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COKE FORMATION ON HYDRODESULPHURIZATION CATALYSTS*

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(Received April 10th, 1978)

ABSTRACT

The extent of coke formation was measured on a number of different hydrodesulphurization catalysts, primarily as a function of the catalyst chemical composition. Variations in the concentration of MoO₃ on the alumina, the type of catalyst promoter, the promoter/MoO₃ ratio, the presulphiding material and the reaction temperature were made. Increases in the reaction rate caused by either changes in the catalyst composition or by moderate changes in the reaction temperature were compared to the catalyst coke content. It was suggested that two types of coke were present on the catalyst, a reactive coke which is subsequently converted to reaction products and an unreactive coke which blocks catalytic sites.

INTRODUCTION

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76-65 was rewritten as 77-17(J) which has now been published in the journal *Fuel Processing Technology*. A copy of the reprint is attached. The title has changed slightly from the first version.

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The extent of coke formation was measured on a number of different hydrodesulphurization catalysts, primarily as a function of the catalyst chemical composition. Variations in the concentration of MoO₃ on the alumina, the type of catalyst promoter, the promoter/MoO₃ ratio, the presulphiding material and the reaction temperature were made. Increases in the reaction rate caused by either changes in the catalyst composition or by moderate changes in the reaction temperature were compared to the catalyst coke content. It was suggested that two types of coke were present on the catalyst, a reactive coke which is subsequently converted to reaction products and an unreactive coke which blocks catalytic sites.

INTRODUCTION

Catalysts used for the hydrocracking and hydrodesulphurization of heavy residual oils and bitumens have been studied in our laboratories for several years. The deposition of coke and of nickel, vanadium and iron metals on the catalysts generally causes a rapid decline in reaction rate. At high conversions of the high boiling hydrocarbons to lower boiling distillates, catalyst fouling caused by coke formation is several times greater than that caused by metals deposition. Appreciable coke formation also occurs during the hydrodesulphurization of distillate materials such as heavy gas oils which are relatively free of metals.

The purpose of this work was to examine the effect of the catalyst chemical composition on catalyst coke content. A series of unpromoted catalysts containing varying amounts of molybdenum on the support was studied. In addition, molybdenum—alumina catalysts promoted with transition metal compounds were investigated.

EXPERIMENTAL

In these studies, laboratory prepared catalysts were compared with a

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commercial catalyst. The alumina catalyst supports (Catapal N and Catapal SB) were obtained from the Continental Oil Company. Both were high purity Boehmite (α -alumina monohydrate) produced by the hydrolysis of aluminum alkoxides during the manufacture of alcohols. The N type was kiln-dried material in the form of relatively large particles, more than 60% of which were in the size range 100–1000 μm . The SB type was a spray-dried material in the form of relatively small particles, the bulk of which were in the size range 30–100 μm . The commercial catalyst was cobalt–molybdenum on alumina (15 wt. % MoO_3 and 3 wt. % CoO) manufactured by the Harshaw Chemical Co. (HT-400).

The methods and equipment used to make the laboratory prepared catalysts and to perform the reaction experiments have been described in detail previously [1, 2]. The properties of the feedstocks are listed in Table 1. The bitumen was obtained from Great Canadian Oil Sands Ltd. of Fort

TABLE 1

Properties of the feedstocks

Feedstock	Heavy gas oil	Athabasca bitumen
Boiling range ($^{\circ}\text{C}$)	343–525	—
Pitch (+525 $^{\circ}\text{C}$) (wt.%)	0	52
Conradson carbon residue (wt.%)	0.97	12.6
Pentane insolubles (wt.%)	0.3	15.8
Resins (wt.%)	20.6	23.4
Sulphur (wt.%)	3.6	4.7
Nitrogen (wt.%)	0.38	0.4

McMurray, Alberta, Canada. The 343–525 $^{\circ}\text{C}$ heavy gas oil was a distillate fraction of the liquid product obtained by thermally hydrocracking the bitumen. A result obtained with bitumen is presented in Table 2. All of the data shown in the figures were obtained with heavy gas oil. The data for the temperature series shown in Fig. 5 were obtained by presulphiding the catalyst with the feedstock at 400 $^{\circ}\text{C}$ followed by a single reaction experiment at the temperature indicated. The rest of the heavy gas oil data were obtained by presulphiding at 400 $^{\circ}\text{C}$ followed by a sequence of reaction experiments at 420, 400 and 380 $^{\circ}\text{C}$. The presulphiding procedure was described previously [3]. During reaction the oxide form of the catalyst was converted to a sulphide form. However, for the sake of simplicity all catalyst concentrations will be referred to in their oxide form.

