2 \longrightarrow CH_3CH_2CH_2CH_3 + H_2S$$
8, 9, 13, 22, 23,
26, 36, 48

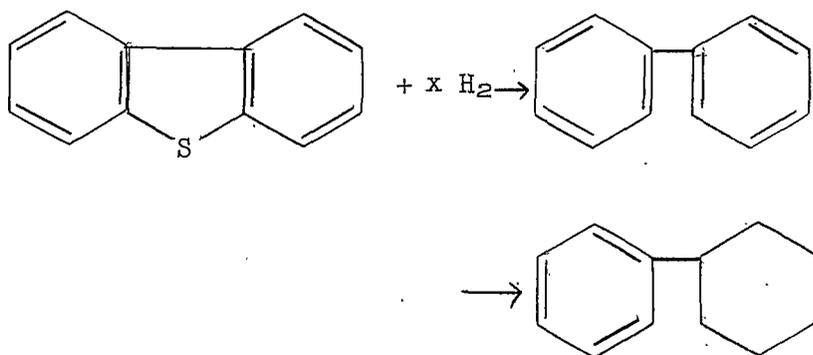
V. Benzothiophenes:

$$\begin{array}{c}
 \text{C}_6\text{H}_4 \\
 | \\
 \text{C}_2\text{H}_2\text{S}
 \end{array}
 + 3H_2 \longrightarrow \text{CH}_3\text{-CH}_2\text{-C}_6\text{H}_5 + H_2S$$
14, 29

TABLE I (continued)

VI. Dibenzothiophenes:

Reference



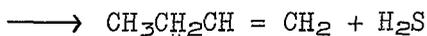
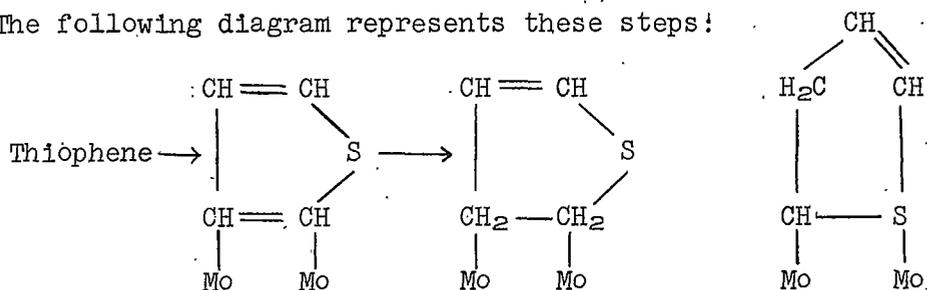
*R = alkyl or aryl group

Examination of this table and other data indicate the major reaction to be simple carbon-sulfur bond rupture and saturation of the free valencies. Diolefins and the majority of mono-olefins are usually saturated. Ordinarily, aromatic double bonds are not saturated due to the inactivity of the catalyst for the reaction. However, in the case of dibenzothiophenes partial ring saturation may precede the rupture of the carbon-sulfur bond.

These reactions have been substantiated by a great deal of pure compound work. The references in Table I are to the pure compound work on each type of compound. Particularly interesting is the work of Griffith, Marsh and Newling,²³ who proposed the mechanism of thiophene hydrodesulfurization over the $\text{MoO}_2\text{-MoS}_2$ catalyst they used. Their mechanism is:

1. Two point absorption of the thiophene on a pair of adjacent Mo atoms in an exposed plane of the MoS₂ lattice;
2. Conversion to the half-hydrogenated state by reaction with hydrogen atoms absorbed on an adjacent site;
3. Rupture of the carbon-sulfur bond by reaction of more hydrogen atoms with the half-hydrogenated molecule in which the sulfur atom has become linked to a molybdenum atom.
4. Conversion of the absorbed molecule to butane or butene by continued reaction with more hydrogen atoms.

The following diagram represents these steps:



Kinetics of Hydrodesulfurization:

Pure compound work by several investigators has shown that in general non-thiophenic compounds react much more rapidly than thiophenic compounds.

