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Conversion of Athabasca Bitumen with Dispersed and Supported Mo-Based Catalysts as a Function of Dispersed Catalyst Concentration

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A hydrocracking study of Athabasca bitumen using a batch reactor with varying concentrations of a microdispersed metal sulfide catalyst (MoS_2) in the presence and absence of a common commercial supported catalyst is reported. The work compares the effects of a wide range of MoS_2 dispersed catalyst concentrations (0−6000 ppm) on the conversion of residuum and the effects of using that dispersed catalyst with a commercial extruded hydrogenation catalyst. Hydrocracking runs using only the MoS_2 microdispersed catalyst showed reduced coke formation only at low Mo concentrations. In the presence of the supported catalyst, solids formation increased significantly and overall catalyst performance was lowered as a function of increased MoS_2 microdispersed catalyst concentration.

Introduction

Hydrocracking of Athabasca bitumen residuum is normally carried out with finely dispersed transition metal sulfide catalysts[1] or with catalysts in which the metals are supported on a porous alumina or alumina/silica base.[2] A mechanism which describes the role of supported catalysts during hydrocracking has recently been proposed[3,4] and supporting evidence was provided by stable isotope studies.[5] The modified mechanism is reproduced in Figure 1 and assumes that the main role of catalyst is to activate hydrogen toward reaction with an aromatic carbon radical to give a cyclohexadienyl type intermediate (step III). Once the intermediate is formed, the molecule decomposes through a series of reactions to form distillate and gases. Gaseous hydrogen is not incorporated into the residuum fraction indicating hydrogen capping reactions (step IV) are not dominant in the hydrocracking mechanism. If the CCR forming molecule which is being decomposed contains sulfur in a thiophene type structure, then hydrodesulfurization (HDS) of the liquids could result with the production of hydrogen sulfide as one of the products.

With dispersed catalysts, concentrations are generally kept low (50−250 ppm), and the main observable effect is a reduction in solids formation in the reactor. Organically soluble dispersed catalysts containing a complexed transition metal (Ni, Co, Fe, Mo, Sn) are typically added as a catalyst precursor to the feedstock. Under reaction conditions a highly dispersed metal sulfide catalyst forms. According to the proposed mechanism (Figure 1), solids formation (step II) would be reduced by capping radical intermediates with hydrogen (step IV). Gaseous hydrogen would be incorporated into the unreacted residuum. At Mo concentrations of 250 ppm, hydrogen incorporation into the residuum was observed.[5] Sulfur and CCR conversions are low, indicating that the next step, addition of a hydrogen atom to the aromatic center, does not take place at these Mo concentrations.

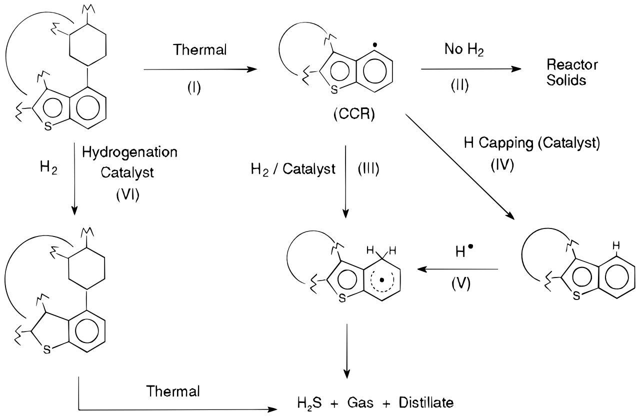

Figure 1. Proposed mechanism of hydrocracking.

Very few studies have looked specifically at the effects of the concentration of dispersed catalysts. Fixari et al.[6] found that coke formation decreased to a low level at relatively low Mo concentrations and remained constant as the Mo concentration increased. Sulfur removal rose as a function of Mo concentration up to a certain point and then leveled off. Both coke formation and sulfur

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(1) Bearden, R.; Aldridge, C. L. US Patent 4,134,825, 1979.

(2) Beaton, W. I.; Bertolacini, R. J. *Catal. Rev.—Sci. Eng.* **1991**, *33* (3, 4), 281−317.

(3) Sanford, E. C. *Ind. Eng. Chem. Res.* **1994**, *33*, 109−117.

(4) Sanford, E. C. *Energy Fuels* **1995**, *9*, 549−559.

(5) Sanford, E. C.; Steer, J. G.; Muehlenbachs, K.; Gray, M. R. *Energy Fuels* **1995**, *9*, 928−935.