To determine the amount of coke on the catalyst, stainless steel screen boxes were filled with pellets and placed into a chamber. Hydrogen at atmospheric pressure flowed continuously over the pellets as the temperature was raised to 525 $^{\circ}\text{C}$ during a 7.2 ks (2 hour) period and kept at this temperature for an additional 3.6 ks (1 hour). Then the chamber was allowed

to cool in the presence of H_2 . Air was not permitted to contact the catalyst pellets until they had reached ambient temperature. The change in catalyst weight during the hydrogen treatment was ascribed to the removal of distillable oil. The catalyst was then left overnight in a muffle furnace at $600^\circ C$. The second weight change, after correction for conversion of metals in the catalyst from the sulphide to the oxide form, was ascribed to coke being burned from the catalyst. This empirical definition of coke was used throughout the present work.

RESULTS AND DISCUSSION

The amount of coke per unit surface area of $MoO_3-Al_2O_3$ catalysts is expressed as a function of the MoO_3 content in Fig. 1. Two different types of alumina supports were used. The SB alumina, which had a slightly larger surface area, also contained slightly more coke per unit catalyst weight.

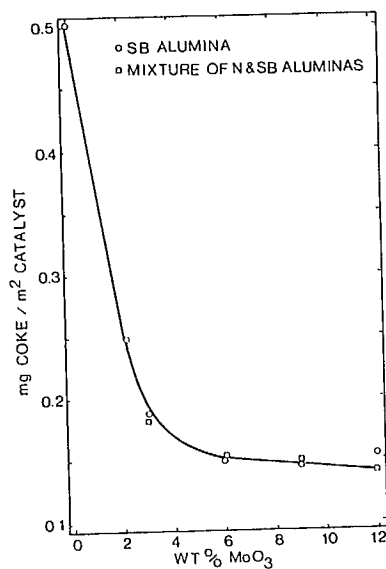


Fig. 1. Amount of coke per unit surface area of catalyst (mg coke/m² catalyst) versus weight per cent MoO_3 in a $MoO_3-Al_2O_3$ catalyst. The circular data points represent catalysts prepared with SB alumina. The square data points represent catalysts prepared with a mixture of 20 wt. % SB alumina and 80 wt. % N alumina.

When the catalyst coke content was expressed per unit of catalyst surface area, both types of support produced similar results. The addition of small amounts of MoO_3 to the support caused a dramatic decrease in coke content. The decrease in coke content with increasing MoO_3 content was much more gradual when the catalyst contained more than 6 wt. % MoO_3 .

Sulphur removal data have been reported elsewhere for both the SB alumina [1] and the N-SB alumina mixture [2] supported catalysts. The

weight per cent sulphur removed from the liquid hydrocarbon increases sharply up to 3–6 wt. % MoO_3 for both supports. Thereafter it increases much more gradually. The catalysts which produced the low conversions contained the greatest amount of coke. The ones which produced the highest conversions contained the least amount of coke.

Fig. 2 shows the amount of coke per unit catalyst surface area on promoted $\text{MoO}_3\text{--Al}_2\text{O}_3$ catalysts. All of the data points in Fig. 2 were obtained with catalysts composed of SB alumina and 2.2 wt. % MoO_3 . It is apparent that the amount of coke on the catalyst did not vary greatly with the type of promoter used. The amounts of coke on the promoted catalysts represented in Fig. 2 were similar to the amount of coke on the unpromoted catalyst containing 2.2 wt. % MoO_3 , shown in Fig. 1. This indicates that it is the molybdenum content of the catalyst rather than the promoter which controls the coke level.

