

Cold Lake bitumen upgrading using exfoliated MoS₂

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Exfoliated MoS₂ has been investigated as a dispersed catalyst for Cold Lake bitumen upgrading. The results are compared with MoS₂ prepared *in situ* by the decomposition of molybdenum naphthenate. Although liquid yield and coke suppression were similar among the catalysts, better hydrogenation activity, especially hydrodenitrogenation, and asphaltene and microcarbon residue (MCR) removal, were obtained with the exfoliated MoS₂. The improved hydrogenation is suggested to be a consequence of increased rim-edge sites associated with the exfoliated MoS₂. The potential for recycle of the exfoliated MoS₂ is also reported.

KEY WORDS: catalyst; exfoliation; MoS₂; heavy oil upgrading; bitumen; hydrogenation; hydrocracking.

1. Introduction

Heavy oil upgrading has attracted worldwide attention because of decreasing conventional sweet crude reserves and the large reserves of available heavy oil, the latter being approximately equivalent to one third of the world's total oil and gas reserves [1]. Heavy oils have high concentrations of heteroatoms (S, N) and metals (Ni and V) and they have a propensity for coke formation (as measured by the MCR – microcarbon residue content), all of which challenge existing oil refining technology. Furthermore, ever more demanding environmental regulations increase pressure on the refining industry to produce cleaner fuels, despite the use of a lower grade feedstock.

MoS₂ catalysts are used to activate molecular hydrogen and thereby suppress coke formation during heavy oil upgrading. Deposition of coke and metals on supported MoS₂ catalysts results in rapid deactivation in commercial plants. One approach to limiting the effect of catalyst deactivation is to perform the reaction in slurry hydrocracking reactors using unsupported MoS₂ dispersed in the heavy oil. Several such hydrocracking technologies have been developed [2–5]. High levels of catalyst dispersion, and hence activity, can usually be achieved by introducing water- or oil-soluble catalyst precursors to the feed that decompose and form the active metal sulfide *in situ* [6]. Molybdenum naphthenate is reported to be one of the most promising catalyst precursors [7,8] that yields MoS₂ crystallites 1–5 nm in size [3]. Although the catalyst may be used on a once-through basis, the possibility of either catalyst recycle or regeneration has also been considered because of issues associated with catalyst cost, especially if the Mo concentration in the feed oil is above 200 ppm [3].

A number of studies have reported on the relationship between MoS₂ structure and activity, especially with respect to the hydrogenation and hydrodesulfurization (HDS) activity of MoS₂. According to the rim-edge model of MoS₂ catalysts put forward by Daage and Chianelli [9], rim sites catalyze hydrogenation reactions while both rim and edge sites are responsible for HDS activity. The basal plane of MoS₂ is considered to be inert catalytically. Iwata *et al.* [10] demonstrated that the hydrogenation rate of 1-methylnaphthalene on dispersed MoS₂ was proportional to the number of rim sites. Consequently, creating more rim sites by dismantling the layered MoS₂ structure should increase the ratio of hydrogenation to HDS reactions. In the context of bitumen hydrocracking, improved hydrogenation should provide for high conversions of MCR, asphaltenes and nitrogen removal from aromatics, while maintaining low coke yields.

Joensen *et al.* [11] has described a chemical exfoliation method to separate bulk MoS₂ into single molecular layers (or exfoliated, two-dimensional material), that would produce a significant increase in the rim sites versus edge sites per unit mass of MoS₂. This technique has been used in catalyst preparation and tested for methanation by supporting the exfoliated MoS₂ on Al₂O₃ [12–14]. Exfoliated MoS₂ catalysts have also been tested for their hydrogenation activity in coal liquefaction and residue upgrading [15,16]. However, for Hondo residue upgrading the results did not show any consistent correlation between catalyst properties, such as surface area and MoS₂ stack height, and the HDS activity. More recently, Del Valle *et al.* [17,18] investigated the activity of exfoliated MoS₂ for the HDS of thiophene and dibenzothiophene. Catalytic activity of the crystalline MoS₂ and exfoliated MoS₂ catalyst did not show any correlation between catalyst properties and activity either. Del Valle *et al.* [18] suggested that residual Li, introduced during the exfoliation, may be responsible for the unexpectedly low hydrogenation activity of the

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exfoliated MoS₂. However, it is also noted that the exfoliated MoS₂ was dried prior to dispersion in the reactant oil and the exfoliated MoS₂ will likely undergo some degree of re-stacking during the drying process.

