CHEMICAL ORIGIN OF COKE DEPOSITED ON CATALYST SURFACE

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by

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ABSTRACT

A marked difference has been observed in the chemical composition of coke deposits formed during catalytic hydrotreatment of bitumen and heavy gas oil. In the case of the latter, nitrogen and oxygen accumulate in the deposit to a greater extent as compared to the bitumen feed. This is attributed to different coke precursors, i.e., heterocyclic compounds in the gas oil and heavy asphaltenous species in the bitumen, respectively. In addition to this, metals, when present in the feed, concentrate in the deposits as well. The vanadium/nickel ppm ratios in the deposits are almost 9, while the ppm ratios in the bitumen feed is only about 3. This suggests that vanadium, when present in the feed, will have a much more detrimental effect on catalyst activity than nickel.

INTRODUCTION

Limited resources of conventional crudes are the main reason for the increasing attention being paid to heavy crudes and distillation residuums. Processing of these materials is essential in order to fulfil future energy requirements. Catalytic hydrotreatment is one of several upgrading processes. Economic feasibility of this technology is affected markedly by the cost of catalyst. Metals, such as vanadium, nickel and iron, as well as high contents of resinous and asphaltenous species, have deteriorating effects on catalyst life. The level of the metal contents in some cases might exceed 1000 ppm (heavy Venezuelan crudes). Any catalytic treatment of such feedstock is impossible unless a major part of the metals is removed prior to the processing.

The activity of these catalysts diminishes mainly because of the formation of carbonaceous deposits. Metals, if present in feeds, concentrate in the deposits which then represent the most complex material to deal with. Their structure is unknown and the amount determined on the catalyst surface depends on the analytical procedure. In scientific literature, these deposits are usually referred to as coke and this has been done in this publication.

In the present work, an attempt was made to obtain information on the origin of the coke from its chemical composition. A marked difference in

properties of the feedstocks might result in cokes of different struc-
tures. Therefore, some speculation on the mechanism of coke formation can
be made. The experimental work is based on a series of extractions with
various solvents performed on a commercial cobalt molybdate catalyst used in
hydrotreatment of either heavy gas oil or Athabasca bitumen. In the case of
the bitumen feed, special attention is also paid to V, Ni and Fe. A possibil-
ity of removing the metals from used catalyst pellets by extraction will be
shown.

EXPERIMENTAL

The reaction experiments were performed in a bench-scale fixed
bed reactor having a volume of 155 cm^3 and a length to diameter ratio of 12.
The reactor was filled sequentially from the bottom with 42 cm^3 berl saddles,
100 cm^3 catalyst pellets and 13 cm^3 berl saddles. The mixture of hydrogen
and heavy gas-oil flowed continuously into the bottom of the reactor and up
through the catalyst bed. Each experiment was performed at a pressure of

13.9 MPa (2000 psi), or liquid hourly space velocity of 2 h^{-1}. Experiments
involving the catalyst consisted of a series of successive runs in the
temperature ranges of 380-420°C for the gas oil and 440-460°C for the
bitumen, respectively. The catalyst, a cobalt molybdate (3 wt% CoO_3 -12 wt%
MoO_3), 1/8" x 1/8" cylindrical pellet type was a product of the Harshaw
Chemical Co. Catalyst pellets were removed from reactor after 43 Ks on
stream.

The properties of the feedstocks are listed in Table 1. The bitumen
was obtained from Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta.
The 343-524°C heavy gas oil was a distillate fraction of the liquid product
obtained by thermally hydrocracking the bitumen.

Boiling Range	°C	343–524	–
Pitch (+524°C),	wt %	Nil	52
Conradson Carbon			
Residue	wt %	0.97	12.6
Pentane Insolubles	wt %	0.3	15.8
Benzene Insolubles	wt %	Nil	0.9
Sulphur	wt %	3.6	4.7
Nitrogen	wt %	0.38	0.4
Oxygen	wt %	0.44	0.84
Vanadium	ppm	Nil	189

EXPERIMENTAL

The methods and equipment used to perform the reaction experiments have been described in detail previously by Parsons and Ternan (1977). The properties of the feedstocks are listed in Table 1. The bitumen was obtained from Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta. The 343-524°C heavy gas oil was a distillate fraction of the liquid product obtained by thermally hydrocracking the bitumen.

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Properties of the Feedstocks

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Oxygen	wt %	0.44	0.84
Vanadium	ppm	Nil	189
Nickel	ppm	Nil	68

Extractions of pellets were carried out in a Soxhlet apparatus. A clean solvent indicated the end of extraction. Extracts, after evaporation of solvents, were subjected to high vacuum at 100°C to remove remaining solvent. The high vacuum treatment was also applied to catalyst pellets after extractions.