TABLE II

SULFUR COMPOUNDS ARRANGED IN DECREASING ORDER OF REACTION RATE
AS REPORTED BY VARIOUS WORKERS

<u>Compounds</u>	<u>Reference</u>
Benzene thiol-ethane thiol 3 me-1 butane thiol - debenzyl sulfide - di-isopropyl sulfide - di-isoamyl sulfide	47
Benzene thiol - carbon disulfide - thiophene	13
Di-isopropyl sulfide - thiophene	22
1-butane thiol - thiophene	46
Thiacyclopentane - thiophene	23

Several papers^{9,22,45} deal with the desulfurization of thiophene in benzene over MoS_2 catalysts. They state that the reaction varies from zero to first order with respect to sulfur.

Griffith, Marsh, and Newling²³ concluded that the rate controlling step was the absorption of hydrogen on the MoS_2 surface.

Work on petroleum fractions^{10,12,44} also indicates the following order of stability: thiols - disulfides - sulfides - thiophenes.

There is little work available to show what effect aromatic structure has on reaction rate. About all that can be said from the available data^{28,32} is that stability increases with molecular weight.

Hoog²⁸ showed that the desulfurization data for narrow boiling fractions of petroleum could be correlated by assuming a first order reaction

with respect to sulfur. This seems to be generally true with respect to petroleum desulfurization at commercially used conditions where hydrogen is always present in large excess.

Mahugh⁴¹ investigated the effect of the structure of the oil in which sulfur compounds were dissolved, upon the rate of desulfurization. He showed that a paraffinic oil solvent resulted in a faster rate than an aromatic one. Furthermore, he found the reaction to be further retarded by the presence of condensed ring aromatics in the solvent oil.

Hydrodesulfurization Catalysts:

The literature on hydrodesulfurization catalysts is too voluminous to be reported here. For a good review of the literature up to 1956, see reference 44. For more recent data the yearly reviews of progress in hydrogenation in Industrial and Engineering Chemistry should be consulted.

The catalysts almost universally used at present consist of 5-8% MoO promoted by 0.1 to 1.0 percent CoO deposited on a gamma alumina carrier. Almost all commercial catalysts are variations of this formula.

Table III shows the hydrogen reduction equilibria of cobalt and molybdenum at 600 and 900°F. These data are abstracted from the computation of McKinley⁴⁴ from the data of Rossini⁵⁶, Kelly^{37,38}, Rosenquist,⁵⁵ Sudo⁵⁹ and Hulsmann³³.

TABLE III

HYDROGEN REDUCTION EQUILIBRIA OF COBALT AND MOLYBDENUM SULFIDES

$\log_{10} \frac{\text{Moles H}_2\text{S}}{\text{Moles H}_2}$	Molybdenum Species	Cobalt Species
below -4.6	T = 600°F	Co
-4.6 to -0.3		Co ₉ S ₈
-0.3 to 0.5		Co ₃ S ₄
above 0.5		CoS ₂
below -5.6	Mo	
-5.6 to 3.2	MoS ₂	
above 3.2	MoS ₃	
	T = 700°F	
below -4.1		
-4.1 to -0.3		Co
-0.3 to 0.7		Co ₉ S ₈
above 0.7		Co ₃ S ₄
below -4.9	Mo	CoS ₂
-4.9 to 3.2	MoS ₂	
above 3.2	MoS ₃	

The data shown are for the pure metals in a H₂-H₂S atmosphere and probably are not precisely accurate for a catalyst in which the Mo and Co are deposited on a catalyst support and the atmosphere is oil-H₂-H₂S. However, analysis of commercial operations shows that the catalyst is usually in the form MoS₂, Co₉S₈. That the most active form of the catalyst

is obtained when the metals are sulfided is borne out by the fact that sulfiding with H_2S increases the initial activity¹⁶.

Catalyst Activity:

The fact that the catalyst loses its ability to catalyze the desulfurization reaction with use has been recognized for many years. Hale, Simmons, and Whisenhunt²⁴ thought that the activity decline of their Co-Mo on bauxite catalyst was due to the carbon deposited on the catalyst during use. Similarly, Cole and Davidson¹⁶ thought that the activity decline of tungsten-nickel sulfide catalyst was due to "tarry deposits".