In the present study, the activity of exfoliated MoS₂ prepared in a water or decahydronaphthalene (DHN) suspension has been tested for bitumen upgrading. The properties of the exfoliated MoS₂ and the effect of operating conditions are reported. In addition, the properties and activity of the Mo catalyst recovered in the coke, have been determined.

2. Experimental

2.1. Materials

The heavy oil used in the present study was Cold Lake bitumen from Esso Resources, Canada. The bitumen properties are presented in table 1. MoS₂ (< 2 μ m powder) and *n*-butyllithium/hexane used for exfoliation were obtained from Aldrich and the molybdenum naphthenate (MoNaph) was supplied by ICN Biomedicals Inc.

2.2. Catalyst preparation procedure

MoS₂ was exfoliated using a slightly modified method to that of Joensen *et al.* [11]. In brief, MoS₂ was intercalated with lithium by mixing the MoS₂ powder with *n*-butyllithium in hexane under argon atmosphere. The mixture was left to age for at least 72 h. The supernatant was subsequently decanted and the remaining Li-intercalated MoS₂ material was exfoliated by adding water and sonicating for 30 min. The exfoliated MoS₂ was collected by centrifuge and washed until the pH reached 7. The final catalyst contained 2 wt% MoS₂ dispersed in water, and is designated herein as exfoliated MoS₂.

The exfoliated MoS₂ was also dispersed in DHN. Accordingly, the exfoliated MoS₂ suspended in water was re-washed, first in isopropanol and then DHN. The washing procedure in isopropanol and DHN was the same as that used with water.

Table 1
Properties of Cold Lake bitumen used in the present study

Elemental analysis	
C (wt%)	80.54
H (wt%)	10.61
N (wt%)	0.34
S (wt%)	4.09
Ni (ppm)	67
V (ppm)	179
Asphaltene content (wt%)	17.9
MCR wt%	13.6
Boiling point (%)	
<177 °C	0
177–350 °C	17.2
350–525 °C	27.1
>525 °C	55.7

2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns of the MoS₂ were recorded with a Siemens D5000 powder diffractometer with power settings of 40 kV and 30 mA using CuK α radiation ($\lambda = 1.5406$ Å). The step-scan (0.01°) was taken over the range 2θ from 5° to 70°. Samples were prepared by diluting the exfoliated MoS₂ suspension in ethanol followed by drying a few drops of the suspension on a glass slide.

BET surface areas were measured by N₂ adsorption at –196 °C using a FlowSorb II 2300 Micromeritics analyzer. A 30% N₂/70% He mixture, fed at 15 mL/min, was used for surface area measurement. Samples were degassed at 125 °C for 2 h prior to the measurement.