Analyses for carbon, hydrogen, nitrogen and oxygen were performed on a Perkin Elmer 240 analyser and a Dohrman microcoulometer. Sulphur was determined by either Leco or an X-ray fluorescence technique. Atomic absorption spectroscopy was applied to determine metals content.

RESULTS AND DISCUSSION

After the reaction, product and feed fractions, as well as some heavy species, remain adsorbed on the catalyst surface. Confusion exists in defining carbonaceous deposits. In the present work the pre-extraction with benzene has been chosen as a basis assuming that the light fractions and soluble asphaltenes are removed by this treatment. Because of the low content of benzene insolubles in both feeds, the assumption is made that all carbonaceous material left over on the surface after the benzene pre-extraction was a result of a degrading process. Further attention will be restricted to these deposits.

In order to obtain information on the chemical structure of the remaining deposit, an attempt was made to isolate some of its fractions by applying a stronger solvent. Thus pyridine extractions always followed the pre-extraction by benzene. The composition of pyridine extracts from catalyst pellets previously extracted by benzene are summarized in Table 2. The results of pre-extractions are not presented as the yields and compositions of the extracts have little meaning, i.e., the amount left on the surface can be markedly affected by draining of the reactor.

TABLE 2

Chemical Analysis of Pyridine Extracts from Catalyst Pellets

| | | Feedstock | |
		Bitumen	Gas Oil
Yield	wt %	3.4	2.6
Carbon	wt %	81.0	79.3
Hydrogen	wt %	7.8	8.3
Sulphur	wt %	5.0	3.1
Nitrogen	wt %	1.8	3.4
Oxygen	wt %	2.5	5.5
S/C ratio		0.023	0.015
N/C ratio		0.019	0.035
O/C ratio		0.023	0.052
Ash	wt %	1.8	trace
Vanadium	ppm	1070	Nil
Nickel	ppm	1330	Nil
Iron	ppm	820	Nil

The higher content of N and O heteroatoms in the extracts from the coke formed during catalytic treatment of the gas oil is rather unexpected. In view of the fact that some pyridine might have been left in the extract this was checked by C and N analysis performed on crushed pellets being previously extracted by benzene. The higher nitrogen content in the coke layer after the gas oil treatment (Table 3) is another confirmation of the same trend. A similar analysis of S and O could not have been obtained.

TABLE   3

Carbon and Nitrogen Analysès of Deposits

		Feedstock	
		Bitumen	Gas Oil
Carbon	wt %	13.9	4.6
Nitrogen	wt %	0.29	0.48
N/C ratio		0.018	0.089

Another interesting observation is a relatively small difference in the carbon levels in the deposits (Table 3).   On the basis of asphaltene content, one would expect this difference to be significantly larger.   Then there must be an additional source of coke besides asphaltenes and other heavy species contained in feeds.

The accumulation of heteroatoms, especially N and O in the deposits, suggests that compounds containing these elements act as precursors of coke formation.   In the case of gas oil, it is a good assumption that the N and O containing compounds are those of heterocyclic origin.   It is unlikely that other less stable species would have much chance to survive conditions of thermal hydrocracking.   Dibenzofuran, carbazole and dibenzothiophene can easily be converted to coke in the presence of either Lewis acid type catalysts or some metals, shown by Mochida et al. (1977).   If it is assumed that a type of Lewis acid sites is present on the surface of supported cobalt molybdate catalysts, then a coupling mechanism leading to higher molecular weight species can be proposed.   The aforementioned authors have shown that the accumulation of N and O in the coke for dibenzofuran and carbazole was significantly larger than that of S in the case of dibenzothiophene.   This might be attributed to the thermal cleavage of the C-S bond, resulting in removal of S.   The C-S bonds in the heterorings are weaker than those of C-N and C-O,

respectively. The heteroring containing compounds are strongly adsorbed on the surface because of their polar nature. Because the coke-forming reactions occur on the surface, the hetero-cyclics will play a predominant role as compared to non-polar hydrocarbons.

In the bitumen, asphaltenes represent the main part of polar and unstable species. They might disintegrate in liquid phase even without contacting the catalyst surface. This was confirmed by a marked decrease in asphaltenes content during thermal hydrocracking of the bitumen (Khulbe et al., 1976) under conditions (temperature and pressure) similar to those applied in the present work. In the presence of a catalyst, a part of the asphaltenes adsorbs on the surface. A steady-state level is reached during the initial stages on-stream. Subsequently, adsorbed asphaltenes react further to coke. During this reaction, elimination of sulphur, nitrogen and oxygen may occur, especially through splitting off unstable groups, e.g., carboxylic, amine, thio, etc., which are frequently considered in proposed models for asphaltenes. This might explain the lower content of sulphur, nitrogen and oxygen in the deposit after the catalytic hydrotreatment of bitumen.

