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CATALYST TECHNOLOGY FOR REACTORS USED TO HYDROCRACK
PETROLEUM RESIDUA
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CATALYST TECHNOLOGY FOR REACTORS USED TO HYDROCRACK PETROLEUM RESIDUA

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ABSTRACT

In this paper, the phenomena occurring in catalysts used to hydrocrack petroleum residua are discussed. Reaction sites are provided by the catalyst sulphide phase (Mo is the majority cation) and by the catalyst oxide phase (Al is the majority cation). The influence of the promoter cations (typically Co or Ni) is also described. The catalyst is deactivated by coke and by metals. Furthermore, the reaction rate is often controlled by the rate of diffusion of the large carbonaceous molecules in the residua. All of these factors have been considered in mathematical simulations of the phenomena occurring in the catalyst.

INTRODUCTION

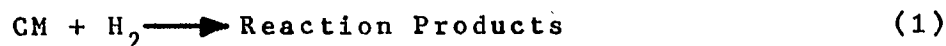
Catalysts are an important technological factor in many chemical reaction systems. Although catalysis is not yet a precise science, it has progressed far beyond its former image of being a black art. The catalyst commonly used to hydrocrack heavy oils and petroleum residua, promoted molybdenum-alumina, will be discussed here, in order to illustrate this point.

The technological history of the hydrocarbon processing industry contains several instances of catalytic processes replacing thermal ones. Fluid catalytic cracking, reforming and lube oil processing are examples. This transition may now be occurring in Canada, for heavy oil conversion. Previously the primary processes used to convert the bitumen from the Canadian oil sands were thermal (delayed coking and fluid coking). At the present time two catalytic hydrocrackers which will process residual oil are under construction, and a third one is at the design stage.

Four distinct topics related to the catalytic hydrocracking of residual oil will be discussed, the catalytic mechanism (or how the catalyst works), catalyst deactivation, diffusion in the catalyst pores, and catalyst modelling.

THE CATALYTIC MECHANISM

Several types of reactions occur on residual oil hydrocracking catalysts[1], molecular weight reduction (hydrogenation and bond cleavage), hydrodemetallization (Ni and V), and heteroatom removal (S, N, and O). These DESIRABLE REACTIONS can all be generalized as a reaction between a carbonaceous molecule, CM, and hydrogen, as follows:



Polymerization and dehydrogenation, also occur on residual oil hydrocracking catalysts. These UNDESIRABLE REACTIONS do not involve hydrogen as a reactant and can be generalized as follows:



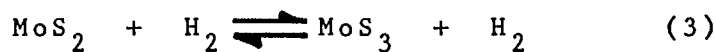
In Equation 1, hydrogen can be considered to be chemisorbed by electron holes (represented as \oplus) in the catalyst. Wise and co-workers [2-6] have reported experimental evidence for the relationship between desirable reactions and p-conductivity in sulphided cobalt-molybdenum-alumina catalysts.

The carbonaceous molecule in Equation 1 is chemisorbed by electron acceptor states (represented as □) in the catalyst. Examples of electron acceptor states include anion vacancies in molybdenum sulphides and Lewis acid sites in alumina. Heckelsberg and Banks [7] have explained catalytic cracking in terms of electron transfer which occurs via electron acceptor states.

In alumina, the Al^{3+} cations are the adsorption sites, or electron acceptor states.