2.4. Catalyst activity tests

The catalyst activity tests were conducted using a 300 ml autoclave reactor operated in batch mode. The autoclave was loaded with 80 g of Cold Lake bitumen to which the desired amount of exfoliated MoS₂ was added. Note that typically the MoS₂ was added as a 2% MoS₂ in water suspension, unless otherwise noted. The reactor was pressurized with H₂ to 3.5 MPa after purging with N₂ and H₂, before heating at a rate of 5 °C/min to the desired reaction temperature. The reaction temperature was then maintained for 1 h followed by rapid quenching of the reactor to room temperature. Product gas was trapped in a gas bomb before the autoclave was depressurized. The reactor liquid product was recovered via extraction in methylene chloride followed by evaporation of the solvent in a rotary evaporator. The coke produced during the hydrocracking reaction was defined as methylene chloride insoluble material. It was collected through 3.0 and 0.2 μ m size membrane filters and dried at 110 °C for 18 h. The gas collected after reaction was analyzed by a Shimadzu gas chromatograph using a thermal conductivity detector. The liquid product was analyzed for its C, H, N and S content and MCR content following ASTM D5373, ASTM D4239 and ASTM D4530 procedures, respectively. The asphaltene content was analyzed according to the Syncrude asphaltene analytical method [19] and the metals content was determined by ICP analysis.

The gas produced after the reaction was mainly CH₄, C₂H₆, C₂H₄, C₃H₈, C₄H₁₀, and H₂S, the balance being un-reacted H₂. H₂ consumption for each reaction was estimated from the gas analysis. This was done by calculating the weight of gas before and after reaction from the initial and final reactor pressures, respectively.

Several of the activity measurements were repeated and analysis of the data from these experiments yielded estimates of the experimental errors associated with the reported data. Overall mass balances were better than 95% and errors associated with the conversion and yield

data were $\pm 5\%$, except for the asphaltene conversion ($\pm 10\%$) and coke yield ($\pm 10\%$) data.

3. Results

3.1. Catalyst characterization

Figure 1 shows the XRD patterns of: (a) untreated MoS₂ before exfoliation, (b) exfoliated MoS₂ dispersed in water and (c) exfoliated MoS₂ re-dispersed in DHN. All of the peaks for the untreated MoS₂ are sharp and have high intensity especially the peak corresponding to the (002) plane. The average MoS₂ crystallite size, estimated using Scherrer's equation applied to the (002) peak, was 35.8 nm. After exfoliation in water and drying (sample b), the (002) peak broadened and the estimated average particle size decreased to 4 nm. Correspondingly, the number of MoS₂ layers per particle (N_s) decreased from about 57 layers to 6 layers (Table 2). The latter result suggests that a certain degree of re-stacking occurred when the sample was dried during the XRD sample preparation procedure. The XRD data also indicated that the washed and dried catalyst was free of intercalated lithium following exfoliation, since the inter-planar spacing (6.3 Å) of the exfoliated MoS₂ was much less than that expected (11.8 Å) if lithium hydrate were intercalated [20]. The small increase in the average interplanar spacing from 6.2 (MoS₂) to 6.3 Å (exfoliated MoS₂) is due to the presence of water between the MoS₂ layers [21].

Single-layered exfoliated MoS₂ remains in suspension for several days due to the formation of a hydroxylated MoS₂ surface. The MoS₂ will eventually re-stack to form multilayer particles [21]. When the exfoliated MoS₂ was re-dispersed in the non-polar organic solvent

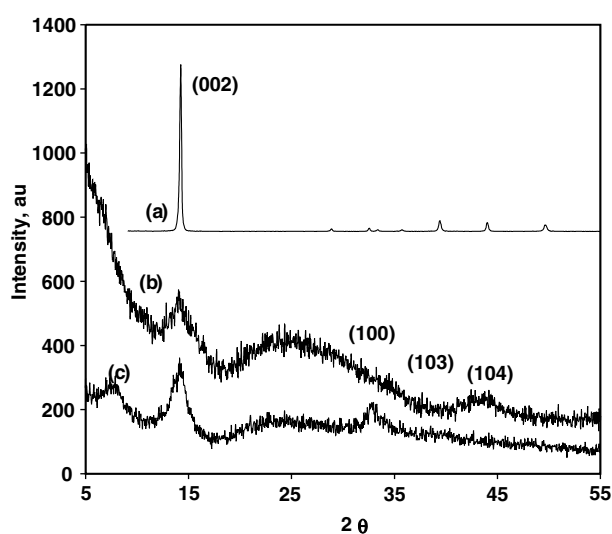


Figure 1. XRD pattern of (a) untreated MoS₂; (b) MoS₂ after exfoliation and dispersed in water; (c) MoS₂ after exfoliation and redispersion in DHN.

