

DISPERSION AND ACTIVITY OF INORGANIC CATALYST PRECURSOR IN HEAVY OIL

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ABSTRACT

Compared to supported catalysts, highly dispersed catalyst particles suspended in heavy oil are less susceptible to deactivation during heavy oil upgrading. Oil soluble catalyst precursors produce highly dispersed catalyst particles but can be expensive even when used at low concentrations. The dispersion of an aqueous catalyst precursor using an atomizing nozzle suspended in Cold Lake heavy oil has been carried out in the laboratory and the activity of the resulting catalyst was verified in semi-batch autoclave tests. The activation of the catalyst could be achieved simply by heating the heavy oil and catalyst precursor to reaction temperature. Although the catalyst particles are larger than those produced by oil soluble precursors their activities appear to be as good. The catalyst particles were shown to maintain their activity when recycled in sequential batch tests. Some details of the catalyst preparation, testing and properties are presented.

INTRODUCTION

Hydrocracking catalysts for upgrading heavy oil and bitumen are typically composed of metal sulphides dispersed on a porous oxide support in the form of extrudates. These types of catalysts suffer loss of activity due to the deposition of coke and metals, such as nickel and vanadium present in the heavy oil. Eventually, the fixed bed reactors employing these catalysts must be shut down and the catalyst replaced at a significant expense. Process technologies, such as moving bed and ebullated bed catalysts, which avoid shutdown by continuous addition of fresh catalyst are available but they can be expensive in capital and operating costs. Other processes have included the continuous addition of small amounts (< 5wt%) of finely dispersed catalysts and oil soluble catalyst precursors such as molybdenum naphthenate [1] to the heavy oil. The use of highly dispersed catalysts to upgrade heavy feeds has been recently reviewed by Del Bianco *et al.* [2]. The active catalysts are generally considered to be in a colloidal state and range in size from sub-micron to several microns. Typically, the concentration of catalyst on metal basis is 50 - 1000ppm but even at these concentrations they can be expensive to use. The ability to recycle the catalyst is important for the economics of the process especially if the metal catalyst is used in high concentrations (>100ppm).

Molybdenum is the basic constituent of the most active catalysts. The major source of molybdenum is the mineral molybdenite (crystalline molybdenum sulphide) which is roasted to produce molybdenum oxide, purified by dissolution in aqueous ammonia to produce ammonium heptamolybdate and separated by fraction crystallization. Thus, ammonium heptamolybdate is one of the cheapest sources of molybdenum. An active dispersed catalyst precursor produced from this material in a simple process could have low cost compared to oil soluble catalyst precursors.

EXPERIMENTAL

Catalyst Dispersion: An atomizing nozzle was used to sparge an aqueous solution of ammonium heptamolybdate into the heavy oil held in a stirred heated tank. The temperature and pressure of the aqueous solution and hydrocarbon were maintained such that the water was immediately vapourized during the injection. A nitrogen purge tube was inserted at the top of the tank to minimize air oxidation and to aid in removal of water vapour and ammonia liberated during the process. The degree of dispersion was

controlled by adjustments in the solution concentration and, the pressure and flow rate of the atomizing nozzle.

By varying the concentration of Mo in the aqueous solutions while maintaining similar injection conditions, it is possible to produce products with suspended particulates having the same total surface area but different mass percent concentrations. Thus, two feeds were produced with different Mo concentration but with the same calculated total surface area for ammonium heptamolybdate particles and by extension MoS_2 surface areas.

Materials: The feedstock (F-0) used was Cold Lake heavy oil (Table 1). The catalyst precursor was ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. This salt was dissolved in de-ionized distilled water to the desired concentration and then injected into the heavy oil. Two feeds, F-1 and F-2, were produced having Mo concentrations of 212 and 611ppm, respectively. The oil soluble catalyst used was molybdenum naphthenate obtained as a 6wt.% Mo solution in oil. The required amount was added to the heavy oil after dilution in 21g of a diluent (BP: 200-343°C).