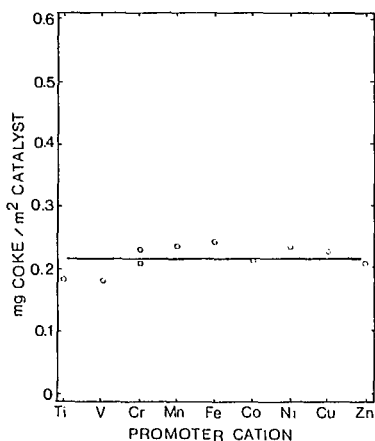


Fig. 2. Amount of coke per unit surface area of catalyst (mg coke/m^2 catalyst) versus the promoter cation contained in the catalyst. All of the catalysts were prepared with SB alumina, 2.2 wt. % MoO_3 , and a promoter/molybdenum atomic ratio of 1. The circles represent catalysts calcined at 500°C . The square represents a catalyst which was calcined at 900°C .

The chromium catalyst calcined at 900°C , and represented by the square data point, had a surface area which was approximately one-quarter the value of the surface area for the same catalyst calcined at 500°C . In spite of this large difference in surface area the amount of coke per square meter was almost the same in both cases. This suggests that the coke may be formed in some uniform manner on the catalyst surface.

Sulphur removal data, for the catalysts represented in Fig. 2, have been reported previously [1]. The catalysts promoted with nickel and cobalt removed substantially more sulphur from the feedstock than the others. This indicates that although the promoter has a large effect on sulphur removal, it does not affect the coke level in the catalyst. For the un-

promoted catalysts represented in Fig. 1, sulphur removal was somewhat inversely related to the catalyst coke content. For the promoted catalysts in Fig. 2, no relation between sulphur removal and catalyst coke content is apparent.

Fig. 3 shows some results obtained with promoted catalysts having a nickel to molybdenum ratio of 1. The sulphur removal from the feedstock increased and the coke content per unit surface area decreased as the amounts of molybdenum and nickel in the catalyst increased. The sulphur removal with the nickel promoted catalysts in Fig. 3 was much greater than the sulphur removal previously reported [1] for the unpromoted catalysts in Fig. 1. In spite of the difference in magnitude of the results the shape of the sulphur removal curve in Fig. 3 is similar to the shape of the one for the unpromoted catalyst [1].

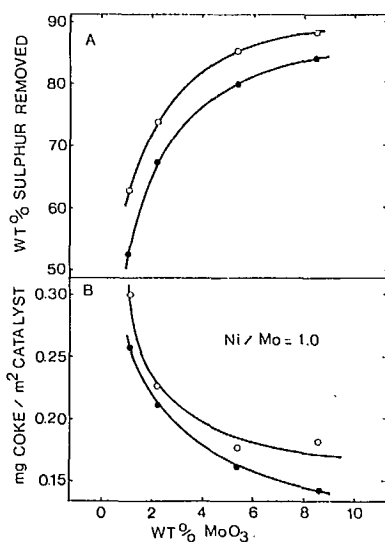


Fig. 3. (A) Weight per cent sulphur removed from the liquid hydrocarbon feedstock versus the weight per cent MoO_3 in catalysts having a nickel/molybdenum atomic ratio of 1. The catalyst support was a mixture of 20 wt. % SB alumina and 80 wt. % N alumina. The open circles represent catalysts which were presulphided with the feedstock. The solid circles represent catalysts which were presulphided with an $\text{H}_2\text{S}/\text{H}_2$ mixture. (B) Amount of coke per unit surface area of catalyst ($\text{mg coke}/\text{m}^2$ catalyst) versus weight per cent MoO_3 in a $\text{NiO}-\text{MoO}_3-\text{Al}_2\text{O}_3$ catalyst.

Both the nickel promoted catalysts in Fig. 3 and the unpromoted catalysts in Fig. 1 contained similar amounts of coke per unit catalyst surface area. Also the shapes of the curves in Figs. 1 and 3 are somewhat similar. This indicates that the amount of coke is controlled by the molybdenum content and not by the presence of nickel. The data in Fig. 3 are consistent with those in Fig. 2 in that the promoter has a minor effect if any on coke level. The nickel promoter appears to enhance the reaction rate without greatly changing the amount of coke on the catalyst.