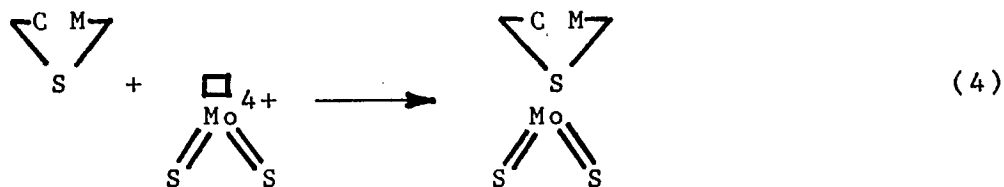


Thermodynamic equilibrium calculations for the reaction

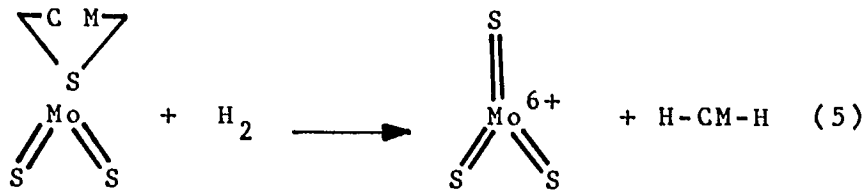


indicate [1] that at reaction conditions, molybdenum sulphides should be predominantly present as MoS_2 with a small amount of MoS_3 .

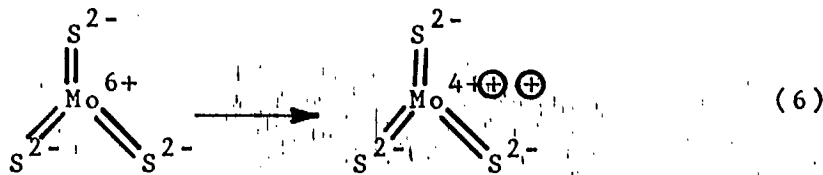
The carbonaceous molecule will be adsorbed at anion vacancies [8-10] which in this case are sulphur vacancies in MoS_3 . As an example, a carbonaceous molecule in a residual oil would probably be a polycyclic aromatic containing a thiophenic ring, CM-S



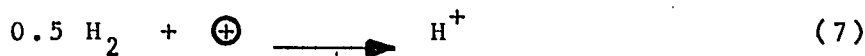
The sulphur containing carbonaceous molecule could be chemisorbed by an electron acceptor state, which is a sulphur vacancy in MoS_3 , as indicated in Equation 4. The chemisorbed species can react with hydrogen as shown in Equation 5.



The hydrogen which reacts is also chemisorbed on the catalyst in a manner to be described below. The reaction products are MoS_3 and a hydrogenated carbonaceous molecule. The MoS_3 can also be considered to be MoS_2 containing non-stoichiometric sulphur. The non-stoichiometric MoS_2 , containing excess sulphur anions, must also contain electron holes in order to preserve electron neutrality, as shown in Equation 6



Hydrogen chemisorption has been associated with electron holes [3] as shown in Equation 7

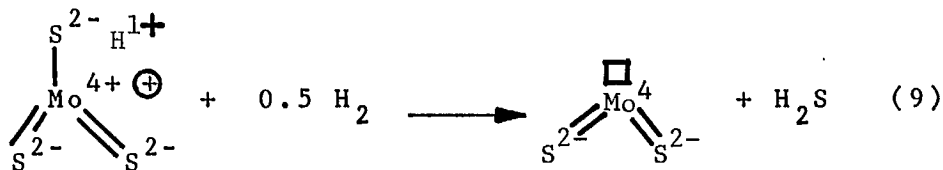


Wright et al [11] have reported experimental evidence for hydrogen chemisorption on sulphur anions. These concepts are combined, in Equation 8.



Continued reaction with chemisorbed hydrogen leads to the formation of hydrogen sulphide and the regeneration of the original electron acceptor state (sulphur anion

vacancy), as shown in Equation 9.



If the desirable reaction, shown in Equation 1, was an elementary reaction, then its rate could be expressed as

$$\text{Rate} \propto [\text{CM}] [\text{H}_2] \quad (10)$$

In terms of the reaction sites this would be

$$\text{Rate} \propto [\square] [\oplus] \quad (11)$$

Two site mechanisms of this type have been proposed previously [12-14]

Similarly, the rate of the undesirable reaction can be expressed as

$$\text{Rate} \propto [\text{CM}] \quad (12)$$

Expressed in terms of reaction sites on the catalyst, it becomes

$$\text{Rate} \propto [\square] \quad (13)$$

Equations 10-13 are based on the carbonaceous molecules being chemisorbed by electron acceptor states and on hydrogen being chemisorbed by electron holes.

