Catalysis Today 150 (2010) 244–254

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

A study of Cold Lake Vacuum Residue hydroconversion in batch and semi-batch reactors using unsupported MoS_2 catalysts

Hooman Rezaei [a], Xuebin Liu [a], Shahrzad Jooya Ardakani [a], Kevin J. Smith [a,*], Maureen Bricker [b]

[a] *Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, British Columbia V6T 1Z3, Canada*
[b] *UOP LLC, Des Plaines, IL, USA*

ARTICLE INFO

Article history:
Available online 13 November 2009

Keywords:
Hydroconversion
Bitumen upgrading
Catalyst
Catalyst recycle
Coke formation
Coke characterization
MoS_2
Reversed micelle

ABSTRACT

Hydroconversion of Cold Lake Vacuum Residue (CLVR) in both batch and semi-batch slurry reactors using unsupported MoS_2 catalysts is reported. The MoS_2 catalyst precursors were added to the CLVR either as an aqueous solution of ammonium heptamolybdate (AHM) or as molybdenum chloride dispersed in reversed micelles that were stabilized in n-hexane using a surfactant. At the reaction conditions studied in both the batch and semi-batch reactors, the MoS_2 catalyst prepared in the reversed micelles had lower coke yield (toluene-insoluble material), lower gas yield, higher liquid yield and higher H_2 consumption, compared to the AHM-derived MoS_2 catalyst. The coke–catalyst mixture recovered after reaction, characterized by chemical and energy dispersive X-ray analysis, confirmed that most of the added catalyst was captured by the coke. Analysis of the coke by X-ray diffraction and transmission electron microscopy confirmed the presence of highly dispersed MoS_2 that suggests the possibility of catalyst–coke recycle.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The demand for petroleum products continues to increase whereas the supply of light crude oils needed to generate these products continues to decline. Hence, the conversion of residue oils to more valuable products using technologies that provide high liquid yields is of increasing interest to refiners. Furthermore, increased environmental concerns require improved processes to meet stricter environmental regulations associated with the use of fossil fuels. Consequently, the development of new processes that convert heavier oil fractions into lighter and cleaner products more efficiently is of increasing importance [1].

High coke and gas yields associated with existing coking processes, as well as severe catalyst deactivation associated with hydroconversion processes used to upgrade residue oils, have led to the development of slurry phase hydroconversion (HCR) technology. HCR uses unsupported catalysts dispersed directly in the residue oil. Since the catalysts are used once-through, the impact of catalyst deactivation is reduced significantly compared to conventional hydroconversion methodologies. A variety of slurry based processes have been developed although none has yet been commercialized. Three processes reached the demonstration stage with a production capacity of at least 200 bbl/d. Veba Combi Cracking (VCC) [2,3] operated for a number of years, while the CANMET process [4,5] was demonstrated at a scale of 5000 bbl/d at the Petro-Canada Montreal refinery beginning in the 1990s. Development of these technologies had largely ceased by 2000, with the exception of the ENI Slurry Technology (EST) [6]. This process is currently being demonstrated at a plant in Italy. The sulfided, unsupported metal catalysts used in HCR are typically generated *in situ*, with the catalyst precursor added to the residue oil as a water-soluble salt, oil-soluble metal complex or as a finely powdered solid. Sulfided transition metals (Mo, Ni, Co, W, Cr, V, Fe, Cu and Zn) are active for hydroconversion among which MoS_2 is the most commonly used catalyst [7]. Under hydroconversion conditions, thermal decomposition and sulfidation of the catalyst precursors yields the active (sulfided) catalyst. Although the performance of different metal sulfides introduced in the form of oil-soluble precursors for hydroconversion of heavy feeds has been investigated [8–12], there are fewer reports on the use of water-soluble precursors. Most studies suggest a better dispersion and smaller particle size in the case of oil-soluble catalyst precursors compared to water-soluble precursors [13]. Liu et al. [14] used different water-soluble precursors for residue hydroconversion and characterized the catalysts recovered after the reaction. Due to the complexity of the characterization and the presence of large amounts of coke, a relatively light feed was used to minimize coke formation. The authors showed that at the reaction conditions, Mo, Ni and Fe were in sulfided form. XRD analysis of the recovered catalysts showed that the catalysts were completely crystalline.

---

* Corresponding author. Tel.: +1 604 8223601; fax: +1 604 8226003.
E-mail address: kjs@interchange.ubc.ca (K.J. Smith).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.10.005

An alternative approach to using water-soluble catalyst precursors is to prepare the water-soluble precursor in reversed micelles such that the water pool containing the metal salt solution is stabilized in an organic solvent, such as n-hexane, using an appropriate surfactant. This approach provides for the possibility of a better control of the catalyst size and better dispersion of the catalyst precursor in the residue oil, compared to direct addition of the water-soluble precursor in the oil.

Although using the catalyst once-through has the advantage of minimizing deactivation effects during slurry phase hydroconversion, the cost of catalyst, especially in the case of more active and expensive metals like Mo, is prohibitive. For example, to process 75,000 bbl/d of heavy oil feed with 600 ppm metal catalyst, about 7.2 ton of metal would be required per day. Clearly recovery, regeneration and recycle of the spent catalyst would be needed to make slurry phase processes economically viable. An understanding of the state of the catalyst after the hydroconversion reaction and the interaction between the catalyst and the coke is needed before an appropriate catalyst recovery and recycle strategy can be implemented.

In the present study, we demonstrate the effectiveness of preparing water-soluble catalyst precursors in reversed micelles for use in hydroconversion of Cold Lake Vacuum Residue oil. Catalyst activity measurements are reported in both batch and semi-batch reactors. The study is part of a larger study on regeneration and recycling of unsupported catalysts in slurry phase hydroconversion reactors and therefore we also report on the catalyst after reaction and its interaction with the generated coke.

2. Experimental

Molybdenum (V) chloride ($MoCl_5$) (Sigma–Aldrich, 99%) was used as the metal source for the preparation of the reversed micelle catalyst precursors. n-Hexane (Acros Organics, 95%) and polyoxyethylene-4-lauryl-ether (PE4LE) (Sigma–Aldrich) were used as solvent and surfactant, respectively. A 2.0 M solution of lithium borohydride in tetrahydrofuran ($LiBH_4$) (Sigma–Aldrich) was used as reducing agent. Since molybdenum chloride is hygroscopic, no water was added during the micelle preparation. To obtain 600 ppm Mo in 80 g of the feed oil, the catalyst precursor was prepared from 6 mL of n-hexane and 1.92 mL of PE4LE added to 0.1366 g of $MoCl_5$. The mixture was placed in an ultrasonic shaker for 1–2 min to yield a transparent micelle dispersion. The metal salt was subsequently reduced by adding 5 times excess $LiBH_4$ prior to the addition of the catalyst to the reactor. All the micelle preparation steps were done at ambient temperature. To obtain different Mo concentrations in the feed oil, the amount of each component of the emulsion was adjusted proportionally. Mo micelles were used at concentrations of 100 ppm, 300 ppm, 600 ppm, 900 ppm Mo in the batch reactor experiments and at 100 ppm, 300 ppm, 600 ppm, 1800 ppm Mo in the semi-batch reactor experiments. Comparative tests were done using a water-soluble catalyst precursor prepared by dissolving appropriate amounts (8.9167 g) of ammonium heptamolybdate (AHM, Alfa Aesar, 99%) in 100 mL of de-ionized water so that 1 mL of this solution provided 600 ppm of Mo metal in 80 g of feed. Water-soluble AHM was used at a single concentration of 600 ppm Mo in the residue oil.

The diameter of the prepared reversed micelles was determined using dynamic light scattering (DLS). A Scitech Instruments ST-100 variable angle light scattering system using the 514 nm line of an Ar ion laser was utilized to determine the reversed micelle size distribution in the emulsion. The Mo micelle catalyst precursor, produced by reduction with $LiBH_4$, was also examined using a Tecnai G2 STEM with field emission of 200 keV and point/lattice resolution of 0.24/0.14 nm.