It has been reported³² that heavy reduced crude oils deactivate the catalyst more rapidly than distillates. Also, the decline in sulfur conversion seems to be linear with the logarithm of throughput². Hughes, et. al.,³² report that space velocity has little effect on the rate of activity decline. Another important conclusion by these investigations is that the extent of vaporization of the oil has little effect on activity decline. The effect of nitrogen in the feedstock has received some attention. The harmful effect of nitrogen compounds on cracking catalysts has been known for some time.^{42,45} Ballard, et. al.,² report that acid washing of the feedstock reduced the rate of activity decline. They thought that this was because of the removal of basic nitrogen compounds. However, they did not measure the nitrogen content. Kirsh, Shalit, and Heinemann³⁹ showed that the addition of pyridine to a thiophene-heptane mixture reduced the catalyst's ability to remove sulfur. Also, quinoline

reduced the activity for sulfur removal from cracked naphthas. They were using a presulfided Co-Mo on alumina catalyst.

Opprecht⁵⁰ reports that the higher the aromatic content of oils the more rapid is the catalyst activity decline. He reached this conclusion by blending low and high aromatic content stocks, so it seems that the change in deactivation may also have been due to other parameters since blending also gave various nitrogen concentrations, molecular weights, etc.

Catalyst Activity Measurement:

Hougan³¹ states that "the principles involved in the selection of catalysts and the factors determining catalytic activity still remain obscure." Consequently, there is widespread disagreement on how to measure catalyst activity.

The two predominant methods are basically as shown below:

$$A_1 = \frac{C_O}{C_N}$$

$$A_2 = \frac{k_O}{k_N}$$

Where: A_1 and A_2 are the activities by the two methods.

C_N = conversion of a certain reaction over new or unpoisoned catalyst

C_O = conversion of the same reaction over old or deactivated catalyst

k_0 = reaction rate constant for a specific reaction over deactivated catalyst

k_N = reaction rate constant for the same reaction over new or unpoisoned catalyst

Pozzi and Rase⁵² recommend the first method and give its theoretical justification as follows:

In general, the reaction rate can be expressed

$$r = L_N \phi (P_A, P_B, \dots, t)$$

Where:

r = reaction rate

L_N = the number of active sites per unit mass of catalyst at an arbitrary activity level

ϕ = functional relationship between partial pressure, temperature and rate

Then at any time τ

$$r = L_\tau \phi (P_A, P_B, \dots, t)$$

Where:

L_τ = number of active sites per unit mass of catalyst at any time τ

Then, say,

$$\frac{L_\tau}{L_N} = \text{activity factor}$$

Let the initial conversion = C_N and $L = L_0$

Then:

$$\frac{W}{F} = \int_0^{C_N} \frac{dx}{L_N \phi (P_A, P_B, \dots, t)}$$

Where: W = weight of catalyst

F = weight feed/hour

And at any later time:

$$\frac{W}{F} = \int_0^{C_0} \frac{dx}{L_{\eta} \phi (P_{\mu}, P_{\nu}, \dots, t)}$$

$$\frac{\frac{L_{\eta}}{L_0} \int_0^{C_0} \frac{dx}{\phi (P_{\mu}, P_{\nu}, \dots, t)}}{\int_0^{C_N} \frac{dx}{\phi (P_{\mu}, P_{\nu}, \dots, t)}}$$

The evaluation of this expression requires knowledge of the functional relationship ϕ .

However, we can approximate L_{η}/L_0 .

$$\frac{L_{\eta}}{L_0} \approx \frac{C_0}{C_N}$$

This approximation becomes less accurate as C_0 and C_N become further apart.

$\therefore \frac{C_0}{C_N} = A_I$ is an approximation to the fraction of active sites remaining at time τ .

The second method is widely used.^{50,63} The common method for the evaluation of $A_2 = k_0/k_N$ is shown below.

At a given space velocity $1/(\frac{W}{F})_1$ over new catalyst the reaction rate constant is k_N and a conversion C_N is reached.

$$\frac{1}{SV_1} = \left(\frac{W}{F}\right)_1 = \int_0^{C_N} \frac{dC_N}{kC(1-C_N)}$$

or if volume of reaction mass remain nearly constant

$$\left(\frac{W}{F}\right)_1 = \frac{1}{k_N C} \int_0^{C_N} \frac{dC_N}{(1-C_N)} \quad \therefore k_N = \frac{SV_1}{C} \ln\left(\frac{1}{1-C_N}\right)$$

Where: C is the initial concentration of the reactant.