The role of the promoter ions in the catalyst is to provide additional electron holes [2,6], for the chemisorption of hydrogen, as illustrated in Equation 14.



As described above both the oxide phase (alumina) and the sulphide phase (MoS_2 containing excess non-stoichiometric sulphur) of the catalyst contain electron acceptor states (\square). The data in Figure 1 are for catalysts having different amounts of sulphide and oxide phases. As the proportion of molybdenum increases, the number of molybdenum electron acceptor states will increase and the number of alumina electron acceptor states will decrease.

Figure 1 shows that the sulphur conversion of Athabasca bitumen (see Table 1) increases as the molybdenum content of the catalyst increases. By increasing the molybdenum content of the catalyst, both the number of molybdenum electron acceptor states and the number of electron holes (\oplus) increase, as indicated in Equations 4 to 9. Equation 10 shows that both types of reaction sites are required for desirable reactions. Therefore the increase in sulphur conversion with molybdenum content of the catalyst is consistent with Equation 10.

Figure 1 shows that greater sulphur conversions were attained by adding nickel promoter ions to the catalyst. This experimental result is also consistent with Equation 10 which shows that conversion should increase when the number of electron holes (\oplus) increase. Promoter ions introduce electron holes into the catalyst, as indicated in Equation 14.

The above reaction mechanism (Equation 10) has also been used to describe the influence of hydrogen sulphide [1], alkali metal ions [15], and halide ions [16,17].

CATALYST DEACTIVATION

Deactivation during catalytic hydrocracking of residual oils is caused by the formation of coke, by the deposition of metals (Ni and V), and sometimes by the deposition of clay or sand particles that may be present in the feedstock [18].

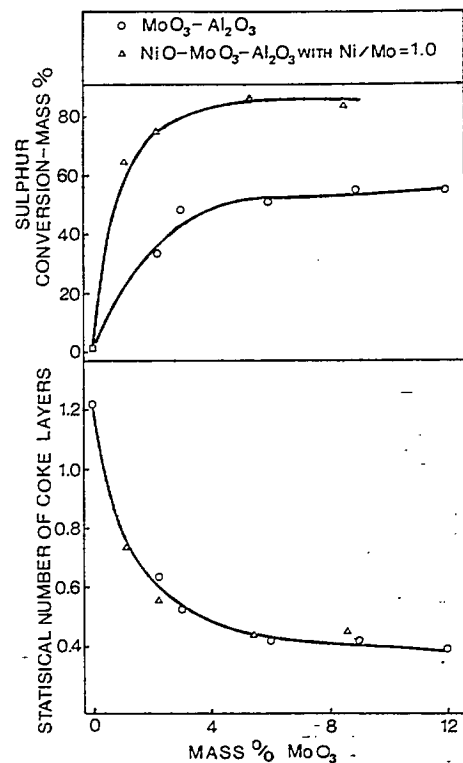


Figure 1 Conversion of sulphur containing carbonaceous species at 400°C (mass %) and statistical number of monolayers of coke on the catalyst versus MoO₃ concentration in the oxide form of the catalyst. Triangles represent NiO-MoO₃-Al₂O₃ catalysts having a Ni/Mo ratio (atomic) of 1, circles represent MoO₃ catalysts. Used with permission (ref 1).