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(7) Bearden, R.; Aldridge, C. L. Presented at the AIChE 90th National Meeting, April 5−9, 1981.

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removal varied as function of the catalyst precursor, which was also observed by Bearden and Aldridge.[1]

Because dispersed catalysts, at the concentrations normally used, mainly prevent coke formation in the reactor, and coke formation is thought to be one of the main contributors to catalyst deactivation with supported catalysts, there was some possibility that there might be a synergistic effect when a mixture of a dispersed catalyst and a supported catalyst was used.

The object of the work reported here is to compare the effects of much higher concentrations of MoS_2 dispersed catalysts on the thermal conversion of residuum and the effects of using that high-concentration dispersed catalyst in conjunction with a commercially available extruded hydrogenation catalyst. To this end, Athabasca bitumen was hydrocracked in the presence of various amounts of the MoS_2 precursor dispersed catalyst (Molyvan-L) ranging in concentration from approximately 0 to 6000 ppm Mo both in the presence and absence of a common commercial supported catalyst.

Experimental Section

All experiments were carried out at 400 °C in a 1.0 L Parr reactor for a period of 4.0 h. The reaction mixture was kept under an atmosphere of hydrogen gas at approximately 1000 psi and thoroughly mixed with a mechanical stirrer at 600 rpm. Enough hydrogen gas was added (450 psi) to the reactor at room temperature to give a pressure close to the desired pressure when reaction temperature was reached. Pressure was then monitored throughout the reaction and either the reactor gas was bled off or fresh hydrogen gas added to maintain approximately 1000 psi.

All experimental runs used 400.0 g of Athabasca bitumen as the feed. The feed contained 4.2% sulfur, 4430 ppm nitrogen, 83.1% carbon, 10.2% hydrogen, 196 ppm vanadium, 74 ppm nickel, and 14.4% CCR. A 400.0 g feedstock charge contains 1.60 g of methylene chloride insoluble solids. This value was subtracted from measured reactor solids in all runs to more accurately reflect the amount of solids produced during the 4 h reaction. In the first series, each run was charged with Athabasca bitumen and a varying amount of Molyvan-L ranging from 0.0 to 20.0 g giving a Mo concentration from approximately 0 to 6000 ppm. Molyvan-L is a mixture of approximately 80 wt % sulfurized oxymolybdenum (V) dithiophosphate of the formula $Mo_2S_2O_2[PS_2(OR)_2]_2$ (where R = 2-ethylhexyl) and 20 wt % of an aromatic petroleum oil. The second series was identical to the first except that 100.0 g of a commercial Co−Mo catalyst on a γ-alumina support was suspended in a catalyst basket in the reactor. The final two runs used molybdenum naphthenate as the microdispersed MoS_2 catalyst source. Detailed experimental conditions are summarized in Table 1.

After the 4-h reaction time, the reactor was cooled to room temperature, the reactor gas was vented, and a methylene chloride slurry was prepared from the reactor contents. Any solids adhering to the reactor walls or internals was carefully scraped off and added to the slurry. Where applicable, the catalyst basket was also washed with methylene chloride and the washings added to the slurry mixture. The slurry was then centrifuged and solids separated and washed with methylene chloride using a 30 μm filter. The solids were dried and weighed. The filtrate solvent was removed by a rotary evaporator and the total liquids were weighed and submitted for analysis. Any washed catalyst was removed from the basket, dried, weighed, and submitted for analysis.

Table 1. Summary of Experimental Conditions and Product Weights

run	Molyvan wt (g)	Mo (ppm)	adjusted solids (g)[b]	liquid product (g)[c]	solids on catalyst (g)[d]
1	0.0	0	15.5	312.5	
2	1.0	325	4.2	349.5	
3	2.5	808	2.1	348.4	
4	5.0	1607	8.6	341.3	
5	10.0	3174	14.6	337.7	
6	20.0	6197	20.3	329.0	
7	0.0	0	0.8	281.3	36.6
8	1.0	325	4.5	292.4	34.0
9	2.5	808	6.7	296.3	34.5
10	5.0	1607	12.5	305.3	32.2
11	10.0	3174	19.4	315.2	26.7
12	20.0	6197	41.2	295.3	24.7
13	5.1[a]	1138	6.0	370.4	
14	19.7[a]	4397	20.7	350.7	

[a] Runs 13 and 14 use molybdenum naphthenate instead of Molyvan-L. [b] Values are ±1 g based on previous runs. [c] Values are ±2 g based on previous runs. [d] Values are ±0.8 g based on previous runs.