For a run over deactivated catalyst $k = k_0$ and at the same space velocity a conversion C_0 is achieved, and:

$$k_0 = \frac{SV_1}{C} \ln(1/1-C_0)$$

$$\frac{k_0}{k_N} = A_2 = \frac{\ln(1/1-C_0)}{\ln(1/1-C_N)}$$

There is a space velocity SV_H such that a run at this space velocity over new catalyst will result in a conversion C_0 .

Thus:

$$1/(SV)_H = 1/k_N C \ln(1/1-C_0) , \quad k_N = (SV)_H / C \ln(1/1-C_0)$$

and by substitution:

$$A_2 = k_O/k_N = SV_1/SV_H$$

This derivation has been for a first order reaction. However, the same result holds if the reaction is other than first order. Thus, if we can determine SV_H , we can find A_2 .

A series of runs is made at a given temperature and pressure, varying the space velocity. Each run is made over new catalyst. A plot of conversion versus space velocity is then made as in Figure 4. This plot is called a profile. When an activity measurement is desired, a run is made at the temperature and pressure of the runs over new catalyst and any given space velocity, SV_1 . The conversion C_0 at this space velocity is measured. From the profile, the space velocity that would have been necessary over new catalyst to give this conversion is determined. This space velocity is SV_H and $A_2 = SV_1/SV_H$.

Orr⁵¹ reports some interesting work on catalyst activity. He studied the desulfurization of several fractions of a West Texas crude. After each fraction was desulfurized, he made a "bench mark" run on the catalyst. This "bench mark" run was made at 700°F, 400 psig, and $SV = 4.0 \text{ hr}^{-1}$, using a heavy diesel fraction of the West Texas crude. He also obtained a profile using this stock at 700°F and 400 psig. Thus, he could measure the activity (A_2) of the catalyst. The idea of using a "bench mark"

for catalyst activity measurement enabled him to compare the effects of many feed stocks on the activity of a given catalyst. The catalyst used in his study was a commercial cobalt molybdate on alumina made by the Houdry Company. The catalyst is called Houdry Series "C" desulfurization catalyst.

He ran each of his stocks at several conditions and measured the activity after each set of conditions. The means of the catalyst activity values after running each stock are tabulated in Table IV.

TABLE IV

EFFECT OF FEEDSTOCK ON ACTIVITY

<u>Feedstock</u>	<u>Mean of Activity Measurement, 100(A₂)</u>
Light Straight Run Naphtha	36.6
Reforming Naphtha	52.2
Kerosene	63.3
Heavy Diesel Fuel	59.5
Heavy Gas. Oil	47.7
Overhead Composite	42.7

The unusual result here is that apparently the lightest stocks were the most effective in deactivating the catalyst. This result contradicts what one normally expects.

OBJECTIVE

The present work was initiated to study the factors that affect catalyst activity using the bench mark method to measure activity. The work of Orr⁵¹ and the general paucity of data on desulfurization catalyst activity indicates that the phenomenon is not well understood. In fact, there is little published data on what factors affect catalyst activity. Thus, we first set out to discover what factors are important. Secondly, we wished to define rather precisely these factors so that one could predict the effect of various operating conditions and feedstock properties on catalyst activity.

EXPERIMENTAL

The desulfurization apparatus used in this study was a typical high-pressure, flow-type reactor. Orr⁵¹ gives a detailed description of this apparatus. Pure hydrogen was used to desulfurize the stocks used. The hydrogen rate in every run was 900 SCF/bbl.

In every case the bench mark samples were washed with a 10% caustic solution to remove dissolved H_2S_x , then water-washed. The washed samples were analyzed for sulfur by an oxidation method.

The present work proceeded in a series of steps with the results of a designed experiment at each step indicating the objectives of the following step. Therefore, the experiment at each step and its results will be treated together in this section as a series of phases.