Table 2
Summary of catalyst properties

	MoS ₂ powder	MoS ₂ from MoNaph ^a	Exfoliated MoS ₂		
			Dispersed in		
			Water	DHN	Literature [17]
BET area (m ² /g)	4.2	—	7.8	—	6.2
d_p (nm)	35.8	39.6	4.0	5.5	14
N_s	57	63	6	9	23

d_p : Estimated MoS₂ particle size based on XRD line broadening of (002) peak; N_s : number of MoS₂ layers per particle, estimated as the particle size divided by the inter-planar spacing.

^aMoS₂ synthesised by *in situ* decomposition of molybdenum naphthenate.

DHN, the period of suspension for MoS₂ was reduced to a few hours. The XRD pattern of exfoliated MoS₂ dispersed in DHN is presented in figure 1(c). Increased stacking was apparent compared to the exfoliated MoS₂ dispersed in water.

The BET area of the untreated MoS₂ powder was 4.2 m²/g. The MoS₂ subjected to exfoliation was analyzed after drying. The surface area showed a small increase to 7.8 m²/g. The low surface area was consistent with previous findings [18].

In an effort to determine the properties of the MoS₂ derived from molybdenum naphthenate, the precursor was decomposed in dodecane/3,5dimethylbenzothiophene at 350 °C in the presence of H₂/H₂S. The resulting MoS₂ particles were recovered and analyzed by XRD, yielding an estimated MoS₂ crystallite size of 39.6 nm. Table 2 provides a summary comparing the properties of the various catalyst samples.

The catalyst characterization data do not provide conclusive evidence for the presence of single layered MoS₂ in the oil during reaction. The catalyst characterization is necessarily done *ex situ*, following a drying step, that may result in partial re-stacking of the MoS₂. A similar conclusion was drawn by Del Valle et al. [18] in their attempts to identify single layer MoS₂ through TEM. However, the XRD analysis clearly shows that the MoS₂ layers were dismantled during the exfoliation treatment. Therefore, according to the 'rim-edge' model [9], hydrogenation of large molecules, catalyzed predominantly by rim sites, should be promoted on the exfoliated MoS₂.

3.2. Catalyst activity

The catalytic hydrocracking of Cold Lake bitumen using exfoliated MoS₂ as catalyst is compared to the activity of crystalline MoS₂ and MoS₂ derived from molybdenum naphthenate in table 3. The data show that the exfoliated MoS₂ and the MoS₂ derived from molybdenum naphthenate (MoNaph) had very similar

Table 3

Cold Lake bitumen upgrading using MoS₂ catalysts of different morphology (Reaction conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h with 600 ppm Mo.)

Catalyst	Coke yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	H ₂ consumed (wt%)	Residue conv. (wt%)	Liquid boiling point (°C)			
						<177	177–343	343–525	>525
						(wt%)			
MoS ₂ powder	2.87	93.8	3.31	34.0	—	—	—	—	—
MoNaph ^a	0.96	96.9	2.14	49.4	26.8	3.50	25.50	30.22	40.78
Exfoliated ^b MoS ₂	1.08	96.8	2.11	56.8	26.0	4.04	25.02	29.71	41.23

^aMoS₂ synthesised by *in situ* decomposition of molybdenum naphthenate.

^bExfoliated MoS₂ dispersed in water.

coke yields and residue conversions. As shown in figure 2, however, the exfoliated MoS₂ had significantly higher activity for N and metals removal, and MCR and asphaltene conversion, compared to the MoNaph derived MoS₂, suggesting that enhanced hydrogenation occurred with the exfoliated catalyst. The enhanced hydrogenation is suggested to be a consequence of the increased number of rim-edge sites associated with the exfoliated catalyst.