A 300 mL stirred autoclave reactor was used for assessing the different catalysts in a batch mode at a reaction temperature of 415 °C, initial H_2 pressure of 5.5 MPa and a reaction time of 1 h. After loading the reactor with the residue oil and the desired catalyst precursor, the reactor was flushed in N_2 and then pressurized with pure H_2 to an initial gas pressure of 5.5 MPa before heating to the desired reaction temperature (415 °C). The reaction temperature and pressure were continuously monitored during the reaction. Depending on the catalyst type and concentration, the initial reactor pressure at reaction temperature (415 °C) varied from about 10.2 MPa for the micelle catalyst to 10.9 MPa for the AHM catalyst. After 1 h reaction, the final pressure was 6.8 and 10.8 MPa for the micelle and AHM catalysts, respectively. After 1 h, the reaction was stopped by rapidly quenching the reactor using the cooling coil placed in the reactor. Solid and liquid products of the reaction were recovered and separated using a Beckman Coulter Allegra 25R refrigerated centrifuge, operated at 12,000 rpm for 30 min. The liquid recovered from the centrifuged samples was tested to make sure that toluene-insoluble content of the liquid was less than 0.5 wt%. The recovered solid was washed with toluene to remove any toluene-soluble material. Coke was defined as toluene-insoluble solids in all experiments. The gas remaining in the reactor (H_2, hydrocarbons and H_2S) was analyzed by a Varian Star 3400 CX gas chromatograph equipped with a 30 m capillary column (i.d. of 0.53 mm) and a thermal conductivity detector. Gas analysis data were used to calculate the H_2 conversion and uptake, and the H_2S and total gas yields.

A 250 mL stirred semi-batch reactor was also used to investigate the effects of higher temperature and pressure on catalyst performance. Reaction temperatures of 415 °C and 445 °C, a H_2 pressure of 13.8 MPa, a H_2 flowrate of 900 mL(STP)/min and a reaction time of 1 h were selected as reaction conditions. The H_2 gas flow to the semi-batch reaction system was controlled with a mass flow controller, and the product gas leaving the reactor was monitored using a mass flow meter. A separator placed in an ice-bath was used in the semi-batch hydroconversion unit to separate and collect C_{5+} hydrocarbons leaving the reactor in the gas phase. After loading the residue oil and catalyst to the reactor, the reactor

Table 1
Properties of Cold Lake Vacuum Residue.

Analyses and properties	CLVR
SARA analysis	
Saturates (wt%)	11.0
Aromatics (wt%)	38.7
Resins (wt%)	32.6
Asphaltene (wt%)	17.7
Elemental analysis	
C (wt%)	81.6
H (wt%)	9.7
S (wt%)	6.0
N (wt%)	0.5
H/C atomic ratio	1.43
HTSD	
<204 °C (wt%)	0.0
204–348 °C (wt%)	0.0
348–524 °C (wt%)	25.2
524+ °C (wt%)	74.8
Metal analysis	
Ni (ppm)	128
V (ppm)	313
Fe (ppm)	65
Mo (ppm)	12
Ash (wt%)	1.4
Molecular weight	765
Specific gravity	1.04

was purged in a 500 mL(STP)/min flow of N_2 and then a flow of H_2. The reactor system was pressurized to the reaction pressure (13.8 MPa) using a back-pressure regulator installed on the exit gas line. The reactor was heated to the desired reaction temperature and after 1 h, the reactor was rapidly cooled to room temperature. Liquid and solid products were recovered and separated using the same procedure followed for the batch reactor. The H_2S free gas, collected after an H_2S scrubber placed in the exit line downstream of the separator, was analyzed by an HP 5890A gas chromatograph. Light gases (C_1–C_4) were separated using a 5 m temperature programmed Porapak Q packed column and quantified with a flame ionization detector. In all experiments, about 80 g of CLVR was used as feed. The properties of the CLVR are listed in Table 1.

Gas yields from both reactors were calculated as the gas produced during the reaction divided by the CLVR feed weight. Liquid and coke yields were defined as the weight of liquid and coke recovered after the experiment divided by the CLVR feed weight, respectively. The product distribution of the liquid product was determined by high temperature simulated distillation (HTSD) using a standardized UOP methodology. Elemental analysis (C, H, N, S) was completed on all liquid products. H_2 conversion was measured by comparison of the H_2 fed to the reactor and the H_2 recovered at the end of the experiment based on the product gas analysis. H_2 consumption was expressed in grams of hydrogen per 100 g of feed. Sulfur removal was also calculated by comparison of the sulfur content in the feed and liquid product. Residue conversion was determined by comparison of the residue content of the feed and the residue content of the liquid product.

Elemental and metal analyses were done on the solid product (coke–catalyst mixture) which was also characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and high resolution transmission electron microscopy (HRTEM). SEM, EDX and EDX-mapping were done using a 120 keV Hitachi S-3000N SEM equipped with a light element EDX detector. Coke samples for TEM analysis were ground to a fine powder using an agate mortar and pestle and dispersed in ethanol ultrasonically, before placing a droplet of the suspension on a 200 mesh copper grid coated with formvar carbon that was left to dry before analysis. X-ray diffraction (XRD) patterns of the prepared catalysts were obtained with a Rigaku Multiflex diffractometer using Cu Kα radiation (λ = 1.5406 Å), a scan range of 2θ from 10° to 90° with a step size of 0.04° and scan rate of 2°/min.

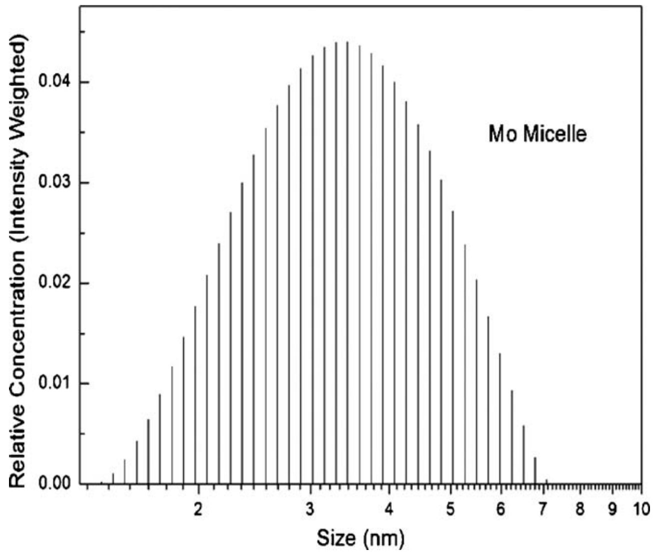

Fig. 1. Micelle size distribution in the emulsion analyzed by DLS. Solvent:surfactant = 3.1:1, Mo concentration in the feed = 600 ppm.

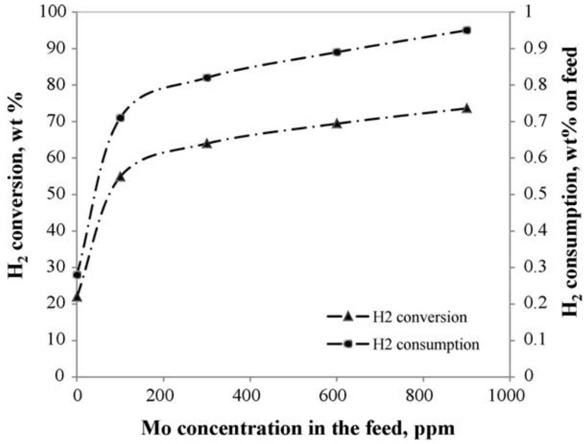

Fig. 2. Comparison of H_2 conversion and consumption in a series of experiments in the batch reactor using Mo micelle precursor with different Mo concentrations. T = 415 °C, $P_{H_2,\text{initial}} \sim 5.5$ MPa and reaction time = 1 h.

3. Results and discussion

3.1. Catalyst characterization

The use of a reversed micelle as the catalyst precursor requires that the metal content of the micelle be as high as possible so that the volume of the microemulsion to be added to the liquid oil is minimized. By adjusting the amount of metal salt, solvent and surfactant, a solvent/surfactant ratio of 3.1:1 was shown to be optimum to obtain stable micelles while also decreasing the microemulsion volume needed to achieve 600 ppm of Mo (48 mg of Mo) in the residue oil to less than 10 mL. The Mo micelle prepared using this ratio of solvent/surfactant was analyzed by DLS and Fig. 1 shows the Mo micelle size distribution in the emulsion with a micelle average diameter of 3.5 nm. Repeated measurements of this analysis for different Mo micelle preparations demonstrated good control of particle size by this procedure.

3.2. Catalyst activity tests

There were three categories of experiments done in the present study to assess catalysts: (i) experiments done in the batch reactor at relatively low temperature and pressure, (ii) experiments done in the semi-batch reactor utilizing low temperature and high H_2 pressure and (iii) experiments done in the semi-batch reactor at high temperature and pressure. Table 2 summarizes the conditions of the experiments investigated in the present study.