Phase I: Preliminary Investigation

The manufacturer of the Houdry Series "C" catalyst claims that their catalyst is in the sulfided state and no pre-sulfiding is necessary to bring it to its full activity level. Orr⁵¹ proceeded on this assumption and did not pre-sulfide his catalysts.

Considering his unusual results, we decided to test this claim. Consequently, a series of three runs using Elk Basin RR Diesel and Elk Basin Heavy Gas Oil as feedstocks were made. The percent sulfur in the product versus throughput was determined at $T = 700^\circ F$, $P = 400$ psig, and space velocities of 2 and 4 hr^{-1} . These results are shown in Figure 1 and Table V.

The pronounced increase in activity at the beginning of the run indicates that the catalyst was not adequately sulfided.

About this time, a new batch of catalyst was received. A difference in the bulk density was noted. The new catalyst was less dense than the old. Two runs using Humble RR Diesel were made to compare the use properties of the two batches. The results of these runs are plotted in Figure 2 as conversion versus throughput and are tabulated in Table VI.

The two batches give appreciably different results. All subsequent runs were made on the new batch of catalyst. Therefore, our results may be slightly different from Orr's⁵¹ because of this.

A run was made on this new catalyst after presulfiding it with a 20% H₂S - 80% H₂ mixture at the reaction conditions. The feedstock used was Humble RR Diesel and the conditions were: T = 700°F, P = 400 psig, SV = 4.0 hr⁻¹. The results of this run are plotted in Figure 3 along with the results of a similar run using non-presulfided catalyst. These data are also reported in Table VII.

There is no activity increase noted using the pre-sulfided catalyst. Furthermore, its activity is higher than the non-presulfided catalyst throughout the run.

In the light of this fact, all subsequent runs were made with pre-sulfided catalyst. The pre-sulfiding was accomplished by passing a 20% H₂S - 80% H₂ mixture over the catalyst until approximately 20 grams of

sulfur had been introduced in this fashion. The sulfiding was always done at the temperature and pressure of the subsequent run. It might be noted here that 40.9 grams of catalyst were used for each run.

Phase II.

Various fractions of Elk Basin crude oil were obtained from the Humble Oil Company in Billings, Montana. One of these fractions, Humble RR Diesel, was selected as an activity standard for activity analysis. The properties of these fractions are shown in Table VIII.

A profile was determined using Elk Basin RR Diesel at a temperature of 700°F and a pressure of 400 psia. The runs for the profile were, of course, made on fresh pre-sulfided catalyst. The data from these runs are shown in Table IX and plotted in Figure 4.

Examination of Figure 4 indicates that a straight line will fit the data rather well above a space velocity of 3.0 hr⁻¹. Since our use for this data will generally be in the region of higher space velocities, a straight line was fitted ignoring the data at SV = 2.0 hr⁻¹. The least squares regression line fitted to these data is

$$\% C = 105.50 - 2.044 (SV)$$

or

$$SV = \frac{\% C - 105.50}{-2.044}$$

Now if we make our bench mark activity measurement at 700°F, 400 psig and SV = 4.0, the activity will be given by the following equation:

$$(100)A_2 = \frac{(-4.0)(2.044)}{C_0 - 105.5}$$

Where: A_2 is defined in the section on activity measurement,
and C_0 = the wt% conversion on the bench mark run.

With this method to measure activity in hand, we wished to determine the effects of several variables on activity. Five variables were selected for this study; i.e., Feedstock, Throughput, Temperature, Pressure, and Space Velocity. We decided to run a half-replicate of a 2^5 factorial experiment and then re-run one-half of this to get an independent estimate of error.¹⁵ The feedstock variable requires some explanation. We wanted to see if the feedstock differences actually affected catalyst activity appreciably. Thus, two feedstocks were selected and one called the high level of this pseudo-variable and the other the low level. These feedstocks were Elk Basin Heavy Gas Oil and Elk Basin Kerosene, respectively. The nomenclature used in the design, the values of the variables and the fractionating of the factorial experiment are shown in Table X.

Thus, each variable was run at each of two levels and 24 runs were made in all. The order of the runs was randomized. Table XI gives the level of all the variables in each run. The results of the bench mark activity measurement at the end of each run are shown in Table XII.

From these data regression equations were fitted to various models. The regression equations for these various models and their associated analysis of variance tables are shown in Table XIII. The dependent

variable in all these equations is $100(A_2)$.