The effect of temperature in the range 400–430 °C on bitumen hydrocracking using exfoliated MoS₂ was also determined and the results are presented in table 4. As expected, the coke and gas yield increased with increasing temperature. Hydrogen consumption also increased as did the sulfur and nitrogen removal. We note, however, that the MCR and asphaltene conversion reached a maximum at 415 °C, and consequently, subsequent catalyst activity measurements were made at this temperature.

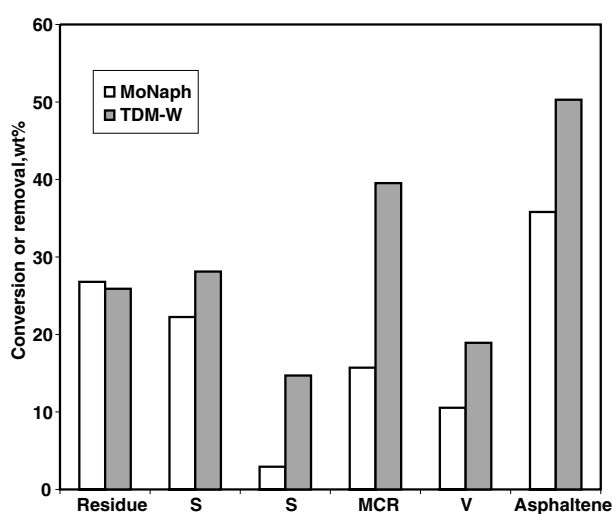


Figure 2. Cold Lake bitumen upgrading using MoS₂ derived from molybdenum naphthenate (MoNaph) and exfoliated MoS₂ dispersed in water (TDM-W) (Reaction conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h with 600 ppm Mo.)

3.3. Effect of Mo concentration

The effect of Mo concentration in the oil was studied at 415 °C using exfoliated MoS₂ with MoS₂ concentrations of 360, 600 and 900 ppm (table 5). In these experiments, increased volumes of the 2% MoS₂-in-water suspension were added to the oil to achieve the desired MoS₂ concentration in the bitumen. Consequently, the corresponding water content in the reaction mixture was approximately 2.8, 4.7 and 6.8 wt%, respectively. Minimum coke was produced at a Mo concentration of 600 ppm. However, the coke yield was found to increase with further increases in Mo catalyst concentration. These results agree with those reported by Panariti *et al.* [22] and are explained by two phenomena taking place concurrently. The high level of hydrogenation of the feedstock achieved in the presence of significant amounts of catalyst reduces asphaltene stability and this promotes coke formation. The MoS₂ microcrystals dispersed in the oil may also be responsible for nucleation that leads to the precipitation of solids. Consequently, as the catalyst concentration increases, coke formation may prevail over coke suppression through hydrogen transfer by the dispersed catalyst.

The data of table 5 also show that the liquid yield was not significantly affected by the MoS₂ concentration and this observation agrees with the kinetic analysis of Panariti *et al.* [22] that demonstrated that since un-

Table 4

Effect of temperature on Cold Lake bitumen upgrading using exfoliated MoS₂ (Reaction conditions: Initial H₂ pressure 3.5 MPa and a reaction time of 1 h with 600 ppm Mo.)

Temperature (°C)	Coke yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	H ₂ consumption (wt%)
400	0.91	97.5	1.6	27.2
415	1.08	96.8	2.1	56.8
430	6.47	89.7	3.3	75.2
	Removal (wt%)		Conversion (wt%)	
	Sulfur	Nitrogen	MCR	Asphaltene
400	14.2	5.9	12.0	27.4
415	28.1	14.7	39.5	50.3
430	30.8	23.5	22.0	45.7

Table 5

Effect of catalyst concentration on Cold Lake bitumen upgrading using exfoliated MoS₂ (Reaction Conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h.)