Fig. 3 also compares catalysts presulphided using H_2S with those presulphided using the gas oil feedstock. Presulphiding with H_2S produced slightly less coke and slightly less sulphur removal than presulphiding with the feedstock which is consistent with earlier work [3]. This shows that there is not a simple relationship between the amount of coke on the catalyst and sulphur removal.

Fig. 3 contained results for catalysts having a constant promoter to molybdenum ratio. In contrast the results in Fig. 4 are for catalysts with different promoter to molybdenum ratios. As before nickel is seen to be a good promoter for sulphur removal. In contrast iron has almost no promotional effect. The sulphur removal curve for the nickel promoted catalysts has a maximum which is similar to results which have been reported previously [4].

The catalyst coke content in Fig. 4 does not change greatly with the promoter to molybdenum atomic ratio. Unfortunately there is a considerable amount of scatter in the coke data particularly for the iron promoted catalysts. As a result, one is not certain if the trend obtained in the coke data for the nickel catalyst is real or if it is merely fortuitous. If the trend is real then the curves representing sulphur removal and catalyst coke content have the same shape. This suggests that the reaction rate may be influenced by the amount of coke on the catalyst.

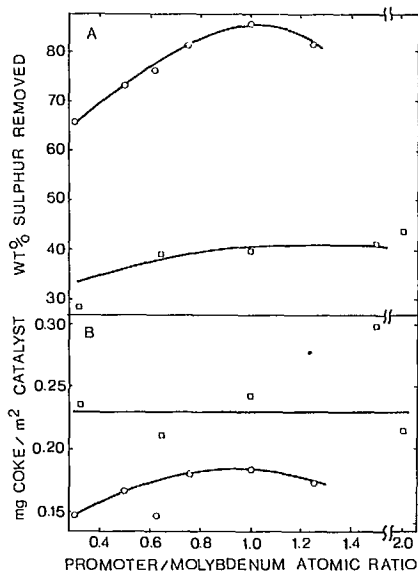


Fig. 4. (A) Weight per cent sulphur removed from the liquid hydrocarbon feedstock versus the promoter/molybdenum atomic ratio. The circles represent catalysts containing 5.4 wt. % MoO_3 , a nickel promoter, and a support which was a mixture of 20 wt. % SB alumina and 80 wt. % N alumina. The squares represent catalysts containing 2.2 wt. % MoO_3 , an iron promoter, and a support consisting entirely of SB alumina. (B) Amount of coke per unit surface area of catalyst ($mg\ coke/m^2\ catalyst$) versus promoter to molybdenum atomic ratio.

In general, the amounts of coke on the iron promoted catalysts are typical of catalysts containing 2.2 wt. % MoO_3 . Similarly the amounts of coke on the nickel promoted catalysts are typical of catalysts containing 5.4 wt. % MoO_3 . Again this indicates that the coke formation is controlled by the molybdenum content and not by the promoter content of the catalyst.

The effect of reaction temperature on sulphur removal and on catalyst coke content is shown in Fig. 5. As expected the sulphur removal increases considerably with temperature. The catalyst coke content also increases substantially with temperature up to approximately 375°C. From 375°C to 440°C it remains approximately constant. Above 440°C the catalyst coke content again increases markedly with temperature.

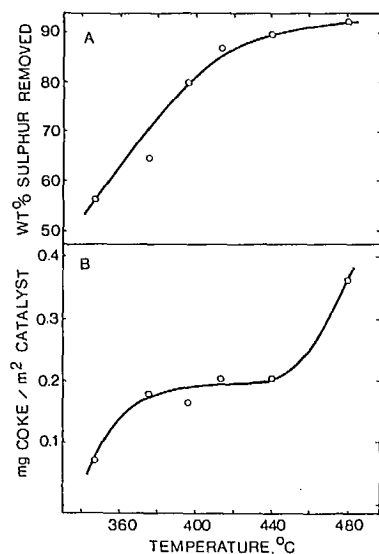


Fig. 5. (A) Weight percent sulphur removed from the liquid hydrocarbon feedstock versus temperature. The catalyst used contained 5.4 wt. % MoO_3 , a cobalt promoter (cobalt/molybdenum atomic ratio equalled 0.75), and a support which was a mixture of 20 wt. % SB alumina and 80 wt. % N alumina. (B) Amount of coke per unit surface area of catalyst (mg coke/m^2 catalyst) versus temperature.