When the model included all the main effects and two-way interaction, the F ratio for testing the hypothesis that all the coefficients of the variables in the regression equation are zero was very low. As successive variables were deleted from the model, the F ratio improved. However, none of these models proved to be significant at the 95% confidence level.

Examination of the raw conversion data leads one to suspect that some of the variables are having a definite effect on the bench mark conversion. It also appears that when the activity is found from this conversion, large errors are introduced. This is because of the small slope of the profile line. Since the bench mark conversion is itself a measure of activity, we decided to use it as the independent variable and see if we could obtain a significant correlation.

Recall that $A_1 = C_0/C_N$ where in this case C_0 is the bench mark conversion and C_N is a constant, being the conversion at bench mark conditions with fresh catalyst. Thus, $A_1 = C_0/C_N$ is just a linear transformation of C_0 and a correlation with C_0 will have the same F ratio as one with A_1 .

The models proposed using C_0 as the dependent variable and their associated analysis of variance tables are shown in Table XIV.

The model containing all main effects and interactions is again not significant at the 95% confidence level. However, when the model that

assumes that pressure and throughput do not affect activity is tested, it is seen to be significant at the 95% confidence level. Furthermore, when the model is tested which assumes that feedstock is the only variable that affects activity, it proves to be significant at the 99% confidence level.

At this point several preliminary conclusions were drawn. These preliminary conclusions from Phase II are:

1. Pressure has no influence on catalyst activity over the range 400-800 psig.
2. Throughput has no influence on activity between 0.0367 li/gram and 0.0734 li/gram.
3. Temperature between 700 and 800°F and space velocity between 4 and 8 hr⁻¹ may or may not have an effect on activity.
4. The feedstock used has a definite effect on activity of the catalyst.
5. The profile method of measuring activity (A_2) introduces large inaccuracies at the conditions used in this phase. This seems to be due to the low slope of the profile line.
6. The data from this phase indicate that the higher the molecular weight of the feedstock the more severe is the catalyst deactivation.
7. One source of error is the high conversion levels at the

bench mark conditions used in this phase. This high conversion leaves little sulfur in the bench mark sample and consequently the sulfur analysis loses accuracy.

Phase III:

It was decided to change the bench mark conditions in order to reduce the bench mark conversion to a level where this sulfur analysis would be more accurate.

Several exploratory runs were made over fresh catalyst varying the temperature and space velocity. Elk Basin RR Diesel was used as the feedstock since it was decided to use it as the activity standard throughout the project. The results of these runs indicated that a temperature of 600°F and a space velocity of 6 hr⁻¹ at a pressure of 400 psig would be satisfactory bench mark conditions. The conversion at these conditions over fresh catalyst was 64 wt %, Thus, C_N = 64.0%. Also a new profile line was determined at these conditions. The data for the profile are shown in Table XV and the profile is plotted in Figure 5. The slope of this profile is considerably greater than that of the previous profile.

A regression line was fitted to these data and used to write an equation for activity (A₂) as before. The resulting equation is:

$$A_2(100) = \frac{39.492}{4.01954 - 2 \log C_0}$$

Where: C_0 = conversion at bench mark conditions over used catalyst.

Also: $A_1 = C_0/64.0$

An experiment was designed similar to that in Phase II. The variables selected were feedstock, temperature, and space velocity. The range of the temperature variable was increased in this phase since it was desired to finally determine whether or not temperature had a significant effect. It was thought that the range used in Phase II might have been too small for a fair test. The feedstocks in this case were fractions of an Oregon Basin crude. They were Oregon Basin Heavy Gas Oil (18) and Oregon Basin Naphtha (15). Their properties are shown in Table VIII. The nomenclature, levels of the variables and design of the 2^3 factorial are shown in Table XVI. Table XVII shows the levels of the variables in each run. A 2^3 factorial was run and all runs repeated. This resulted in 16 runs which were run in randomized order. Since Phase I showed pressure and throughput not to be significant, all runs were made at a pressure of 400 psig and a throughput of 0.049 li/gram.