Mo concentration (ppm)	Coke yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	Atomic H/C ratio	H ₂ consumption (wt%)
360	1.53	95.1	3.4	1.49	27.0
600	1.08	96.8	2.1	1.55	56.8
900	1.83	96.4	1.8	1.61	73.4

	Removal (wt%)			Conversion (wt%)		
	Sulfur	Nitrogen	Nickel	Vanadium	MCR	Asphaltene
360	18.8	5.9	13.5	12.5	13.1	48
600	28.1	14.7	14.3	18.9	39.5	50
900	26.9	11.8	15.6	15.9	36.0	36

ported catalysts do not contain acidic functions, carbon-carbon bond cleavage reactions are thermally controlled. The liquid product showed best quality and the lowest coke yield at 600 ppm Mo in the oil. The S, N and metals removal, as well as asphaltene and MCR conversions were maximum at 600 ppm Mo.

An important difference between the MoS₂ prepared from MoNaph and that prepared by exfoliation is that the exfoliated MoS₂ was dispersed in water, whereas MoNaph is an oil soluble precursor that yields solid MoS₂ dispersed in the bitumen. As noted above, the increased MoS₂ concentration reported in table 5, also corresponds to an increase in water concentration in the slurry. Experiments were therefore carried out at a fixed Mo concentration of 600 ppm using exfoliated MoS₂ dispersed in water, with an MoS₂ concentration in the MoS₂-in-water suspension of 2.0 and 8.4 wt%. In each experiment, the amount of dispersion added to the oil provided 600 ppm Mo in the reactant mixture, but the amount of water in the reactant oil was 4.6 and 1.0 wt%, respectively. The data of table 6 suggest that at the higher water concentration catalyst activity improved, yielding higher asphaltene conversions and reduced coke yield. At much higher concentrations, Yoneyama and Song [24] also reported a beneficial effect of water. They reported that MoS₂ catalysts generated from ammonium tetrathiomolybdate (ATTM) in the presence of

Table 6

Effect of MoS₂ concentration in the MoS₂-in-water suspension during Cold Lake bitumen upgrading using exfoliated MoS₂ (Reaction conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h with 600 ppm Mo.)

MoS ₂ concentration in catalyst suspension (wt%)	2.02	8.37
Water concentration in oil (wt%)	4.6	1.0
Coke yield (wt%)	1.08	1.52
Liquid yield (wt%)	96.8	95.7
Gas yield (wt%)	2.0	2.8
Asphaltene conv. (wt%)	50.3	23.6

Table 7

Effect of solvent used to disperse exfoliated MoS₂ on Cold Lake bitumen upgrading (Reaction conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h with 900 ppm Mo.)

Exfoliated MoS ₂ dispersion medium	Coke yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	Atomic H/C ratio	H ₂ consumption (wt%)
DHN	2.18	95.9	1.9	1.45	43.7
Water	1.83	96.4	1.8	1.61	73.4

n-tridecane solvent with added water under H₂ pressure at 300–400 °C, was much more active than catalyst prepared from ATTM alone. These catalysts were tested for C–C bond cleavage and naphthalene ring hydrogenation using the model compound 4-(1-naphthylmethyl)biphenyl (NMBB). Although the results indicate that water promoted hydrogenation or hydrocracking reactions, the amount of water added in this system (the NMBB : water weight ratio was 0.56) was much greater than the amount of water used in the present study.

3.4. Effect of dispersing solvent

The exfoliated MoS₂ could be re-dispersed in non-polar DHN prior to being added to the heavy oil. The effect that different dispersing solvents (water versus DHN) may have on activity was investigated at 900 ppm Mo and the results are compared in table 7 and figure 3. Similar liquid and gas yields were obtained from both catalysts. The MoS₂ dispersed in water gave lower coke yield and higher MCR removal compared to the MoS₂ dispersed in DHN. The results are consistent with the positive effect of water noted above. However, the exfoliated MoS₂ dispersed in DHN also had a larger stack height than that dispersed in water (table 2). The results of figure 3 are consistent with a higher MCR removal because of an increased number of rim sites associated with the catalyst dispersed in water (MoS₂-in-water suspension) versus that dispersed in DHN (MoS₂-in-DHN suspension).