Table 2
Summary of the experimental conditions in the batch and semi-batch reactors.

Catalyst precursor	Catalyst concentration (ppm)	Batch reactor[a]	Semi-batch reactor[a]	
		$P_{H_2,\text{initial}} = 5.5$ MPa	$P_{H_2} = 13.8$ MPa[b]	
		T = 415 °C	T = 415 °C	T = 445 °C
Mo micelle	100	✓	–	✓
	300	✓	–	✓
	600	✓	✓	✓
	900	✓	–	–
	1800	–	–	✓
AHM	600	✓	✓	✓
	1800	–	–	✓
Thermal experiment	0	✓	–	✓

[a] Reaction time for experiments in both reactors was 1 h.
[b] Hydrogen flowrate: 900 mL(STP)/min.

Table 3
Result of CLVR hydroconversion experiments in the batch reactor using dispersed catalysts compared to literature data.

Catalyst type, Mo Concentration (ppm)	H_2 conversion (wt%)	H_2 consumption (wt% on feed)	Coke yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	Sulfur removal (wt%)	Reference
Thermal[a]							
0	22.0	0.3	8.6	84.3	3.0	35.0	This study
Mo micelle[a]							
100	54.8	0.7	1.2	96.7	2.2	35.0	This study
300	64.0	0.8	1.4	97.1	2.1	31.7	This study
600	69.4	0.9	1.2	98.9	1.9	38.3	This study
900	73.6	1.0	1.6	101.4	2.0	41.7	This study
AHM[a]							
600	28.2	0.4	8.2	87.1	3.2	26.7	This study
Exfoliated MoS_2[b]							
360	27.0	N/A	1.5	95.1	3.4	18.8	[10]
600	56.8	N/A	1.1	96.8	2.1	28.1	[10]
900	73.4	N/A	1.8	96.4	1.8	26.9	[10]
Mo naphthenate[c]							
1000	N/A	1.2	0.8	N/A	N/A	N/A	[6]

[a] H_2 pressure = 5.5 MPa, temperature = 415 °C, reaction time = 1 h, atomic H/C ratio of the feed = 1.43.
[b] H_2 pressure = 3.5 MPa, temperature = 415 °C, reaction time = 1 h, atomic H/C ratio of the feed = 1.58.
[c] H_2 pressure = 9.0 MPa, temperature = 410 °C, reaction time = 1 h, atomic H/C ratio of the feed = 1.41.

Batch reactor data measured at low temperature (415 °C) and pressure (5.5 MPa) are discussed first. The low temperature data emphasize differences in catalyst activities since the contribution of thermal cracking was low at 415 °C (as evidenced by residue conversions <60 wt%). Fig. 2 shows the H_2 conversion and consumption as a function of the Mo concentration for catalysts prepared from Mo micelle precursors. H_2 conversion and consumption both increased with increasing Mo concentration in the oil. Note, however, that the H_2 conversion did not increase linearly with catalyst concentration because at high H_2 conversion, the H_2 supply was limited in the batch reactor. At 100 ppm Mo, about 55 wt% of the H_2 in the reactor was converted after 1 h. This rapid H_2 consumption decreased both the H_2 concentration in the gas phase in contact with the residue oil in the reactor and the system total pressure. The reduced pressure will decrease H_2 solubility in the residue oil and the mass transfer rate between the gas and liquid phase, both resulting in reduced H_2 conversion. Another explanation for the trend shown in Fig. 2 is that at 415 °C, a relatively low temperature for hydroconversion and thermal cracking, the rate of reaction is limited by the concentration of hydrocarbon free radicals, so that further increases in H radical generation (due to increased Mo concentration) do not result in a significant increase in H_2 consumption. In this case, increasing the reaction temperature to increase the rate of hydrocarbon free radical generation, while catalyst concentration remains fixed at a relatively high value (i.e. 600 ppm Mo), will result in increased H_2 consumption. Although not done in the present study, Tye and Smith [15] reported a 32.4% increase in the H_2 consumption as the reaction temperature increased from 415 °C to 430 °C at the conditions of their study (initial H_2 pressure of 3.5 MPa, reaction time of 1 h and 600 ppm Mo using exfoliated MoS_2).

A comparison of the H_2 conversion and H_2 consumption using MoS_2 prepared from the reversed micelles and AHM precursors of the present study showed that at 600 ppm Mo, the catalyst prepared from the reversed micelle precursors had higher H_2 conversion and consumption than the water-soluble AHM catalyst precursor (Fig. 3). Note that although both catalysts were tested under the same operating conditions (T = 415 °C, $P_{H_2,\mathrm{initial}} \sim 5.5$ MPa and reaction time = 1 h), the reactor pressure was higher with the AHM precursor than the Mo micelle at all reaction times due to lower H_2 conversion. This suggests that even at lower H_2 pressures, the Mo micelle-based catalyst had better performance than the AHM in terms of H_2 consumption.

Since H capping of free radicals generated by thermal hydrocarbon cracking reactions is the main mechanism of coke prevention in hydroconversion [11], the higher H_2 conversion

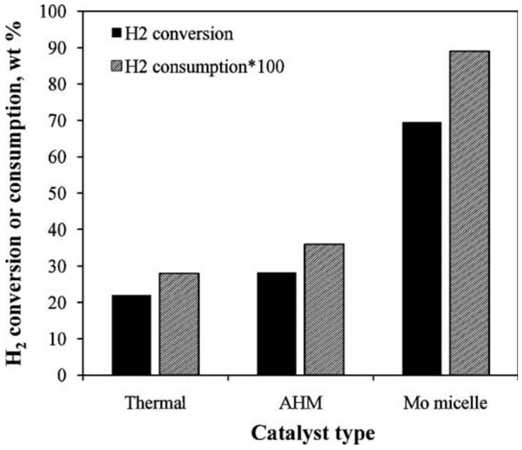

Fig. 3. Comparison of H_2 conversion and consumption in two experiments in the batch reactor using 600 ppm Mo in the form of micelle and water-soluble AHM precursors. T = 415 °C, $P_{H_2,\mathrm{initial}} \sim 5.5$ MPa and reaction time = 1 h.

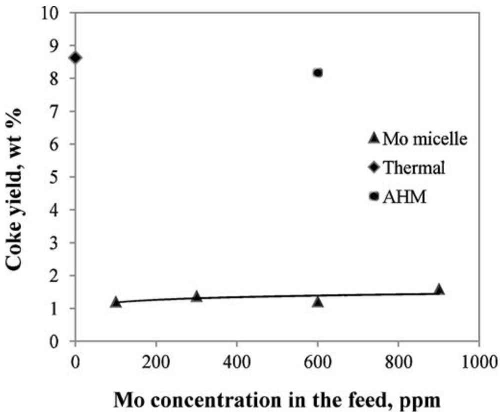

Fig. 4. Coke yield in a series of experiments in the batch reactor using different concentrations of Mo micelle precursor and 600 ppm of Mo using AHM precursor. T = 415 °C, $P_{H_2,\mathrm{initial}} \sim 5.5$ MPa and reaction time = 1 h.

achieved using the Mo micelle catalyst precursor versus the AHM precursor suggests that a significant difference in the coke yields from these two catalysts should also be observed. Fig. 4 shows that the coke suppression in the case of AHM catalyst precursor was very poor. At a concentration of 600 ppm Mo in the feed, the coke yield was much higher with the AHM catalyst precursor than the Mo micelle precursor. Changes in coke yield over the range of Mo concentrations in the case of Mo micelle catalyst were very small for experiments in the batch reactor at low temperature (415 °C). Since both catalysts were prepared using water-soluble precursors, the noticeable difference in catalyst activity shows the distinct advantage of using the reversed micelles to disperse the precursor. One likely reason for the poor activity of the AHM precursor compared to the Mo micelle catalyst precursor is agglomeration of Mo particles due to rapid evaporation of water from poorly dispersed AHM during heat up of the reactor. The well-dispersed Mo salt stabilized in the reversed micelle was much less likely to agglomerate during the heat up period. Also note that in the present study, the AHM catalyst may not have been utilized to its maximum potential. Catalytic properties of ammonium molybdates can be significantly increased by pre-sulfidation of AHM using H_2S at low, moderate and high temperatures [16].