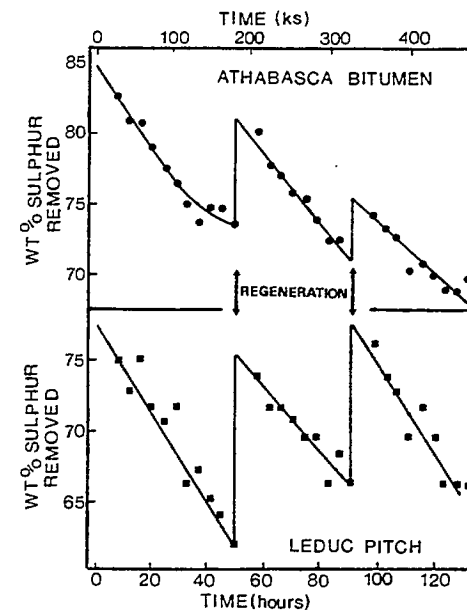


Figure 2 Mass % sulphur removed versus time, for Athabasca bitumen and Leduc pitch. Regenerations were performed after 180 ks (50 h), 328 ks (91 h) and 475 ks (132 h). The reaction temperatures were 450°C and 460°C for Athabasca bitumen and Leduc pitch respectively. Reprinted by permission of the copyright owner (ref 18).

The lower part of Figure 1 shows the amount of coke on the catalyst as a function of the catalyst molybdenum content. Equation 13 indicates that undesirable reactions are only dependent upon the number of electron acceptor states (\square) in the catalyst. In Figure 1, as the number of sulphide phase electron states increase, the number of oxide phase (alumina) electron acceptor states decrease. It has been shown [1] that the Fermi level of the oxide phase is much lower than the Fermi level of the sulphide phase. This means that coke will be bonded much more strongly to the oxide phase. Therefore, as the number of oxide phase electron acceptor states decrease, the quantity of coke on the catalyst also decreases, as shown in Figure 1.

The lower part of Figure 1 also shows that the presence of nickel promoter ions in the catalyst had no influence on the catalyst coke content. This is consistent with Equation 13 which shows that undesirable reactions are not influenced by the number of electron holes (\oplus) in the catalyst.

The separate effects of coke formation and metals deposition have been described in a study with two different residual oil feedstocks [18]. Their properties are listed in Table 1. They have a similar tendency to form coke (Conradson Carbon Residue) but much different contents of organometallic compounds (nickel and vanadium).

TABLE 1 FEEDSTOCK PROPERTIES

	Athabasca Bitumen	Leduc Pitch
Specific Gravity 15/15°C	1.000	0.991
Ash (m %) 700°C	0.70	0.013
Nickel (ppm)	68	13
Vanadium (ppm)	189	10
Iron (ppm)	358	28
Conradson Carbon Residue (m %)	12.6	14.7
Pentane Insolubles (m %)	15.8	6.1
Benzene Insolubles (m %)	0.90	0.09
CS ₂ Insolubles (m %)	0.88	0.05
Sulphur (m %)	4.72	0.92
Nitrogen (m %)	0.42	0.55
Residuum (+525°C)	51	63

Results from reaction experiments are shown in Figure 2. For both feedstocks, the sulphur conversions decrease with increasing time on stream. After 50 hours on stream, both catalysts were regenerated by burning the coke. When the catalysts were put back on stream, deactivation continued. Regeneration was performed again, after 90 hours on stream. This was followed by another on stream period, during which deactivation continued.

After each deactivation, the catalyst processing the Leduc pitch returned to its original sulphur conversion. In contrast after each regeneration, the catalyst processing the Athabasca bitumen produced progressively lower and lower sulphur conversions. The Leduc pitch contained no metals. Therefore after the coke was removed by regeneration, the catalyst returned to its original conversion level. However the Athabasca bitumen contained large quantities of metals. Even after the coke was removed by regeneration, the metals would remain on the catalyst. The metals which were not removed were responsible for the lower sulphur conversions obtained after each regeneration.

Deactivation by metals deposition is also reflected in the measured metals contents of the catalysts. Figures 3 and 4 show electron microprobe measurements of metals as a function of radial position in the catalyst. It is apparent that large amounts of metals are deposited on the outer edge of the catalyst pellets, while the interior contains very little metal. At sufficiently long times on stream, the pores at the outer edge of the catalyst pellets become completely blocked. This phenomena is referred to as pore mouth plugging. When the pores become plugged there is a catastrophic decrease in conversion.

In Figures 3 and 4 the nickel and vanadium were originally present in the feedstock as organometallic compounds. The iron was probably associated with the clay or sand. It is reflected in the ash content of the bitumen in Table 1 being greater than that of the pitch.