As results indicate, asphaltenes are not the only source of carbonaceous deposits. Their content is not a measure of the deposit level formed. This was pointed out earlier by Beuther and Schmidt (1964). Theoretically, all hydrocarbon groups in feeds have a chance to be converted to coke. The rates of these reactions will differ depending on conditions. It is assumed here that, for the bitumen, the rate of asphaltene conversion will be high, i.e., the steady-state level is attained in the early stages. However, more stable species such as those present in the gas oil will be more resistant. In this case, deposit levels might increase continuously for a longer period of time, until the final steady-state is attained. The difference in the

ultimate amount deposited from various feeds does not have to be large under an assumption that a maximum coke level exists, given by available surface area and other catalyst properties.

Another aspect of coke, of most crucial importance, is the presence of metals. Metals, particularly vanadium and nickel, are known to poison the catalyst surface irreversibly (Ternan et al., 1977). A small portion of metals can be removed from coke deposits by a solvent extraction. This is illustrated in Tables 2 and 4. The amount of metals removed depends on the solvent applied. It is expected that strong solvents, for example, quinoline, will remove more metals when compared to pyridine. This was confirmed by the lower content of metals in pellets extracted directly by quinoline relative to those extracted by pyridine (Table 4). However, a pronounced increase in metals concentration was observed when the total metal amounts were related to coke deposits left over after extractions when compared to the unextracted pellets.

TABLE 4

The Amounts of V, Ni and Fe
in Extracted Catalyst Pellets

Solvent	Carbonaceous Deposit wt %	Amount of Metals, ppm x 10^{-2}					
		V		Ni		Fe	
		A	B	A	B	A	B
None	27.0	182	674	21	78	8	30
Pyridine	13.8	165	1196	19	138	5	36
Quinoline	11.8	159	1350	18	153	4	34

A – total amount of the corresponding metal in crushed pellets
B – amount of A related to the coke deposit left after extractions

The results in Table 4 are in support of high accumulation of metals in coke. Here, V/Ni ppm ratios for all three cases shown are almost 9, compared to about 3 in the bitumen. This indicates that V might have a predominant role in poisoning catalyst surface rather than Ni. According to Constantinides and Arich (1964), most V can be removed by precipitation of asphaltenes. This suggests that V content increases relative to Ni in the direction of heavy asphaltene fractions. This is supported by a number of experimental results on deasphalting of crudes and residuums published by Riediger (1976). In his work the V/Ni ratios in the "asphalite" precipitated by normal alkanes, was always higher than that in the de-tarred oil. In addition to this, the V/Ni ratios increased when the de-tarring process was conducted on low "asphaltite" yield, i.e., only the heaviest asphaltene fractions were precipitated.

In scientific literature, little attention has been paid to Fe. Present results show that the amount of Fe relative to V and Ni is small. During catalytic hydrotreatment, the Fe is most likely converted to sulphides. These are known to be catalytically active. Therefore, the contribution of Fe to poisoning of catalyst surface is less significant.

A portion of the metals in crudes is assumed to be porphyrin type. According to Costantinides and Arich (1964), this represents about one-third of the metals present. The molecular weight of the porphyrins is seven to ten times that of the metal's atomic weight. This would indicate that, after the pyridine or quinoline extractions, the amount of the carbonaceous material left on the pellet surface is nearly equal to the amount of porphyrins containing this amount of metals (Table 4). Assuming four nitrogens per one metal atom in porphyrins, the amount of nitrogen in the coke deposit after the pyridine extraction which may originate from the porphyrins is almost

4.7 wt %. However, the amount of nitrogen in the deposit, determined after the catalyst pellets were extracted by pyridine, was only 1.8 wt %. This suggests that less than 1/3 of total V and Ni in the feed is porphyrin type. Otherwise, porphyrins would have to undergo extensive changes on the surface resulting in nitrogen removal, to account for the low nitrogen content.

There is an almost total lack of information on the behaviour of vanadium and nickel porphyrins and other metal compounds under conditions of catalytic hydrotreatment. Thus one cannot escape speculation as to their contribution to coke. To clarify this problem, extensive model compound studies are needed. This can be accomplished by blending sulphur-, nitrogen- and oxygen-containing model compounds with pure metals-containing compounds in a convenient solvent. Here the effect of the metals on sulphur, nitrogen and oxygen removal, as well as other catalytic reactions, can be followed. These experiments might be extended to no-metals-containing crudes and resid-uums, i.e., metals-containing crudes could be simulated by doping these feeds with vanadium and nickel compounds. In view of increasing needs for process-ing high metallic feeds, such information would be of great value.

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