The increased coke yield at a Mo concentration of 900 ppm in the feed, shown in Fig. 4, is consistent with results from experiments done in the semi-batch reactor at high concentration of Mo in the feed (1800 ppm) described below. Furthermore similar increases in coke yield were reported by Tye and Smith [15] and Del Bianco et al. [11]. Using exfoliated MoS_2 and Mo naphthenate, respectively, these authors reported a small increase in coke yield as the Mo concentration increased from 600 ppm to 900 ppm [15] and from 200 ppm to 5000 ppm [11]. Table 3 compares results from the present study, using the batch reactor, to literature data reported at operating conditions similar to those of the present study. Although Table 3 shows higher activity of MoS_2 prepared from a water-soluble precursor prepared in reversed micelles, compared to exfoliated MoS_2, water-soluble AHM and oil-soluble Mo naphthenate catalyst precursors, not all studies used the same residue oil as reactant. The apparent advantage of the Mo micelle catalyst precursor over the exfoliated MoS_2 is more significant considering that the Mo micelle precursor was evaluated using a feed with a low H/C atomic ratio (1.43) that has a much higher tendency for coke formation, compared to the feed used by Tye and Smith [15], which had a H/C atomic ratio of 1.53.

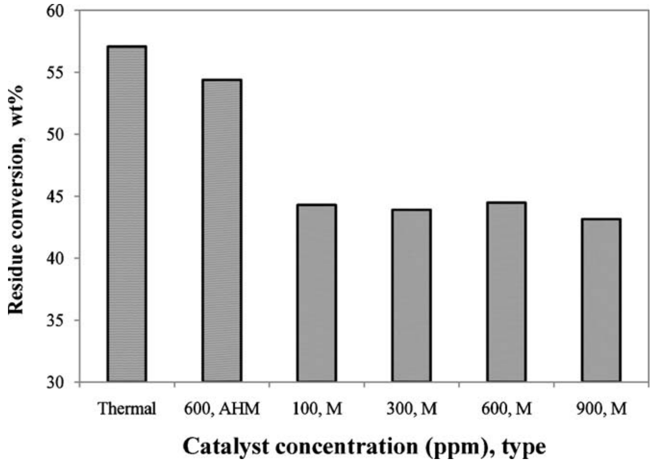

Fig. 5. Comparison of residue conversion in the experiments done in the batch reactor using different Mo precursors and concentrations with thermal experiment (M: micelle precursor). $T = 415\ ^\circ C$, $P_{H_2,\text{initial}} \sim 5.5$ MPa and reaction time = 1 h.

Table 3 also allows comparison of results from experiments using 900 ppm Mo catalyst prepared from the Mo micelle precursor (this work) and a Mo naphthenate precursor [11]. The data suggest that the Mo micelle precursor had almost the same H_2 consumption but higher coke yield than the Mo naphthenate at a Mo concentration of 1000 ppm in the feed. However, note that Del Bianco et al. [11] utilized a much higher H_2 pressure (9 MPa) and a lower temperature (410 °C) compared to that used in the batch experiments of the present study (5.5 MPa and 415 °C), further evidence of the efficiency of the Mo micelle catalyst precursor.

Residue conversion using the Mo micelle catalyst precursors over a range of Mo concentrations showed no improvement with increased catalyst concentration (Fig. 5). In addition, the Mo micelle at the highest Mo concentration had a lower residue conversion compared to the thermal experiment and the experiment using 600 ppm Mo derived from (AHM). Noting that the latter two experiments had the highest coke yield among all the

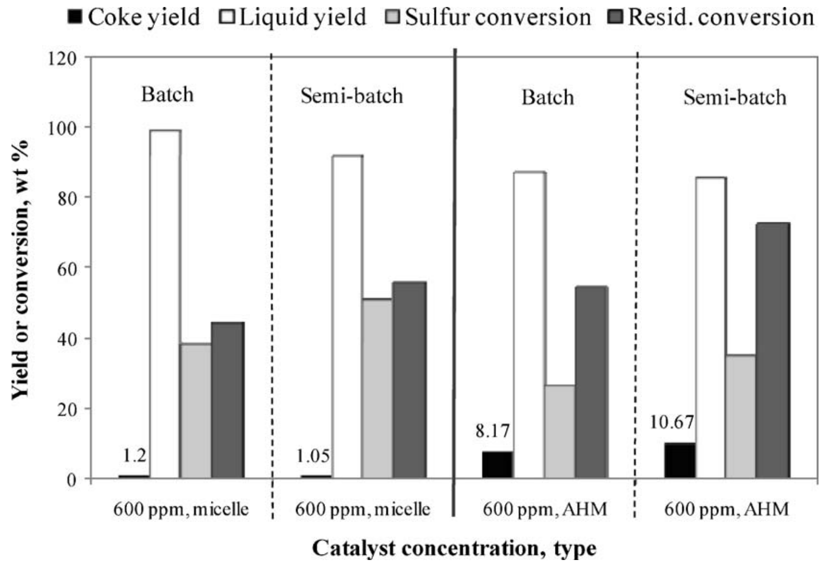

Fig. 6. Comparison of coke and liquid yields, sulfur conversion and residue conversion in the batch and semi-batch reactors using Mo micelle and catalyst prepared *in situ* using AHM. Reaction conditions—batch: $T = 415\ ^\circ C$, $P_{H_2,\text{initial}} \sim 5.5$ MPa and 1 h reaction time; semi-batch: $T = 415\ ^\circ C$, $P_{H_2,\text{initial}} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction.

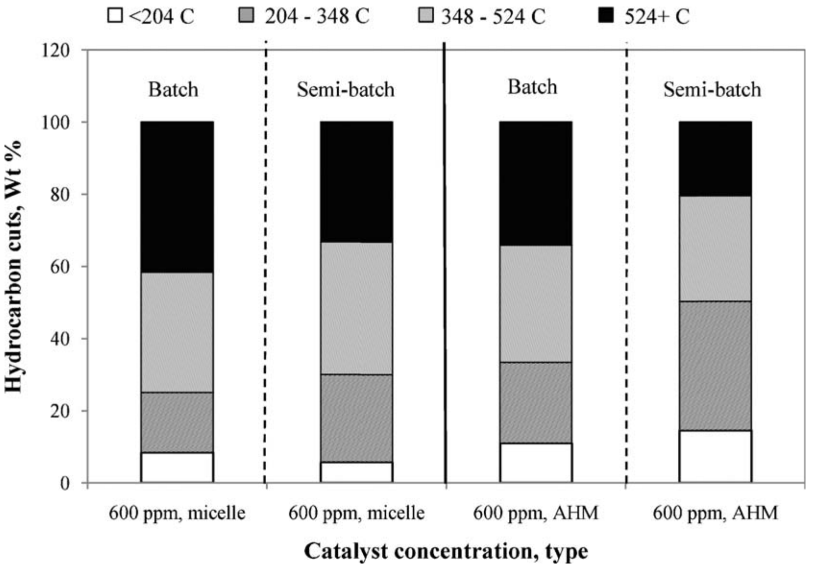

Fig. 7. Comparison of different hydrocarbon cuts in liquid products from experiments in the batch and semi-batch reactors using Mo micelle and catalyst prepared *in situ* using AHM. Reaction conditions—batch: $T = 415\ ^{\circ}C$, $P_{H_2,\text{initial}} \sim 5.5$ MPa and 1 h reaction time; semi-batch: $T = 415\ ^{\circ}C$, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time.

experiments, we conclude that the main reason for the high residue conversion in these systems is a higher rejection of residue in the form of coke and a higher gas yield, at the expense of more valuable liquid product fractions (Table 3).

The batch reactor experiments of the present study were limited by H_2 supply and low temperature and consequently, residue conversions were low (<60 wt%). To investigate the effect of H_2 supply and reaction temperature, experiments were done in a semi-batch reactor system at more severe conditions (Table 2). To investigate the effect of H_2 supply and H_2 pressure on the catalytic activity, two experiments using 600 ppm Mo prepared via reversed micelles and water-soluble AHM precursors, were done at 13.8 MPa H_2 and a H_2 flowrate of 900 mL(STP)/min. Other operating conditions were unchanged. Residue conversion in the experiments using Mo micelle and AHM precursors both increased in the semi-batch reactor compared to the batch reactor. The residue conversion increased from 54.4 wt% to 72.7 wt% in the case of the AHM precursor, due to both increased coke yield and H_2 pressure. In the case of the Mo micelle precursor, the residue

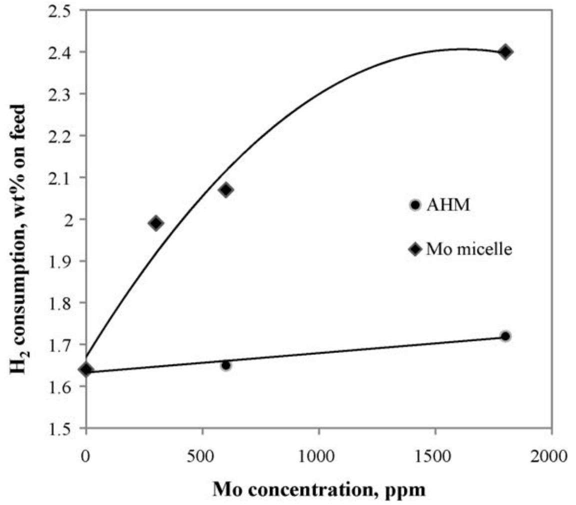

Fig. 8. Comparison of H_2 consumption in experiments using different concentrations and types of catalyst in the semi-batch reactor. $T = 445\ ^{\circ}C$, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time.