The carbon content of the catalyst, determined by a special electron microprobe technique, is shown

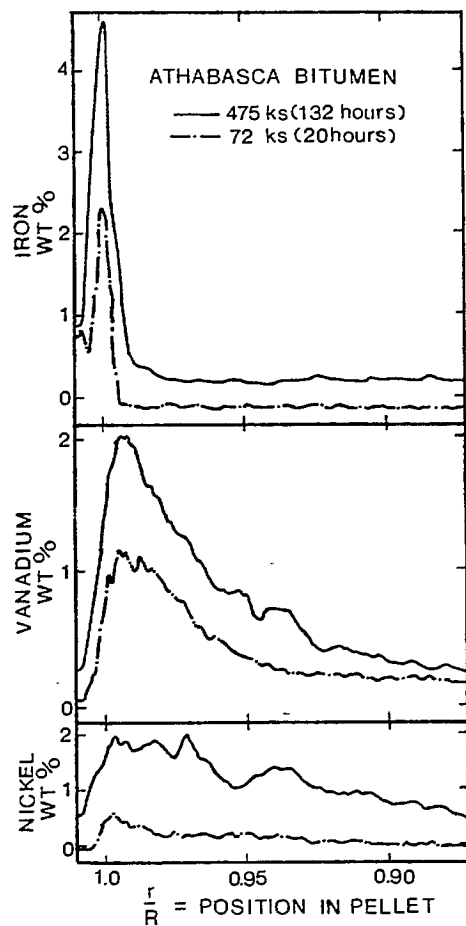


Figure 3 Fe, V and Ni concentrations versus radial position in catalyst pellets used to process Athabasca bitumen

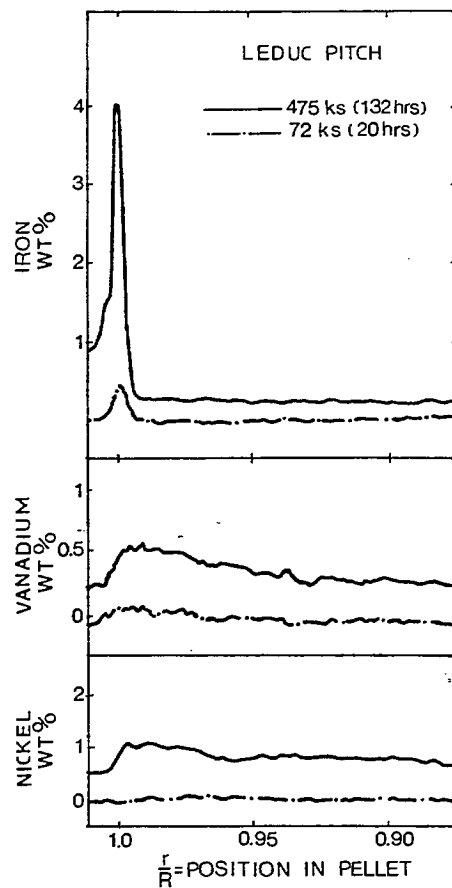


Figure 4 Fe, V and Ni concentrations versus radial position in catalyst pellets used to process Leduc pitch.