It was assumed loss in total product weight compared the amount of feed added would be due to gases and light hydrocarbons produced in the reaction and vented off during product workup.

The conversions shown in Figures 2−9 are defined by the general equation

$$\%\ \text{conversion of A} = \{[(\%\ A_F wt_F) - (\%\ A_{LP} wt_{LP})]/[\%\ A_F wt_F]\} \times 100$$

where A is one of residuum, CCR, S, N, Ni, or V, % A_F is percent of A in feedstock, wt_F is weight of the feedstock, % A_{LP} is percent of A in liquid product, and wt_{LP} is weight of the liquid product.

Results

A summary of batch reactor experimental conditions and mass of liquid and solid products for these runs are given in Table 1. The batch reactor runs are grouped into three series. The first six runs (runs 1−6) represent a series in which increased amounts of Molyvan-L have been added to Athabasca bitumen. The next six runs (runs 7−12) form a series using similar amounts of Molyvan-L as the first series, but this time in the presence of 100 g of a commercial supported catalyst (Co−Mo on γ-alumina). The final two runs (runs 13−14) represent the introduction of highly dispersed MoS_2 using molybdenum naphthenate as the organically soluble precursor instead of Molyvan-L.

In the first series using only Molyvan-L (Figure 2), the percent residuum conversion increased with increasing Mo concentration to about 71% for the higher Mo concentrations. This maximum residuum conversion using Molyvan-L was approximately the same, within normal scatter, as that found for the supported catalyst used in the absence of dispersed MoS_2. However, when the MoS_2 dispersed catalyst and the supported catalyst were used together, the residuum conversion decreased significantly as a function of Mo concentration with a slight increase again at the last data point (6000 ppm Mo).

The use of Molyvan-L alone increases CCR conversion significantly compared with the run having 0 ppm Mo (Figure 3). After the initial rise, CCR increases only slightly as a function of Mo concentration and levels off at approximately the same conversions obtained with supported catalyst alone. However, we again see a

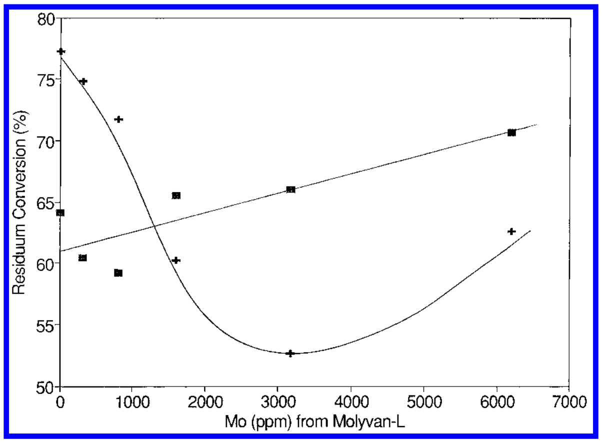

Figure 2. Residuum conversion vs Mo concentration: Molyvan (■), Molyvan + supported catalyst (+).

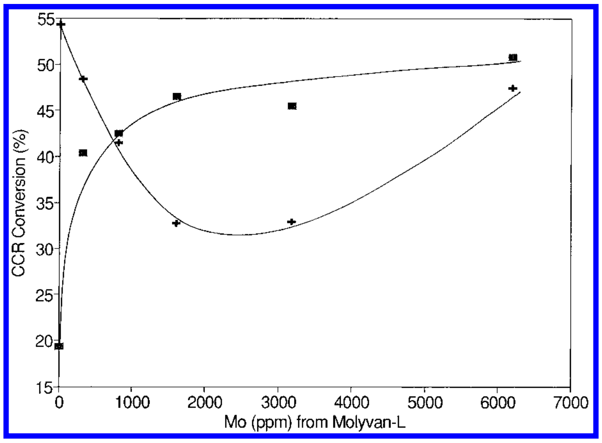

Figure 3. CCR conversion vs Mo concentration: Molyvan (■), Molyvan + supported catalyst (+).