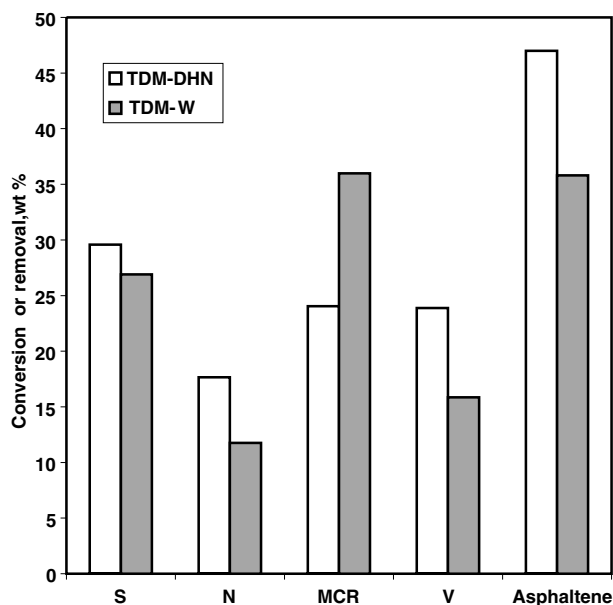


Figure 3. Effect of decalin (TDM-DHN) and water (TDM-W) solvent used to disperse exfoliated MoS₂. (Reaction conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h with 900 ppm Mo.)

Table 8
Activity of recycled MoS₂ during Cold Lake Bitumen upgrading (Reaction conditions: 415 °C at an initial H₂ pressure of 3.5 MPa and a reaction time of 1 h.)

	Thermal coke	Recycled exfoliated MoS ₂ in coke	Exfoliated MoS ₂
Mo (ppm)	0	600	600
Coke yield (wt%)	2.71	1.03	1.08
Sulfur removal (wt%)	9.8	10.3	28.1
MCR Removal (wt%)	0.2	10.4	39.5
Asphaltene conv. (wt%)	21.8	30.2	50.3

3.5. Catalyst recycle

As already noted, the possibility of catalyst recycle in heavy oil upgrading using a slurry reactor may be an important consideration at high Mo concentrations (> 200 ppm) in the oil slurry. Consequently, we have examined the possibility of recycling the exfoliated MoS₂. Analysis of the product oil and coke showed that > 90% of the Mo resided in the coke after a batch reaction time of 1 h. XRD and SEM-EDX analysis of the coke (not shown), confirmed that the Mo was well distributed throughout the coke. Consequently, the activity of the produced coke was tested to determine the possibility of catalyst/coke recycle.

Table 8 reports the results obtained from heavy oil upgrading using the coke produced from a previous experiment using exfoliated MoS₂ catalyst. The amount of coke added to the oil was set to provide an equivalent 600 ppm Mo in the oil. The results are compared with an experiment in which coke produced from thermal

hydrocracking of the same heavy oil with no detectable Mo content, was added to the Cold Lake feed. The data clearly show that the recycled coke had significant activity, although it was lower than the exfoliated MoS₂ catalyst but higher than when the coke added was free of Mo.

After 1 h reaction in the batch reactor, the results of table 8 show that the MoS₂ dispersed in the produced coke remains active for hydrocracking, albeit at a lower level than the original exfoliated MoS₂. Although the coke yield remained low with the recycled exfoliated-MoS₂, the removal of S, MCR and asphaltene conversion all decreased. These results suggest that the exfoliated-MoS₂ remains effective for hydrogen transfer to limit coke production. However, since the MoS₂ is dispersed within the coke, diffusion effects probably limit the catalyst effectiveness for hydrogenation and HDS reactions.