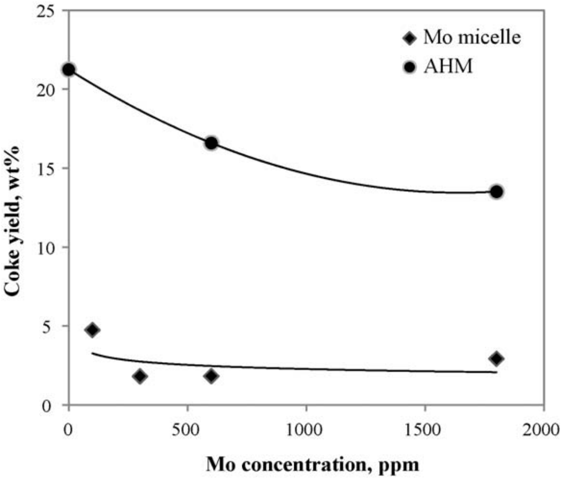

Fig. 9. Coke yield comparison between experiments using different catalyst types and concentrations in the semi-batch reactor. $T = 445\ ^{\circ}C$, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time.

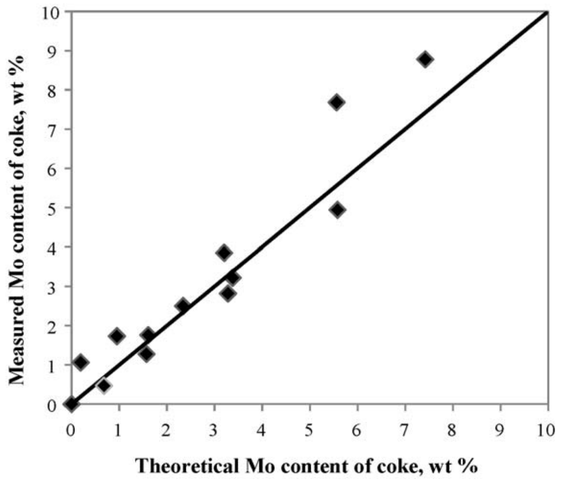

Fig. 10. Comparison of Mo content in different coke samples measured by EDX and theoretical amount calculated assuming all Mo added to the CLVR is associated with the coke.

Table 4
Results of CLVR hydroconversion experiments using dispersed catalysts in the semi-batch reactor.

Catalyst type, Mo Concentration (ppm)	H_2 conversion (wt%)	H_2 consumption (wt% on feed)	Coke yield (wt%)	Liquid yield (wt%)	Gas yield (wt%)	Sulfur removal (wt%)
Thermal[a]						
0	12.8	1.6	21.2	64.2	9.1	N/A
Mo micelle[a]						
100	N/A	N/A	4.8	81.4	7.4	55.2
300	15.6	2.0	1.8	87.5	5.0	53.5
600	16.2	2.1	1.8	90.0	5.6	67.3
1800	18.8	2.4	2.9	88.8	5.9	N/A
AHM[a]						
600	13.0	1.6	16.6	68.6	7.6	N/A
1800	13.7	1.7	13.5	73.1	7.7	N/A

Experimental conditions in semi-batch reactors:

[a] H_2 pressure = 13.8 MPa, temperature = 445 °C, reaction time = 1 h, atomic H/C ratio of the feed = 1.43.

conversion increased from 44.5 wt% to 55.6 wt%, a consequence of increased H_2 pressure, since the coke yield decreased from 1.2 wt% to 1.05 wt%. Sulfur conversion also significantly increased at the higher H_2 pressure in the semi-batch reactor compared to the experiments at lower H_2 pressure in the batch reactor. These results are summarized in Fig. 6.

Fig. 7 summarizes the HTSD results from the experiments using Mo micelle and AHM as catalyst precursors in the batch and semi-

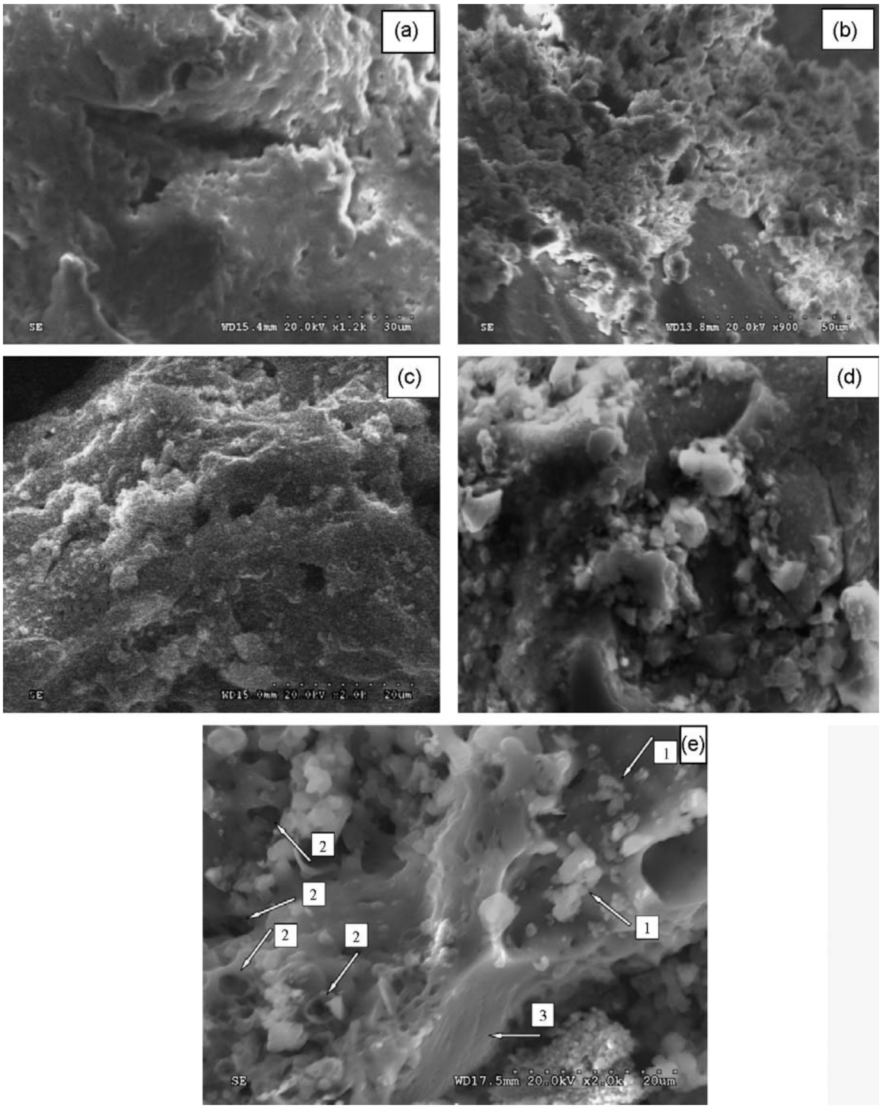

Fig. 11. SEM micrographs of different coke samples from hydroconversion reactions: (a) and (b) batch reactor, 600 ppm Mo using AHM, $T = 415$ °C, $P_{H_2,\text{initial}} \sim 5.5$ MPa and 1 h reaction time. (c) and (d) Semi-batch reactor, thermal experiment, $T = 445$ °C, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time. (e) Batch reactor, 600 ppm Mo micelle, $T = 415$ °C, $P_{H_2,\text{initial}} \sim 5.5$ MPa and 1 h reaction time. Numbers 1–3 are described in the text.

Table 5
Mo recovery from the coke samples recovered from the batch reactor experiments after reaction.