Activity Testing: The feedstocks containing the dispersed catalysts were processed in a 2L semi-batch autoclave that was purged with N_2 , charged with approximately 750g of the feedstock and pressurized to 1000psig with H_2 at room temperature. In order to ensure sulphiding of the catalyst before hydrocracking conditions were reached, the autoclave system was modified to allow the injection of dimethyldisulphide (DMDS) at high pressure. The autoclave was heated to 350°C at which point the pressure was about 2000psig. The flow of H_2 commenced at 2L/min., was maintained for 30 minutes then stopped. DMDS was introduced from the bottom of the reactor and the system held at 350°C for 30 minutes without H_2 flow. Following this period, H_2 flow was restarted and increased to 6.0slpm as the temperature increased to 450°C. These final conditions were maintained for a fixed period and then the reaction was quenched in less than 5 minutes. A comparison test was also performed using molybdenum naphthenate as the catalyst precursor. Tests were also performed without this activation procedure and without addition of DMDS by heating straight to 450°C.

Vapour flow from the autoclave was passed through a series of three condensers, two held at 0°C and the third at -78°C. Dry gas (C_1 - C_3) passing through these condensers was accumulated in a tank. C_4 - C_5 product liquid was taken as the volatiles lost at atmospheric pressure and room temperature from the three condensers after let-down to sample collection bottles.

Asphaltene were determined by precipitation using n-pentane in a ratio of 40:1 with the oil. The 525°C+ pitch contents were determined by crude simulated distillation ASTM D5307.

RESULTS AND DISCUSSION

The results of autoclave tests are summarized in Table 2. The first three tests were carried out under identical conditions using the prepared feedstocks (Test-1 and -2) and the as-received heavy oil containing the oil soluble organometallic precursor (Test-3). In terms of coke and liquid yields, the catalyst formed from water-soluble precursor provided comparable performance to that from the oil soluble precursor. Slightly higher asphaltene and CCR conversions were obtained with the water soluble catalyst precursor.

Test -1 and -3 show that nearly identical product distributions can be obtained using similar Mo concentrations prepared from either water or oil soluble precursors. The small differences lie in the C_4 - C_5 and C_{6+} liquid yields. Asphaltene conversion was 10% higher in Test-1 using the water-soluble precursor compared to Test-3 with the oil soluble precursor. Thus, if the dispersion can be made high enough water-soluble catalyst precursors can be used in place of more expensive organometallic precursors.

The flexibility of the injection process to achieve a range of dispersions is illustrated by Test-1 and -2. In this case, the feedstocks F-1 and F-2 were prepared so that the calculated total surface area of the precursor per gram of oil was identical but the Mo

concentrations were different. Identical precursor and catalyst surface areas should exhibit the same activity. While the apparent catalyst activities were similar in Test-1 and -2, a slightly higher activity was exhibited in Test-2 which also had the higher Mo concentration. However, if feedstock F-2 was diluted with additional oil so as to make the Mo concentration similar to that of F-1, the lower activity per mass of Mo is evident in Test-4 where coke yield is higher while liquid yield and, CCR and asphaltene conversions, are lower than in Test-1.

As detailed in the experimental section, dimethyldisulphide (DMDS) was added to the feedstock in Tests 1-4 and a complex temperature program was used to ensure conversion of the catalyst precursor to the active MoS_2 phase. In Test-5, no DMDS was added and the feedstock was heated room temperature straight to 450°C . The results from Test-5 are almost identical to those from Test-2 and indicate that a complex sulphiding process is not required for proper catalyst activation.

Test-6 and -7a illustrate the performance of the catalyst at longer residence time and higher $525^\circ\text{C}+$ pitch conversion. Compared to Test-2, higher pitch conversions in Test-6 and -7a resulted in greater amounts of dry gas, naphtha and gas oil but solids increased from 0.5 to a maximum 0.8wt.% of feed. Liquid yield was reduced slightly at the highest conversion. In Test-6, the pitch conversion determined was 94.3%. This high value for pitch conversion is probably misleading and reflects the limitation of the crude simulated distillation. Based on the conversion in Table 2, the asphaltene content was 6.7wt.% whilst the $525^\circ\text{C}+$ pitch content was only 3.8wt.% and this is not reasonable. The true pitch conversion is probably between 78% and 90%.