4. Conclusions

The concept of increased rim-edge sites associated with exfoliated MoS₂ that promote hydrogenation reactions provides a suitable explanation of the observed activities of exfoliated MoS₂ and MoS₂ prepared *in situ* from the decomposition of MoNaph. Following a 1 h batch reaction, > 90% of the catalyst was found to be associated with the produced coke, and this material was shown to be active for bitumen upgrading, suggesting that catalyst/coke recycle is possible for the MoS₂ catalyst.

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References

- [1] D. Lanier, UNITAR Centre for Heavy Crude and Tar Sands (1998) 1.
- [2] A. Del Bianco, N. Panariti, S. Dicarlo, J. Elmouchnino, B. Fixari and P. Leperchec, *Appl. Catal. A: Gen.* 94 (1993) 1.
- [3] A. Del Bianco, N. Panariti and M. Marchionna, *Chemtech* 25 (1995) 35.
- [4] R. Lott and L.K. Lee, 2003 AIChE Annual Meeting 2nd April, New Orleans (2003).
- [5] Anon, *Hydrocarbon Process.* 82 (2003) 32.
- [6] N. Panariti, A. Del Bianco, G. Del Piero and M. Marchionna, *Appl. Catal. A: Gen.* 204 (2000) 203.
- [7] A. Del Bianco, N. Panariti, S. Dicarlo, P.L. Beltrame and P. Carniti, *Energy Fuels* 8 (1994) 593.
- [8] S. Peureux, S. Bonnamy, B. Fixari, F. Lambert, P. Leperchec, B. Pepindonat and M. Vrinat, *Bull. Soc. Chim. Bel.* 104 (1995) 359.
- [9] M. Daage and R.R. Chianelli, *J. Catal.* 149 (1994) 414.

- [10] Y. Iwata, Y. Araki, K. Honna, Y. Miki, K. Sato and H. Shimada, *Catal. Today* 65 (2001) 335.
- [11] P. Joensen, R.F. Frindt and S.R. Morrison, *Mater. Res. Bull.* 21 (1986) 457.
- [12] B.K. Miremadi and S.R. Morrison, *J. Catal.* 103 (1987) 334.
- [13] B.K. Miremadi and S.R. Morrison, *J. Catal.* 112 (1988) 418.
- [14] G.A. Scholz and S.R. Morrison, *Can. J. Chem.* 67 (1989) 862.
- [15] B.C. Bockrath and D.S. Parfitt, *Coal Sci. Tech.* 24 (1995) 1343.
- [16] B.C. Bockrath and D.S. Parfitt, *Catal. Lett.* 33 (1995) 201.
- [17] M. Del Valle, J. Cruz-Reyes, M. Avalos-Borja and S. Fuentes, *Catal. Lett.* 54 (1998) 59.
- [18] M. Del Valle, M. Avalos-Borja, J. Cruz and S. Fuentes, *Molecularly Designed Ultrafine/ Nanostructured Materials*, Vol. 351 (Materials Research Society, 1994) p. 287.
- [19] D. Wallace, *A Review of Analytical Methods for Bitumens and Heavy Oils* (Alberta Oil Sands Technology and Research Authority, Alberta, 1988).
- [20] W.M.R. Divigalpitiya, R.F. Frindt and S.R. Morrison, *Science* 246 (1989) 369.
- [21] P. Joensen, E.D. Crozier, N. Alberding and R.F. Frindt, *J. Phys. C: Solid State Phys.* 20 (1987) 4043.
- [22] N. Panariti, A. Del Bianco, G. Del Piero, M. Marchionna and P. Carniti, *Appl. Catal. A: Gen.* 204 (2000) 215.
- [23] B. Fixari, S. Peureux, J. Elmouchnino, P. Leperchec, M. Vrinat and F. Morel, *Energy Fuels* 8 (1994) 588.
- [24] Y. Yoneyama and C.S. Song, *Catal. Today* 50 (1999) 19.