The results of these 16 runs are shown in Table XVIII. These results are in the form of C_0 , $A_1(100)$, $A_2(100)$. Table XIX shows the regression equations and their associated analysis of variance tables when various models were used to correlate the data. The dependent variable in these equations is $A_1(100)$.

When the full model is tested (all main effects and two-way interactions), the F ratio, for testing the hypothesis that all the coefficients of the variables in the equation are zero, is significant at the 95% confidence level but not at the 99% level. When space velocity is dropped from the model, the F ratio becomes barely significant at the 99% level. When only the feedstock variable is considered in the model, the F ratio becomes highly significant. The "lack of fit" term in the analysis of variance table for this model indicates that the model adequately describes the data.

The results of a similar analysis using $100(A_2)$ as the dependent variable are shown in Table XX. The same conclusions are reached from this analysis as for the analysis in which $A_1(100)$ was used as the dependent variable.

These results allow us to draw several conclusions:

1. Changing the bench-mark conditions allows us to use A_2 as a measure of activity. Evidently, the greater slope of the profile and the greater accuracy of sulfur analysis are sufficient to reduce the error in using this method to a point where it can be used for correlation.
2. Space velocity variation between 4 hr^{-1} and 8 hr^{-1} has little effect on activity.
3. Temperature variation has little effect on activity between 600 and 800°F compared to the large effects of the feedstock.

4. The feedstock has a highly significant effect on catalyst activity.
5. The heavier feedstock definitely deactivates the catalyst to a greater extent than the lower molecular weight stock.

Phase IV:

The results of the previous phases have produced two satisfactory methods for measuring activity. Also, we have found that the feedstock used was by far the most significant variable affecting the catalyst activity.

Thus, in Phase IV we decided to try to determine precisely what properties of the feedstocks were important in determining the activity of the catalyst.

Fractions of crude oils representing some of the most important sources of the world were obtained. The properties of these stocks are shown in Table VIII. The crude oils represented by these stocks are from Oregon Basin, Wyoming; Elk Basin, Wyoming; Central Kansas; Four Corners (New Mexico); Kuwait; Venezuela (Gach Saran); South Louisiana; and West Texas.

The range of the significant properties covered by these stocks are shown below in Table XXI.

TABLE XXI

<u>Feedstock Property</u>	<u>Range</u>
Wt % Sulfur	0.02 - 2.545
Wt % Nitrogen	0.000 - 0.2585
K Factor	11.01 - 12.46
API Gravity	22.20 - 76.68
Boiling Point	156 - 745
Molecular Weight	88 - 340

The K factor listed above is defined as the cube-root of the molal average boiling point in degrees Rankine divided by the specific gravity. It is a measure of the aromaticity of the oil. The more aromatic the oil, the lower is its K factor. The boiling point reported is the volumetric average boiling point determined by ASTM D-158 or D-86 and corrected to 760 mm of Hg. Nitrogen is the total nitrogen content.

A total of 35 stocks were run in this phase. Each stock was run twice and the runs performed in a randomized order. Thus, there are a total of 70 runs in this phase.

Each run was made over pre-sulfided catalyst at $T = 600^{\circ}\text{F}$, $P = 400$ psig, $SV = 6.0$, and $\text{Throughput} = 0.0368$ li/gram. After each stock was run the activity of the catalyst was measured by passing Elk Basin RR Diesel over it at the bench mark conditions determined in Phase III.

The results of these 70 runs are shown in Table XXII as C_6 , $100(A_1)$, $100(A_2)$.

Five variables were picked to characterize each stock. These were sulfur content (wt %), nitrogen content (wt %), K factor, API gravity, and boiling point. We wished to fit a second degree polynomial in these variables to correlate catalyst activity. The full model then would contain five main effects, five second degree terms, and ten two-way intereactions.

An examination of the results in Table XXII disclosed some confusing comparisons. The data normally show that as the molecular weight of various fractions from a given crude oil increased the resultant catalyst activity decreased. However, some of the lighter stocks deactivated the catalyst very severely. This is the same observation Orr⁵¹ made. We thought that using pre-sulfided catalyst would eliminate this anomaly. We thought that perhaps since Orr⁵¹ used non-presulfided catalyst, his lighter stocks contained insufficient sulfur to sulfide the catalyst and it remained in the low activity, un-sulfided state throughout the bench mark analysis. Our thoughts along this line were further confirmed by the results from Phases II and III, since they showed the lighter stocks to be less severe as catalyst deactivation agents.