Test-7a and -7b illustrate the performance of the catalyst in a simulated recycle operation. Following a run identical to that in Test-7a, the bottoms from this test were left in the autoclave and an additional amount of fresh oil equal to mass of liquid collected in the product condensers was added to the autoclave. The autoclave was then operated at the same conditions as before. The results for Test-7b presented in Table 2 represent the combined products from conversion of 290.33g of bottoms from Test-7a and 483.6g of fresh feed. As shown in Table 2, the amount of solids did not increase from Test-7a to Test-7b. Dry gas yield increased because of additional conversion of the recycled bottoms. This result suggests that this catalyst could be used effectively in a bottoms recycle process. This conclusion would have to be verified in a continuous true-recycle test.

The MoS_2 catalyst was found to be concentrated along with V and Ni in the product coke. The ash contents of the cokes listed in Table 2 varied from about 14wt.% to 33wt.% for runs using 212 and 611ppm Mo catalyst, respectively. Optical microscopy under cross-polarized light indicated that the coke in all cases except for Test-3 consisted of angular and rounded particles that possess a porous and isotropic matrix. The matrix was embedded with a varying amount of anisotropic mesospheres mostly 2 - 10 microns in diameter but occasionally larger. In the case of Test-3, the porous matrix showed an anisotropic (mosaic) texture and the mesospheres were larger, consisting of spheres approximately 30 microns in diameter.

Figure 1 shows the XRD spectrum of the coke produced in Test-2. The peak near $14^\circ 2\theta$ corresponds to scattering perpendicular to the (002) plane in hexagonal MoS_2 . Other MoS_2 peaks include 33.0° , 39.5° and 58.5° attributable to scattering from the (100), (103) and (110) planes [3]. The two sharp peaks at 31.7° and 45.5° are due to sodium chloride that was present in the as received oil. Using the Debye-Scherrer equation, the width of the peak near $14^\circ 2\theta$ can be used to calculate the average stacking height of the hexagonal layers. In this case it corresponds to an average layer height of 35\AA , i.e., 5.6 MoS_6 stacked layers. Daage and Chiannelli [4] have shown that the stacking height is related to catalyst hydrogenation activity and selectivity for hydrogenation compared to hydrodesulphurization. Scanning electron microscopy (SEM) showed that the MoS_2 crystallites are needle shaped and unencumbered with coke. The minor axis ranged from approx. 0.5 - 1.5 microns while the major axis varied from 5 to over 30 microns. The larger dimensions obtained by SEM compared to XRD indicate that the stacked layers

that make up the crystallite were highly folded and disordered. This was confirmed with the aid of transmission electron microscopy (TEM) and selected area diffraction. The needle-like crystals were observed to be composed of a collection of rods that are less than 100nm in diameter. The composition and structure of the particles were confirmed by analysis using energy dispersive x-ray (EDX) analysis and selected area diffraction. The diffraction patterns indicated that the MoS_2 was polycrystalline but had some preferred orientation.

CONCLUSIONS

It has been shown that a water soluble catalyst precursor, ammonium heptamolybdate, can produce highly dispersed and active MoS_2 catalyst. The activity of these catalyst approaches that achieved by oil soluble catalysts which are reported to be highly dispersed even though the catalyst particles were larger than those from the oil soluble catalyst. TEM confirmed that these large catalyst particles (5-30 microns) were made up of smaller particles (0.1 microns). The catalyst maintained its activity in a simulated recycle test. The lower cost of the water soluble catalyst, its larger aggregate size and its activity relative to the oil soluble catalyst make it a potential candidate for upgrading processes which use highly dispersed catalyst and employ bottoms recycle.