Catalyst type, concentration (ppm)	Mo added to the reactor (mg)	Mo concentration in the coke (mg/g coke)	Mo recovered from coke sample (mg)	Mo recovery (wt%)
Mo micelle, 300	24.0	31.3[a]	20.4	84.8
Mo micelle, 600	48.0	25.0[a]	44.8	93.2
Mo micelle, 900	72.0	47.7[b,c]	65.8	91.4

Experimental conditions in the batch reactor: H_2 pressure = 5.5 MPa, temperature = 415 °C, reaction time = 1 h, atomic H/C ratio of the feed = 1.43.

[a] Chemical analysis by Inductively Coupled Plasma (ICP) Spectrometry method.

[b] EDX analysis done by variable pressure 120 keV Hitachi S-3000N SEM.

[c] An average of analysis results of 8 different areas.

batch reactors. The results reveal that the product distribution in the liquid in the case of the AHM was shifted to lighter products compared to the micelle. The results also showed reasonable agreement between the product quality in the batch and semi-batch hydroconversion of CLVR, although differences ascribed to different heat up rates (due to different reactor geometries and heater types) were identified.

An investigation of the effect of temperature on the catalyst activity and hydroconversion products was completed by conducting a series of experiments in the semi-batch reactor utilizing both high temperature (445 °C) and excess H_2 (13.8 MPa and 900 mL(STP)/min). Mo was added at concentrations of 600 ppm and 1800 ppm Mo in the feed using the AHM precursor and 100 ppm, 300 ppm, 600 ppm, 1800 ppm Mo in the feed using the reversed micelle precursor. A thermal experiment in the presence of H_2 was also completed for comparison. At higher temperatures the rate of cracking reactions, which are mostly thermal and sensitive to temperature [17], would be expected to increase significantly, resulting in more hydrocarbon free radicals being produced. A comparison of the H_2 consumption in these experiments using different concentrations of Mo is presented in Fig. 8. In the case of the Mo micelle catalyst precursor, H_2 consumption increased with Mo concentration much more significantly than was seen in the batch reactor (Fig. 2). In the semi-batch reactor, the presence of an abundant amount of H_2 at high pressure and rapid capping of free radicals at the higher reaction temperature likely occurred [11].

Consistent with the trend reported in the batch reactor, the AHM had a much lower H_2 consumption compared to the Mo micelle precursor even at high concentrations. Since the active form of the catalyst in both cases was MoS_2, the poor catalyst activity in terms of H_2 consumption when using AHM precursor is ascribed to low surface area, a result of agglomeration of catalyst particles and poor dispersion of MoS_2 in the reactor. Although H_2 consumption with the AHM precursor was much less than the Mo micelle precursor, increased temperature and pressure in the semi-batch reactor increased the H_2 consumption of both AHM and Mo micelle precursors compared to the batch reactor.

Fig. 9 shows that the coke yield decreased in the semi-batch reactor with increased Mo concentration using AHM or Mo micelle as the precursor. However, consistent with the results from the batch and semi-batch reactors at 415 °C (Table 3), the AHM catalyst precursor showed much lower activity in terms of coke suppression compared to the Mo micelle catalyst (Fig. 9). Although the coke yield in the case of the Mo micelle precursor was higher compared to experiments at 415 °C, the catalyst showed good activity for coke suppression except at a Mo concentration of 100 ppm. Clearly, with a significant increase in the rate of cracking due to increased temperature, 100 ppm of well-dispersed Mo catalyst did not provide sufficient H to hydrogenate all the free radicals. With increased Mo concentration from 100 ppm to 300 ppm and 600 ppm, the hydrogenation reaction rate surpassed the rate of condensation and coke formation reactions and this decreased the coke yield from 4.74 wt% to 1.81 wt% and 1.83 wt%, respectively. Similar to the results in the batch reactor, with further increases in Mo micelle catalyst concentration (to 1800 ppm), a slight increase in coke yield was observed.

Using a concentration of 600 ppm Mo in the semi-batch reactor, liquid yield increased from 68.6 wt% in the case of AHM-based catalyst to 90.0 wt% in the case of the micelle-based catalyst. At a Mo concentration of 1800 ppm the corresponding liquid yields increased from 73.1 wt% to 88.8 wt%. This was a consequence of higher coke and gas yields in the case of the AHM precursor compared to the Mo micelle. The results presented in Table 4 show that 600 ppm Mo derived from the micelle catalyst precursor gave the best results for hydroconversion of CLVR. Although H_2 consumption, coke yield and gas yield using 300 ppm and 600 ppm Mo prepared from the reversed micelle precursors were very similar, 600 ppm Mo gave higher liquid yield and in particular, higher sulfur conversion.

3.3. Coke–catalyst characterization

The main goal of characterization of the coke generated during hydroconversion was to investigate the potential for coke–catalyst

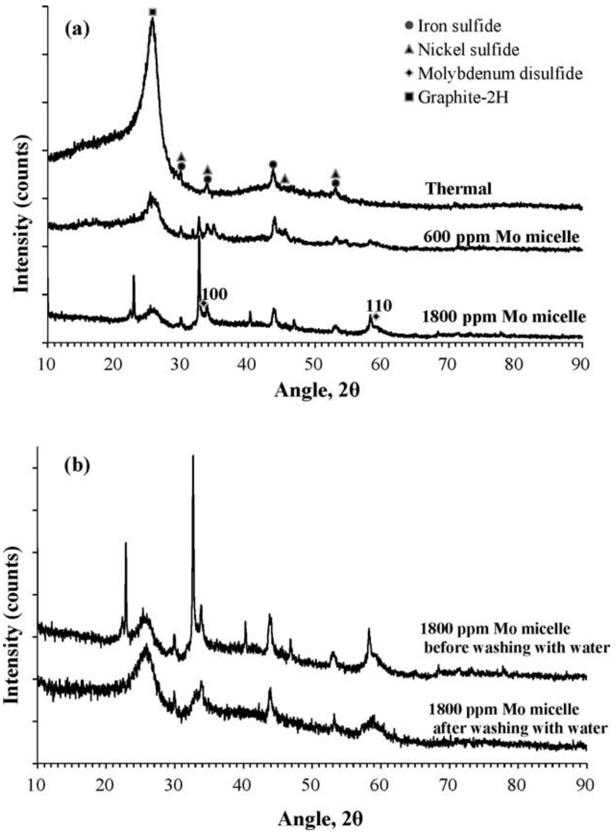

Fig. 12. X-ray diffractogram of coke samples from different experiments in the semi-batch reactor. T = 445 °C, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time.

recycle. To achieve this goal, three main issues need to be addressed: (i) the catalyst added to the reactor must be recovered in the solid product otherwise catalyst recovery and recycle becomes impractical. If the coke does not contain the catalyst, the coke cannot be recycled as the hydrocracking catalyst to the reactor inlet (ii) the metal must be well dispersed within the coke. A high degree of agglomeration of the catalyst particles in the coke–catalyst mixture will result in a very low catalyst surface area and very poor catalytic activity of the recycled catalyst. In this case, some treatment to improve the dispersion of the catalyst within the coke would be required before each recycling step and (iii) since the active form of the hydrocracking catalyst is the sulfided metal phase, the state of the metal before recycling should be investigated to make sure that metal is in its active phase. If not, some pretreatment (sulfidation) of the metals present in coke may be required prior to recycle of the coke–catalyst mixture.

Elemental and EDX analysis were done on selected coke samples to determine the amount of catalyst captured by the coke at the end of the reaction. Results from three experiments (Table 5) revealed that the generated coke captured most of the Mo catalyst. The Mo recovery varied from 85 wt% in the experiment using 300 ppm Mo in the feed to 93 wt% in the experiment using 600 ppm Mo and 91 wt% in the experiment in which 900 ppm Mo was used as catalyst. These results are consistent with results reported by others. Tye and Smith [15] reported that about 95 wt% of Mo using different Mo precursors ended up in the coke generated during hydroconversion. Lee et al. [12] also reported a metal concentration decrease in the liquid phase from 326 ppm to 12–16 ppm when using a fixed bed of extrudates made of microporous activated carbon to capture the catalyst in the hydrodesulfurization of residue oil. In the latter study, high metal adsorption was not surprising due to the high porosity and surface area of the activated carbon.

Fig. 10 shows the theoretical Mo concentration in the coke recovered after reaction versus the coke concentration measured by EDX for a number of experiments done in both the batch and semi-batch reactors. The theoretical amount of Mo in the coke samples was calculated based on the assumption that all of the Mo added to the CLVR was associated with the coke at the end of the reaction. Good agreement between the theoretical and measured concentrations confirmed the results presented in Table 5.