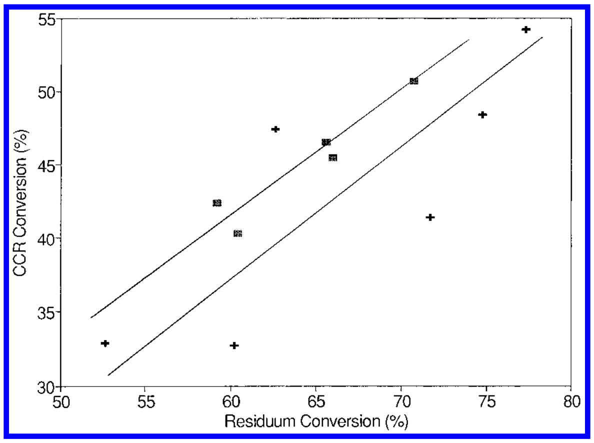

Figure 4. CCR conversion vs residuum conversion: Molyvan (■), Molyvan + supported catalyst (+).

marked reduction in CCR conversion when both dispersed catalyst and supported catalyst are used together rising slightly again at higher Mo concentrations. In all cases, with the exception of the no dispersed catalyst case, CCR conversion follows residuum conversion as observed previously.[4] A plot of CCR conversion versus residuum conversion in these runs (Figure 4) also shows a general linear correlation.

When using exclusively Molyvan-L, there is a rapid increase in sulfur conversion till 1000 ppm of Mo and leveling off at higher concentrations to 50% conversion (Figure 5). The supported catalyst shows much higher sulfur conversions (69%) initially, but when the concentration of Mo increases the sulfur conversions are depressed. After 1500 ppm of Mo sulfur conversions for both series are approximately the same.

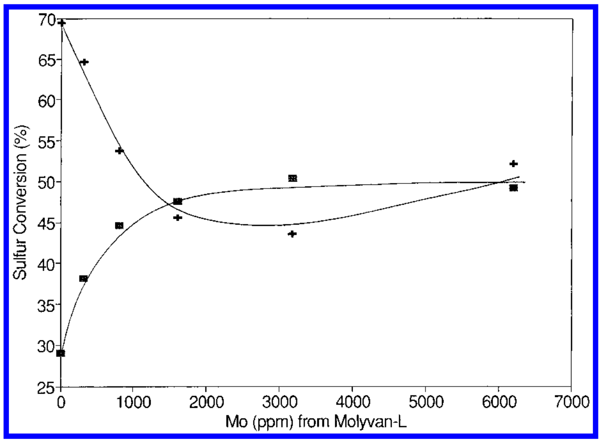

Figure 5. Sulfur conversion vs Mo concentration: Molyvan (■), Molyvan + supported catalyst (+).

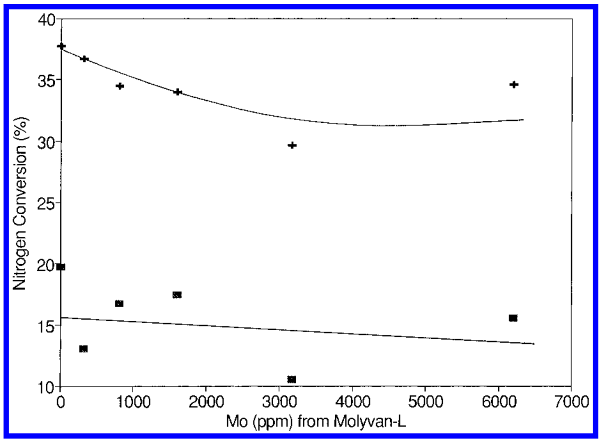

Figure 6. Nitrogen conversion vs Mo concentration: Molyvan (■), Molyvan + supported catalyst (+).

In the series with Molyvan-L, nitrogen conversion is much lower than when supported catalyst is used and is relatively constant at about 16% conversion with minor variations (Figure 6). Although there is a slight depression in nitrogen conversions when the supported catalyst is used in combination with Molyvan-L, the percent conversion is relatively constant and substantially higher (35% conversion) than with Molyvan-L alone.

In the presence of increasing concentrations of Molyvan-L both Ni and V conversions (Figure 7) undergo an initial dip at about 200 ppm Mo followed by a rapid increase to 2000 ppm and then instead of leveling off there is a gradual increase for the rest of the series significantly surpassing the percent conversion obtained when using the supported catalyst by itself. Initially, the Ni and V conversions are higher (77% compared with 58%) when the supported catalyst is used by itself. However, when used in combination with Molyvan-L the Ni and V conversions become depressed.