In an attempt to resolve this difficulty, we used the hydrogen reduction data in Table III to calculate the cobalt and molybdenum compounds present in the catalyst chamber during each run. This calculation assumed complete conversion of sulfur to H₂S during the run. Furthermore, this calculation assumes that thermodynamic equilibrium is attained and that

the data for the pure metals still applies even though they are deposited on an alumina support. The results of this calculation are shown in Table XXIII. Examination of this table shows that for each run from which unusually severe catalyst deactivation resulted, the catalyst is in the form Mo-Co, or MoS₂-Co. The catalyst, used in runs from which normal deactivation resulted, were either in the form MoS₂-Co or MoS₂-Co₉S₈ with the great bulk being in the phase MoS₂-Co₉S₈. It appears that the form Mo-Co is least active, MoS₂-Co more active, and MoS₂-Co₉S₈ most active. The activity data fails to classify the runs precisely into two groups corresponding to catalysts in the phases Mo-Co, MoS₂-Co for one group, and MoS₂-Co₉S₈ for the second group. This is probably due to the fact that the actual system in the reactor is somewhat different from that used to obtain the thermodynamic data.

Apparently the physical phase of the catalyst is different in various runs in this phase. It seemed, then, to be unwise to try to fit one equation to all the data. Therefore, on the basis of the above calculations and examination of the activity data, runs 1, 2, 3, 5, 9, 14, 15, 19, 24 and their duplicates were thrown out for the purpose of regression analysis. This left us with 52 data points which, to the best of our knowledge, were all obtained from runs in which the catalyst was in the phase MoS₂-Co₉S₈.

The results of fitting regression equations to various combinations of the five previously selected feedstock variables as shown in Table

XXIV. These models all use $A_1(100) = 100 C_0/C_N$ as the dependent variable. Similar results using $A_2(100)$ as the dependent variable are shown in Table XXV.

It proved to be impossible to fit the full 20-term polynomial to the data since the matrix which must be inverted for this calculation was singular.

Phase V:

Before the results of Phase IV are discussed, the additional work in Phase V will be presented. Normally, after one feedstock is run the activity standard stock is run for approximately 1 hour to get the bench mark sample for activity measurement. It seemed possible that if one continued to run the activity standard stock at the bench mark conditions, the activity might increase with time. That is, the deactivation caused by the original feedstock might be temporary in nature.

To find out whether or not the activity decline is temporary, a run was made with a West Texas kerosene; then the activity standard stock was run for several hours and samples taken periodically. Thus, data of the form C_0 versus throughput or time were obtained. A similar run was made in which Kansas naphtha was the original feedstock. The results of these two runs are shown in Table XXVI and Figures 6 and 7.

The increase in catalyst activity with time after the bench mark measurement was begun was very small in these runs. It was somewhat

larger with the lighter stock, however. It looks as if we can conclude that the activity we measure by the bench mark method is valid and does not change appreciably with time as the bench mark measurement is run. The poisoning by the original feedstocks seems to be permanent in nature.

We also wanted to test our theory that even pre-sulfided catalysts lose their activity when the feedstock has too little sulfur to keep the catalyst in the phase $\text{MoS}_2\text{-Co}_9\text{S}_8$. If our theory is correct, then introducing H_2S into the hydrogen feed during the run ought to eliminate the severe activity decline noted with some of the very light stocks. Consequently, two runs were made using 20% H_2S -80% hydrogen as the gaseous feed rather than pure hydrogen. One run was made with Kansas naphtha and one with Oregon Basin naphtha as feedstocks. In both runs the bench mark run was continued for several hours and C_0 versus time data taken. The data from these runs are shown in Table XXVII and Figures 8 and 9.

These results are rather surprising. The activity is quite low at the start of the bench mark period but increases rapidly and then levels out at considerably higher levels than when pure H_2 was used as a reactant. It appears, therefore, that our theory is at least partially verified. The catalyst activity is higher when H_2S is introduced into the gas stream. However, the low initial activity is difficult to explain.