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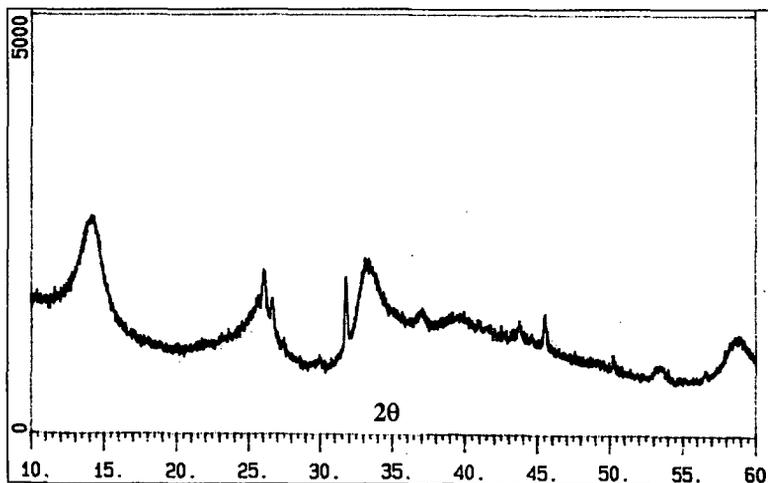


Figure 1. XRD of MoS_2 in coke from Test-2.

Table 1. Properties of Cold Lake heavy oil.

Carbon (wt.%)	82.8
Hydrogen (wt.%)	10.4
Nitrogen (wt.%)	0.40
Sulphur (wt.%)	4.60
Asphaltenes (wt.%)	16.9
CCR (wt.%)	12.6
H ₂ O (wt.%)	1.54
Nickel (ppm)	66
Vanadium (ppm)	178
°API Gravity	10.7
Viscosity @ 38°C (cP)	8,675
IBP – 200°C (wt.%)	0
200 – 343°C (wt.%)	10.7
343 – 525°C (wt.%)	35.5
525°C+ (wt.%)	53.8

Table 2. Results of autoclave activity tests.

Test	1	2	3 ^a	4	5	6	7a	7b
Feedstock	F-1	F-2	F-0	F-2	F-2	F-2	F-2	F-2 ^c
Mo Concentration (ppm)	212	611	200	200	611	611	611	611
Residence Time (min.)	45	45	45	45	45	90	70	70
C ₆₊ Liquids (wt. % feed)	87.5	90.4	89.3	86.7	89.5	86.5	88.2	89.8
C ₄ –C ₅ Liquid (wt. % feed)	5.6	4.6	4.4	4.5	4.3	3.8	4.0	1.6
Dry Gas (wt. % feed) ^b	4.6	4.2	4.7	5.3	3.7	5.9	4.8	6.7
H ₂ S (wt. % feed) ^b	2.4	2.3	2.1	2.2	1.9	2.3	2.0	1.9
Solids (wt. % feed)	0.7	0.5	0.9	2.1	0.6	0.8	0.5	0.5
Ash (wt. % of solids)	14.4	33.1	21.7	11.2	29.8	23.3	35.8	38.4
Simulated Distillation of C₆₊ Liquids								
IBP – 200°C (wt.%)	21.4	17.5	20.0	21.0	18.8	33.0	22.5	20.0
200 – 343°C (wt.%)	34.0	34.2	35.6	33.1	33.7	38.8	37.1	36.2
343 – 525°C (wt.%)	26.7	28.4	26.0	20.5	27.4	24.3	25.9	28.3
525°C+ (wt.%)	17.9	19.9	18.3	25.4	20.1	3.8	14.5	15.6
Conversions (%)								
Asphaltenes	65.7	72.3	56.3	41.3	67.5	66.7	71.0	45.9 ^d
CCR	58.8	63.4	52.5	53.0	61.8	56.6	75.4	54.3 ^d
525°C+	73.5	69.3	69.6	60.3	69.3	94.3 ^e	78.2	60.8 ^d

a. Product yield corrected for 21.7g of added diluent (BP: 200-343°C)

b. Values for Tests 1 to 4 include CH₄ and H₂S products from 10.0g of dimethyldisulphide.

c. Includes a calculated 290.3g of reactor bottoms (containing coke and catalyst) from Test-7a and 483.6g of virgin oil.

d. Conversions based on composite composition of virgin oil and reactor bottoms used in Test-7b.

e. Determined by crude simulated distillation ASTM D5307. See text.