The use of Molyvan-L decreases the amount of solids formed in the reaction for the first 1000 ppm of Mo with the optimal range being 300−800 ppm (Figure 8). After 2000 ppm the amount of solids formed increases again to a slightly higher value than the first run when no MoS_2 was used. The additional two runs (runs 13 and 14) carried out with an alternate MoS_2 source, molybdenum naphthenate, produced similar amounts of solid in the product. In combination with the supported

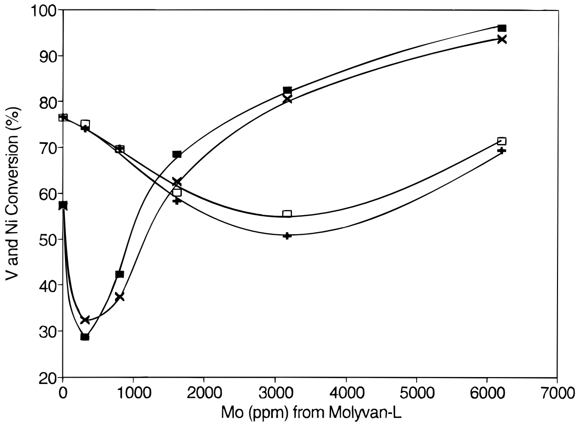

Figure 7. Vanadium and nickel conversions vs Mo concentration: Molyvan: V (■) and Ni (×), Molyvan + supported catalyst: V (+) and Ni (□).

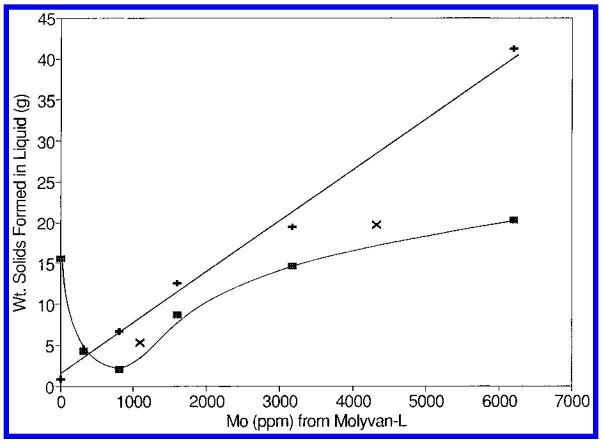

Figure 8. Solids formed in the reaction vs Mo concentration: Molyvan (■), Molyvan + supported catalyst (+), molybdenum naphthenate (×).

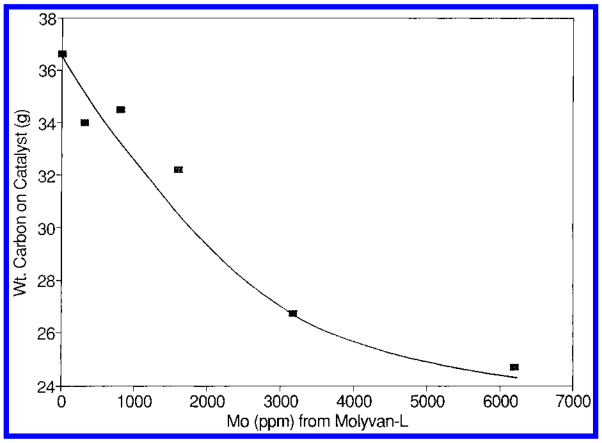

Figure 9. Carbon on catalyst vs Mo concentration: Molyvan + supported catalyst (■).

catalyst, the amount of solids produced increases proportionally with Mo concentration, eventually forming substantial amounts of solids at high dispersed catalyst concentrations. It should be noted that the weight of solids formed has been adjusted to take into account solids normally found in raw feedstock as well as solids due to MoS_2 precipitation.

The amount of carbon found on the supported catalyst after the reaction is completed (Figure 9) decreases gradually with the amount of Molyvan-L used.

Discussion

The experimental results are consistent with the model proposed by Sanford which has been discussed in detail elsewhere.[3,4] A modified form of this model is shown in Figure 1. The early stages of hydrocracking (step I) involve mainly thermal processes resulting in the fission of easy to break bonds to produce mainly distillate with little coke and gas formation. An aromatic radical intermediate is produced as a result of step I and can undergo a number of reactions. With no hydrogen present these radical intermediates can condense with similar radical species leading to a production of coke (step II). In the presence of hydrogen the carbon radical can react with hydrogen to form a capped neutral species (step IV) or it can add to the aromatic ring to form another radical intermediate (step III) destroying the aromaticity of the ring system and which can then lead, through a series of transformations, to the production of gases and distillate. Note that addition of a hydrogen radical to the neutral intermediate (step V) will also form a cyclohexadienyl type radical intermediate. Also, hydrogenation of the feedstock by fresh catalyst has been included as step VI of the process. This process is most prevalent in the early stages of the reaction before the catalyst is deactivated to hydrogenation.