The temperature range where the coke content remains relatively constant is of particular interest. This effect is different than that observed by Voorhies [5] and by Plank et al. [6]. These workers reported that for catalytic cracking catalysts an increase in temperature or conversion was accompanied by an increase in the extent of coke formation. In contrast our hydrotreating studies show that from 375°C to 440°C, increasing the temperature causes an increase in reaction rate without changing the catalyst coke content. One can speculate that some phenomenon related to adsorption or reactivity of hydrogen on the catalyst surface, counteracts the tendency for increased coke formation in this temperature range.

The fraction of the catalyst surface covered with coke was calculated by assuming that all the coke was present as a monolayer, that the coke monolayer had the thickness of an aromatic molecule [7], and that the surface coke had the same density as bulk coke [8]. This procedure has been applied to a catalyst coke content of 0.2 mg/m^2 , which is typical of some results presented in Figs. 1–5. The calculation shows that for this typical result there are 0.49 statistical monolayers of coke covering the catalyst surface.

Although there is no firm evidence that coke actually exists as a monolayer, there are two indications which suggest that a monolayer could be formed. It has been shown experimentally [9, 10] that coke contains a high concentration of oxygen and nitrogen atoms. These polar compounds will tend to be preferentially adsorbed on the catalyst surface. Thus there would be a greater propensity for molecules containing these heteroatoms to be adsorbed directly on the catalyst surface than as a second layer of a carbonaceous deposit.

It has already been mentioned that the two chromium catalysts in Fig. 2, which were calcined at different temperatures, had markedly different surface areas but very similar coke contents per unit area. This shows that the coke is being deposited in a consistent and uniform layer. A monolayer would be one type of uniform layer.

It is unreasonable to suggest that the coke would exist as a perfect monolayer. It seems likely that at least some patches more than a monolayer thick would exist. Nevertheless the two indications described above suggest that it would not be impossible for a structure approaching a monolayer to be formed.

If one accepts the concept that coke is deposited as a monolayer, then a very large fraction of the catalyst surface could be covered. Furthermore quite large reaction rates were observed with some of the catalysts in spite of the presence of coke. One possible conclusion would be that the coke does not interfere with the reaction rate.

Hydrodesulphurization of the same gas oil feedstock for 360 ks (100 hours) of continuous operation using an unpromoted catalyst containing 9 wt. % MoO_3 with SB alumina has been performed in our laboratories [2]. Virtually no change in catalyst activity was observed during the 100 hours. Any coke which may have been deposited on the catalyst surface during this period did not cause the reaction rate to diminish.

In Table 2 the catalyst coke content resulting from hydroprocessing gas oil is compared with that resulting from hydroprocessing bitumen. The commercial catalyst used for these experiments (Harshaw HT-400) contained 15 wt. % MoO_3 and 3 wt. % CoO . The feedstock qualities listed in Table 1 indicate that greater quantities of coke would be expected from the bitumen than from the gas oil. For example, both the Conradson Carbon Residue (an indication of coking tendency) and the pentane insolubles (an indication of asphaltene content) are much greater for bitumen than for gas oil. As expected the data in Table 2 show that the catalyst coke content resulting

TABLE 2

Variation in catalyst coke content with feedstocks

	Heavy gas oil	Athabasca bitumen
Reaction conditions		
Pressure (MPa (p.s.i.g.))	13.9 (2000)	13.9 (2000)
Temperature (°C)	380-420	440-460
Catalyst coke content (wt.%)	4.1	9.2
(mg/m ²)	0.199	0.447
Statistical number of monolayers on the catalyst surface		
	0.49	1.10

from bitumen hydroprocessing is much greater than that resulting from gas oil hydroprocessing. In fact the surface of the catalyst used to process bitumen contained sufficient coke to form a monolayer over its entire surface. In spite of its coke content this catalyst was still removing 96 wt. % of the sulphur in the bitumen. Obviously the presence of coke was not interfering with the reaction rate.