Selected coke samples from the batch and semi-batch reactor experiments were analyzed by SEM to investigate potential differences in the morphology of the coke generated in the thermal and catalytic experiments at 415 °C and 445 °C. Although there were some differences in the general morphology of the coke

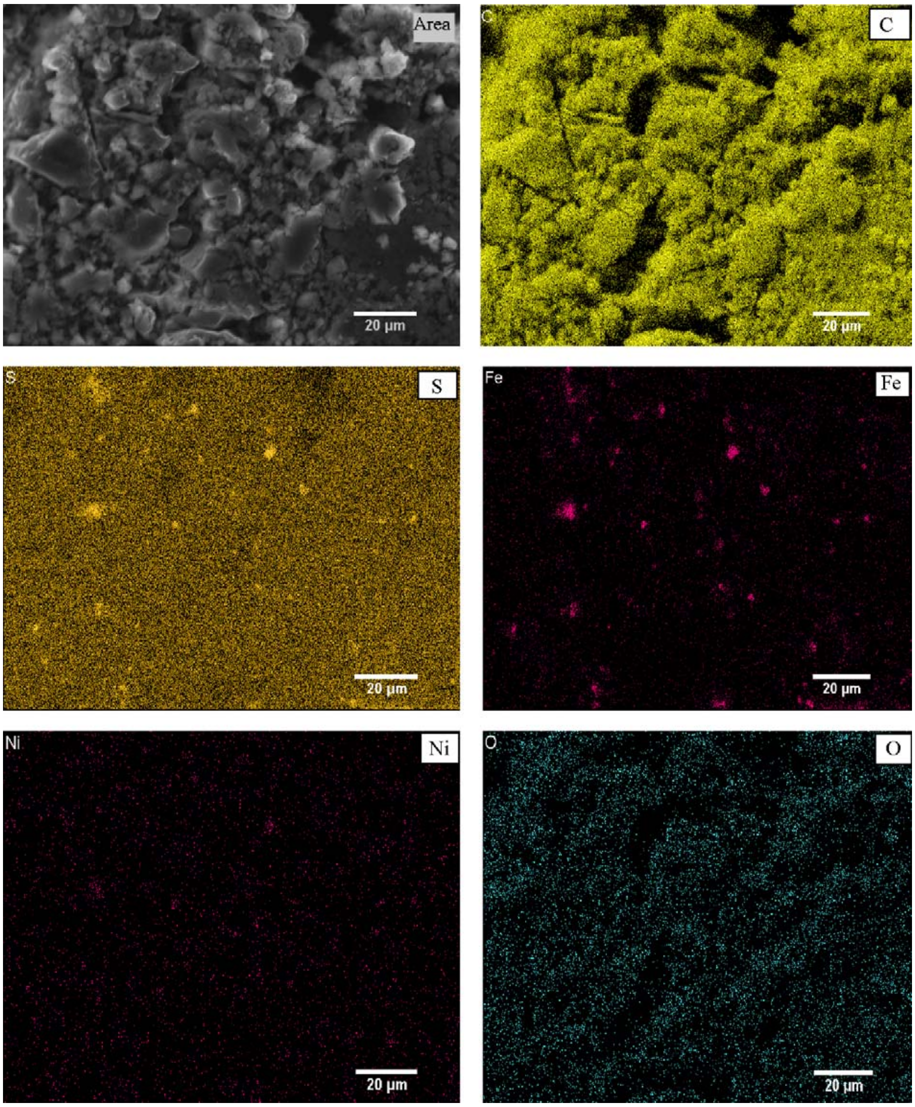

Fig. 13. Elemental mapping of coke sample generated in an experiment using 1800 ppm Mo micelle in the semi-batch reactor. $T = 445$ °C, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time.

samples, the coke samples had very similar features as observed by SEM. For example, Fig. 11a and b shows the coke samples from an experiment in the batch reactor with a Mo concentration of 600 ppm added as AHM. Three main features were apparent in all the coke samples: a continuum phase of coke with some cavities typical of porous materials (Fig. 11a), a relatively smooth surface of carbonaceous material (Fig. 11b), and smaller precipitated and attached particles with size <20 μm on the surface (Fig. 11b). It has been reported that treatment of solid carbonaceous materials with different solvents affects the morphology of the solid [18]. Since Fig. 11a and b shows different morphology of coke in the same sample, with the same reaction temperature and solvent used for solid recovery, the differences observed are ascribed to different stages of coke formation. Small particles on the surface (Fig. 11b) may depict nucleation and growth of the coke particles which result in a continuum phase with some porosity in the structure (Fig. 11a). The porous structure with further coke generation in its pores produced a smooth surface of carbonaceous material (Fig. 11a). The same morphology can be seen in coke samples generated in thermal experiments in the absence of catalyst (Fig. 11c and d). These observations suggest that the use of the catalyst and the different reaction temperatures had little effect on the general morphology of the generated coke. The three steps: (1) coke nucleation and deposition on the surface, (2) agglomeration of small deposited particles and development of a continuum porous phase and (3) production of a smooth surface of coke are also shown in Fig. 11e.

For XRD and TEM analysis of the coke, we used the coke generated in an experiment that used 1800 ppm Mo, added in the form of micelle to the reactor, to increase the Mo concentration in the recovered coke and hence, detection of the MoS_2 crystals and potential MoS_2 agglomeration. Coke generated by thermal reaction and with 600 ppm and 1800 ppm Mo, added via the micelle precursor, were examined by XRD (Fig. 12). MoS_2 has three characteristic peaks corresponding to the (0 0 2), (1 0 0) and (1 1 0) planes at $2\theta \sim 14^\circ$, $2\theta \sim 33.3^\circ$ and $2\theta \sim 59.1^\circ$. Although the coke samples from the latter two experiments had a theoretical Mo concentration of about 3.1 wt% and 5.7 wt%, respectively, no peak corresponding to the (0 0 2) plane of MoS_2 was observed in the diffractograms. Broader peaks corresponding to the (1 0 0) and (1 1 0) planes, which had some overlap with peaks from graphite and other metal sulfides, were identified in the diffractogram of the coke sample of the experiment using 1800 ppm Mo micelle. These peaks were not observed clearly in the XRD pattern of the coke sample recovered from an experiment using 600 ppm Mo micelle, mainly due to the low Mo concentration in the generated coke. The lack of a reflection corresponding to the (0 0 2) plane suggested the presence of highly dispersed crystallites with only a few atomic layers, that have higher hydrogenation activity than crystalline MoS_2 that displays a prominent (0 0 2) peak [19]. Nickel and iron sulfide, present at a lower concentration than the MoS_2, were also identified in the X-ray diffractograms. Since Fe and Ni were present in the feed, the intensity of these peaks was the same in all diffractograms from all coke samples and was independent of catalyst concentration. Agglomeration of these metal sulfides, compared to the highly dispersed MoS_2, suggests that the coke–catalyst mixture recovered after the reaction has a high potential of remaining active in terms of residue conversion, hydrogenation and coke suppression.

Fig. 12 also suggests a change in the crystallinity of the coke with increased Mo concentration. In the coke sample generated in the thermal experiment, a sharp peak at $2\theta \sim 25.68^\circ$ characteristic of graphitic carbon, was observed and the intensity of this peak decreased significantly with increased Mo. This suggests the generation of more amorphous coke when the catalyst was used in the hydroconversion reaction. Note that the unlabeled peaks of Fig. 12 for the micelle catalyst precursor are ascribed to NH_4Cl, a side-product of the micelle catalyst preparation procedure. These peaks disappeared when the coke was washed with de-ionized water.

The dispersion of different metals on the surface of the coke samples generated in the experiment using 1800 ppm Mo micelle was investigated using SEM-EDX elemental mapping. Fig. 13 confirms the conclusion drawn from the XRD analysis: a high dispersion of carbon and sulfur, major elements in the coke samples, was observed in the elemental maps. Fe and Ni were dispersed within the coke sample but in some locations, agglomeration of these metals (especially Fe which had a higher concentration probably due to contamination from the reactor wall during reactor cleaning) was observed. Comparison of the map of the Fe metal with the S map shows that agglomeration of the Fe occurs at the same location as the S. This observation in the case of Fe, which showed good crystallinity in the XRD analysis ($2\theta \sim 29.9^\circ$, 33.9°, 43.6° and 53.1°), confirmed that the metals in the coke were present as metal sulfides.