Finely dispersed metal sulfides, formed in-situ from a variety of precursors, are commonly used to suppress coke formation during hydrocracking of petroleum residua.[8] The pioneering work of Bearden and Aldridge showed that coke formation during cracking of Cold Lake crude decreased as the molybdenum concentration increased up to approximately 500–800 ppm on feed, under a relatively high reactor total pressure of 17.3 MPa.[8] As the concentration of Mo increased above 500 ppm, there was a steady increase in solids formation in batch runs, from 0.5 wt % up to 1.7 wt % of feed at 10 000 ppm Mo. The results reported here using Athabasca bitumen are similar, with a minimum in the reactor solids concentration occurring at 800 ppm and increasing to 20 g per 400 g of feed or 5 wt % at 6200 ppm. There are two likely explanations for the difference in magnitude of the effect. The use of different feeds could contribute, although they are both Alberta oil sand derived feeds. The most likely reason is the hydrogen partial pressure difference: 17.3 MPa in one case and 6.9 MPa in the other case.

The trend of increasing solids formation at higher Mo concentrations would imply that at least two processes are occurring in competition with each other. Since most of the Mo in the reaction is recovered in the solid products and not the liquid, it would suggest that the MoS_2 microcrystals may be responsible for seeding the precipitation of solids as well as catalytically stabilizing coke precursors through hydrogen transfer (step IV, Figure 1). Which process dominates is determined by the concentration of MoS_2 in the reaction mixture. Solids formation also appears not to be dependent on the dispersed catalyst's organic ligand. Two runs using molybdenum naphthanate at the Mo concentrations of 1138 and 4397 ppm resulted in similar amounts of solid

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(8) Dabkowski, M. J.; Shih, S. S.; Albinson, K. R. *AIChE Symp. Ser.* **1991**, *87* (282), 53–61.

formation compared with runs using Molyvan-L as the precursor. Bearden and Aldridge found that most molybdenum precursors gave similar results, although MoO_3 and MoS_2 were not as effective as other precursors.[1,7]

Residuum conversion as a function of dispersed Mo concentration in the absence of the supported catalyst was 64 ± 4% for six runs, including the zero concentration run (Figure 2). This represents the normal reproducibility of these runs.[9] However, when the data are plotted, there appears to be a definite trend to increasing conversion with increasing Mo concentration. In hydroconversion runs with a supported catalyst, there is a small but definite catalytic contribution[10] and the contribution from the dispersed Mo sulfide is in the same direction. The catalytic contribution to residuum conversion is thought to be due to hydrogenation of aromatic rings in complex molecules which would result in structures which are easier to thermally crack.

Sulfur conversion, CCR conversion and metals conversion with a dispersed catalyst all increase rapidly up to approximately 1500 ppm Mo and then level off, giving results comparable to those observed with Athabasca bitumen residuum and supported catalysts in a batch reactor.[10] The indication is that these are catalytic reactions, catalyzed by the dispersed Mo sulfide present. Selective demetallation has been one of the advantages of dispersed catalysts like Molyvan-L,[8] and MoS_2 is known to be an excellent hydrodesulfurization (HDS) catalyst and could promote the destruction of heterocyclic ring systems at sulfur centers.[11] Nitrogen conversion is low in the presence of dispersed molybdenum sulfide, in keeping with previous findings[10] that nitrogen removal is largely due to the incorporation of nitrogen-containing compounds into reactor solids that are formed. Under conditions which produce relatively few solids, nitrogen removal would be low.

When supported catalysts are used during hydrocracking, it has been shown that the active sites for hydrogenation of aromatic rings (step VI, Figure 1), which lead to sulfur, nitrogen, and CCR conversion, are lost very rapidly.[4] There is also a rapid buildup of carbon on the catalyst during this same period, which is the likely cause of the initial deactivation. After the initial deactivation, the catalyst continues to deactivate, probably due to the deposition of metals on the catalyst. If dispersed catalysts and supported catalysts were used together, then there are two likely results. First, the dispersed catalysts, which are normally used to prevent coke formation in the reactor, might prevent coke formation on the supported catalyst, thus decreasing the rate of initial deactivation of the catalyst. This would be very beneficial if it were to happen. The second possibility is that the dispersed metal sulfide would deposit on the active sites of the supported catalyst and deactivate the catalyst through metal poisoning.