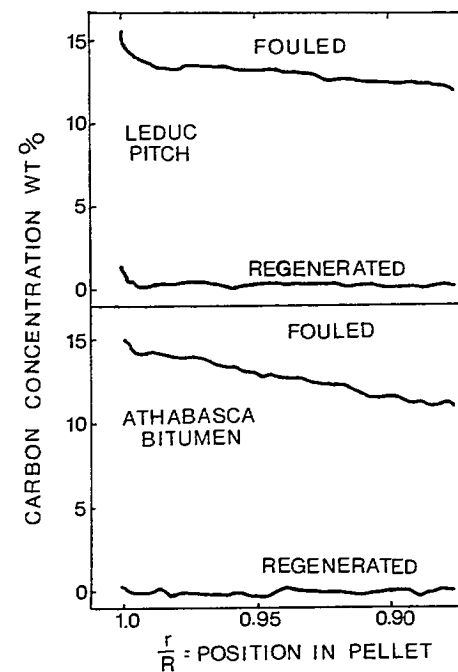


Figure 5 Carbon concentration versus radial position in the catalyst pellet

in Figure 5. It is apparent that carbon deposition is similar with both feedstocks. Furthermore there is very little change in carbon content from the exterior of the catalyst pellet to the interior. This is consistent with Auger results reported by Pollack and co-workers [19]. However these workers also used transmission electron microscopy which is capable of greater resolution. In this way, they were able to determine that on a microscopic scale, the carbon was deposited in patches on the catalyst surface.

DIFFUSION IN CATALYST PORES

Many investigators have reported diffusional limitations in catalysts used for hydroprocessing residual feedstocks [20-22]. Effectiveness factors varying from 0.7 to 0.2 have been reported [23-24].

The Ni and V metals profiles in Figures 3 and 4 can also be interpreted in terms of diffusion. Metals are deposited at the reaction sites at which the large organometallic compounds are converted into smaller molecules. The large quantity of metal deposits at the external edge of the catalyst pellets indicate that the organometallic compounds are reacting near the exterior of the catalyst pellet before they have been able to diffuse to the center.

Most of the measurements on diffusivities of compounds in the liquid phase, in catalyst pores, have been made with small molecules. Recently Chantong and Massoth [26] measured diffusivities of non-metallic porphyrin molecules. Baltus and Anderson [27] made diffusivity measurements using narrow molecular weight fractions of a petroleum residuum. In their work tetrahydrofuran asphaltenes were separated into five fractions by gel permeation chromatography. The polystyrene equivalent average molecular weights they reported were 3000, 6000, 12000, 24000, and 48000.

All of these measurements have been correlated by similar empirical equations having empirical constants. These equations are generally of the form indicated here in Equation 15,

$$D_{\text{eff}} = D_0 \exp(-4.0 d_m/d_p) \quad (15)$$

where, D_{eff} is the effective diffusivity in the catalyst pore, D_0 is the diffusivity in bulk solution, d_m is the molecular diameter, and d_p is the catalyst pore diameter. The molecular diameter used was the diameter of the model compounds in studies which used pure compounds. For asphaltene fractions, the molecular diameter was calculated using the Stokes Einstein equation with measured values of bulk diffusivities [27].

Almost all of the experimental diffusion measurements have been made at room temperature, in extremely dilute solutions (less than 3 m %). Information at reaction temperatures, in real solutions containing dissolved hydrogen, is sparse [28,29]. One known complication is that the molecules tend to agglomerate to form micelles when the solutions are not extremely dilute. For example, values from 885 to 10910 have been reported for average molecular weights of Athabasca bitumen asphaltenes, depending on the concentration of the solution used [30]. Experiments performed by Moschopedis, et al [31] have shown that as the solution concentration increased the molecular weight increased, presumably as a result of micelle formation. Because the diameter of the diffusing species will increase when micelles are formed (as shown by an increase in molecular weight of the diffusing species), slower diffusion rates will be attained, in accordance with equation 15. However, the higher thermal energies in the molecules at reaction temperature may tend to break up micelles. The effects of these factors on diffusion rates is not known quantitatively.

CATALYST MODELLING

A number of papers modelling conversion and deactivation during catalytic residuum hydrocracking have appeared in the literature [32-44]. The conversion has been predicted as a function of pore radius [34,40]. The amount of the deposit has also been predicted as a function of pore radius [33,44]. Profiles have been predicted as a function of radial distance through the catalyst pellet [36]. Deactivation rates have been modelled as a function of catalyst pore size [44] up to the point of poreplugging.

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Recent investigations, both experimental measurements [45,46] and simulation studies (42) have indicated that bimodal catalysts have considerable potential. The large pores provide greater rates of diffusion than the smaller pores. However the small pores provide greater surface area on which the conversion reactions can occur. Ideally, if both large and small pores are combined, an optimum can be attained.

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