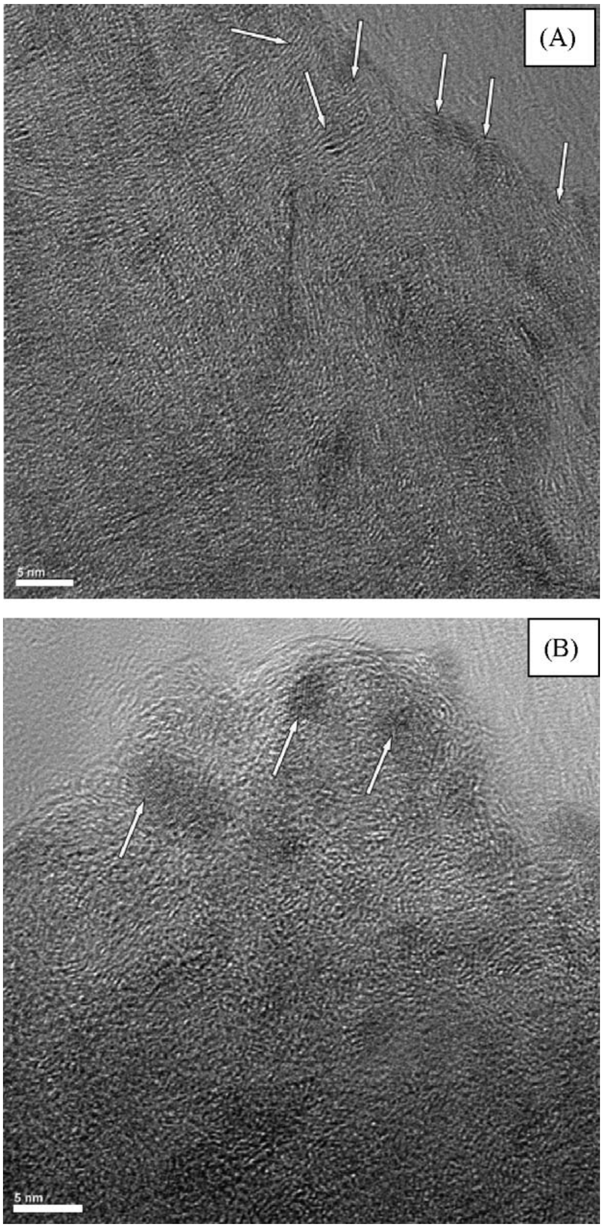

Fig. 14. HRTEM images of coke sample generated in an experiment using 1800 ppm Mo micelle in the semi-batch reactor. $T = 445\ ^\circ C$, $P_{H_2} \sim 13.8$ MPa at 900 mL(STP)/min and 1 h reaction time.

Further insight into the structure and morphology of the coke–catalyst mixture was obtained by HRTEM analysis. Two morphologies were apparent in the coke HRTEM micrographs. In the first micrograph (Fig. 14a), a tangled structure within all the sample was observed, but an interlayer space of 0.357 nm was also identified, in agreement with the $d_{0\,0\,2}$ spacing of graphene corresponding to amorphous material [18]. Edges are well defined in the images and this structure seems to be the dominant structure within the sample. In agreement with the XRD results, stacking of (0 0 2) planes (with 0.62 nm interplanar spacing [20]) was not observed in any of the micrographs, indicating a high dispersion of MoS_2 within the coke sample. No nickel sulfide or iron sulfide was observed either, most probably due to the low concentration of these metals in the sample. The second morphology identified by HRTEM was much more ordered with a smaller interlayer spacing (Fig. 14b) than that identified for the graphene layers. These features are ascribed to graphitic carbon which was also observed in the XRD diffractograms. Alkane-induced disruption is believed to be the main cause of the difference in the two types of structures observed in the HRTEM micrographs.

4. Conclusions

Two types of catalyst both prepared from water-soluble precursors were examined for CLVR hydroconversion in batch and semi-batch slurry reactors. In both reactors, based on higher H_2 consumption, higher liquid yield, lower coke yield and lower gas yields, the Mo micelle catalyst precursor was shown to give higher activity than the water-soluble AHM catalyst precursor. Operating the catalysts at higher temperature showed that the AHM catalyst precursor was not capable of rapid hydrogenation and hence coke suppression, whereas the Mo micelle catalyst precursor had very good coke suppression (coke yield $<$2 wt%).

Chemical and EDX analysis of selected coke–catalyst samples recovered from the reactors revealed that most of the metal added to the reactor at the beginning of the reaction was captured by the coke recovered from the reaction products. The presence of MoS_2, highly dispersed in the coke in a few atomic layers was confirmed by XRD analysis. The presence of other metal sulfides in the coke was shown by XRD and EDX-mapping techniques, but these metal sulfides were more agglomerated in the coke compared to the MoS_2. Two main morphologies were observed in the HRTEM images of the coke, one an amorphous structure and the second a more ordered crystalline structure ascribed to graphitic carbon. No obvious evidence of MoS_2 stacking in the coke sample was observed.

The characterization results indicated that most of the catalyst was highly dispersed in the generated coke, suggesting a good potential for the recovered coke to be recycled and used as the hydroconversion catalyst.

Acknowledgements

The authors gratefully acknowledge financial supports from UOP LLC, Alberta Energy Research Institute (AERI) and National Science and Engineering Research Council (NSERC) of Canada.

References

[1] M.S. Rana, V. Sámano, J. Ancheyta, J.A.I. Diaz, Fuel 86 (2007) 1216–1231.
[2] K. Niemann, K. Kretschmar, M. Rupp, L. Merz, Proc. The 4th Unitar/UNDP International Conference on Heavy Crude and Tar Sands, Edmonton, 7–12 August, (1988), pp. 225–242.
[3] W. Doehler, K. Kretschmar, L. Merz, K. Niemann, Proc. Symposium on Advances in Resid Upgrading American Chemical Society, Denver Meeting, 5–10 April, (1987), pp. 448–489.
[4] M.A. Menzies, A.E. Silva, J.M. Denis, Chemical Engineering (February) (1981) 46–47.
[5] N.K. Benham, B.B. Pruden, M. Roy, US Patent 5,755,955 (1998).
[6] N. Panariti, A. Delbianco, M. Marchionna, S. Rosi, Proc. American Institute of Chemical Engineers, New Orleans, 30 March–3 April, (2003), pp. 664–669.
[7] J.G. Speight, The Chemistry and Technology of Petroleum, Taylor & Francis group, New York, 2007, p. 627.
[8] G.T. Hager, X.X. Bi, F.J. Derbyshire, P.C. Eklund, J.M. Stencel, Preprints of Papers—American Chemical Society, Division of Fuel Chemistry 36 (1991) 1900–1908.
[9] K. Sato, Y. Iwata, K. Honna, Y. Araki, T. Yoneda, Y. Miki, H. Shimada, Studies in Surface Science and Catalysis 121 (1999) 411–414.
[10] B. Shi, D. Lin, L.Q. Wang, G.H. Que, Preprints of Papers—American Chemical Society, Division of Petroleum Chemistry 46 (2001) 410–413.
[11] A. Del Bianco, N. Panariti, S. Di Carlo, P.L. Beltrame, P. Carniti, Energy & Fuels 8 (1994) 593–597.
[12] D.K. Lee, S.K. Park, W.L. Yoon, I.C. Lee, S.I. Woo, Energy & Fuels 9 (1995) 2–9.
[13] E. Furimsky, Catalysts for Upgrading Heavy Petroleum Feeds, Elsevier, Amsterdam, 2007, p. 297.
[14] D. Liu, X. Kong, M. Li, G. Que, Energy & Fuels 23 (2009) 958–961.
[15] C.T. Tye, K.J. Smith, Catalysis Letters 95 (2004) 203–209.
[16] J. Lopez, E.A. Pasek, US Patent 4,710,486, December (1987).
[17] F. Khorasheh, H.A. Rangwala, M.R. Gray, I.G. Dalla Lana, Energy & Fuels 3 (1989) 716–722.
[18] F. Trejo, J. Ancheyta, M.S. Rana, Energy & Fuels 23 (2009) 429–439.
[19] M. Soto-Puente, M. Del Valle, E. Flores-Aquino, M. Avalos-Borja, S. Fuentes, J. Cruz-Reyes, Catalysis Letters 113 (2007) 170–175.
[20] F. Pedraza, J. Cruz-Reyes, D. Acosta, M.J. Yanez, M. Avalos-Borja, S. Fuentes, Journal of Physics of Condensed Matter 5 (1993) A219–A220.