One can hypothesize that some of the coke on the catalyst is a reactive substance which is eventually converted into reaction products. If the concept of a coke monolayer is accepted, then some of the coke which covered the complete surface of the catalyst used for bitumen hydroprocessing, (Table 2) must have been converted into reaction products. If this were not the case, the reactants would not have had access to the catalyst surface and the reaction could not have continued at the high rate which was observed.

Longer term catalytic reaction experiments with bitumen have also been performed in our laboratory [11]. Initially 83 wt. % sulphur was removed from the bitumen. Sulphur removal by the catalyst gradually decreased to 74 wt. % after 180 ks (50 hours). At this point the coke was burned off the catalyst by passing air at 500°C through the reactor. When the reaction experiments were continued with the regenerated catalyst the sulphur removal increased to 81 wt. %. The sequence of catalyst deactivation and catalyst regeneration was repeated three times. A marked increase in sulphur removal was observed after each regeneration. This clearly shows that some of the coke on the catalyst is an unreactive substance which blocks catalytic sites.

The previous hypothesis can be expanded to state that the coke on the catalyst is comprised of at least two species. One is a reactive substance which is subsequently converted into reaction products. The other is an unreactive substance which blocks catalytic sites.

The concept of coke being a reactive substance has been reported in other studies using less complex reactants. Wentrcek et al. [12] have studied the formation of methane from CO and H₂ over nickel catalysts. When a stream

of CO flowed over the catalyst, a carbon species formed on the surface. Subsequently a stream consisting of 100% hydrogen flowed over the catalyst. The hydrogen reacted with the carbon species quantitatively to form methane. Blakely and Somorjai [13] studied the dehydrogenation of cyclohexane using platinum catalysts. Two different types of carbon deposits were observed on the catalyst. They presented evidence to show that benzene was the reaction product formed from an ordered carbon deposit, and that cyclohexene was the reaction product formed from a disordered carbon deposit. Miloudi et al. [14] investigated the conversion of toluene using an alumina catalyst. They found that the formation of benzene was directly related to the amount of coke on the catalyst. Thus the suggestion that some of the coke on our catalyst functions as a reactive substance is consistent with other studies.

Some of the data in Figs. 1–5 can be explained in terms of this hypothesis. As the amount of molybdenum in the catalyst is increased, as in Fig. 1 and Fig. 3, the reaction rate increases. This could be explained by a decreasing amount of unreactive coke on the catalyst which is consistent with the corresponding coke data. In Fig. 3 the catalysts presulphided with the gas oil could contain more reactive coke and therefore have a higher reaction rate than the ones presulphided with H_2S . H_2S is known to compete with the reactant for catalytic sites [15, 16]. Furthermore the sulphur content of catalysts presulphided with H_2S remains at a higher level for some time than the sulphur content of catalysts presulphided with gas oil [3]. Thus it seems plausible that H_2S presulphiding may decrease the amount of reactive coke on the catalyst. This would be consistent with coke data reported in Fig. 3. In Fig. 4 the shape of the curve describing sulphur removal as a function of nickel to molybdenum ratio is similar to the curve drawn through the coke data points. It is possible that the extent of sulphur removal is due to the amount of reactive coke on the catalyst.

CONCLUSIONS

In summary the following statements can be made. It has been shown that the coke content of hydrodesulphurization catalysts is controlled primarily by the molybdenum content in the catalysts. Other effects such as the type and concentration of the promoter, or presulphiding method have less influence. During hydrodesulphurization, it is possible to increase the reaction rate by changing the catalyst composition or the reaction temperature without causing an increase in catalyst coke content. It has been hypothesized that coke contains at least two components. One is a reactive substance which is subsequently converted to reaction products. The other is an unreactive substance which blocks catalytic sites.

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