When the two types of catalysts were used together, the amount of carbon on the supported catalyst did indeed decrease, from 36 to 24 g. Although this is a significant decrease, there is still a large amount of carbon on the catalyst. Much of the initial carbon deposition on the catalyst may be due to acid-catalyzed coke formation by the acid sites on the catalyst.[4]

When the data for residuum, sulfur, CCR, and metals conversions in the presence of dispersed and supported catalysts are compared, they all have one feature in common, a rapid decrease in conversion as the amount of dispersed catalyst in the system is increased. Residuum conversion decreases rapidly from 77% with no dispersed catalyst to approximately 60% at 1600 ppm Mo and then starts to level out. The last three runs at 1600−6200 ppm Mo give residuum conversions of 59 ± 5%, similar to the conversions in the presence of lower concentrations of Mo without any supported catalyst. Although there is some scatter in the data, it appears as though the supported catalyst ties up some of the dispersed Mo, thereby deactivating the supported catalyst, and the conversions are similar to runs with just dispersed Mo, but at lower concentrations.

CCR conversions are similar, with the runs in the presence of supported and dispersed catalyst leveling out at conversions of 34 ± 3%. Again, it appears that the supported catalyst has been completely deactivated and most of the dispersed Mo has been removed as a catalyst by the supported catalyst. When the concentration of dispersed catalyst reaches 6200 ppm, CCR conversion again increases to the level attained with 1600 ppm Mo in the absence of supported catalyst. Sulfur conversion follows a similar trend with conversions becoming similar in both cases at around 1600 ppm Mo. After 1600 ppm Mo, there is no effect of the supported catalyst on sulfur conversions. The trends for metals removal follow the same pattern.

Nitrogen removal is significantly higher in the presence of supported catalyst and decreases only slightly as a result of adding dispersed Mo to the supported catalyst. This is in keeping with the mechanism of nitrogen removal being one of nitrogen being incorporated into the solids which are formed.[10] Solids are formed on the supported catalyst very rapidly in the early stages of the reaction and this leads to a high nitrogen conversion. Although the total solids formed in the reaction, reactor solids plus catalyst solids, increases as the concentration of Mo increases, nitrogen removal appears to follow solids on the supported catalyst up to high dispersed Mo concentrations, when total solids increase rapidly and nitrogen conversion increases again.

Previous studies have shown that with supported catalysts in batch systems, coke forms rapidly on the catalyst but none is formed in the reactor when active catalyst is used.[4] As the catalyst deactivates, coke begins to form in the reactor. In the present studies, coke formation in the reactor in the presence of active supported catalyst was linear with dispersed Mo concentration and was higher than with just the dispersed catalyst. With dispersed catalyst there appears to be a competition between two opposing mechanisms, one which produces coke and one which prevents coke formation. At the lower Mo concentrations, the latter prevails. In the presence of a supported catalyst, the ability of the dispersed catalyst to prevent coke formation appears to have been largely lost while the coke-forming ability of the catalyst is still active.

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(9) Sanford, E. C.; Xu, C. M., submitted to *Can. J. Chem. Eng.*

(10) Sanford, E. C. *Energy Fuels* **1994**, *8*, 1276−1288.

(11) Lui, C.; Zhou, J.; Que, G.; Liang, W.; Zhu, Y. Presented at the Division of Petroleum Chemistry, Inc. 205th National Meeting of the American Chemical Society, Denver, CO, 1993.

Conclusions

1. Dispersed molybdenum sulfide has the ability to both promote and prevent coke formation during hydrocracking of Athabasca bitumen. At concentrations of Mo below approximately 800 ppm, coke formation is prevented, with the coke formation mechanism dominating at higher Mo concentrations.
2. When dispersed Mo sulfide is used together with a supported catalyst, the dispersed molybdenum sulfide rapidly deactivates the supported catalyst and at the same time ties up some of the dispersed catalyst. Thereafter, reactions proceed as if a lower concentration of dispersed Mo sulfide was present. The supported catalyst appears to completely remove the coke suppressing ability of the dispersed catalyst.

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