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Study of MoS_2 Catalyst Recycle in Slurry-Phase Residue Hydroconversion

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ABSTRACT: A study of MoS_2 catalyst recycle during slurry-phase hydroconversion of residue oil, under high hydroconversion conditions, is reported. Different concentrations of MoS_2 (100, 300, 600, and 1800 ppm Mo derived from Mo-micelle and Mo-octoate precursors) were investigated in a semibatch stirred reactor. Catalyst recycle was simulated by reusing the solid coke-catalyst recovered from the reactor in subsequent experiments. The process was repeated several times until the catalyst deactivated. The recycled catalyst had a very similar activity to the fresh catalyst in the early stages of recycling. Experimental results showed that with increased catalyst concentration, an increased number of catalyst recycles with acceptable coke yield (<3 wt %) and toluene insoluble organic residue (TIOR) conversion (>80 wt %) were possible before deactivation was observed. At an initial concentration of 600 ppm Mo (using both Mo-micelle and Mo-octoate precursors), the catalysts were recycled 3 times without any significant loss in catalyst activity. Characterization of the recycled coke-catalyst mixture recovered after each recycle showed that coke aging resulted in significant changes to the properties of the recycled coke. While the MoS_2 catalyst was well-dispersed within the coke matrix, the coke's initial amorphous structure transformed to a more graphitic structure as the number of recycles increased. These changes resulted in catalyst deactivation during hydroconversion.

1. INTRODUCTION

With the depletion of conventional sweet crude oil reserves worldwide, the role of heavy-oil and bitumen in securing a reliable source of energy in the next few decades or centuries has become more important.[1] At the same time, there is a significant decrease in demand for low value petroleum products such as residue-based fuel oils.[2] Furthermore, increased environmental concerns have resulted in more rigorous specifications for petroleum fuels. In order to meet these challenges, a wide variety of processes have been developed and studied during the last few decades to convert heavy-oil and residue feedstocks to light, high value fuels.

Slurry-phase hydroconversion processes use dispersed, unsupported catalysts for upgrading the heavy-oil and residue into lighter petroleum products.[3] A review of slurry-phase hydroconversion using unsupported catalysts has been presented by Del Bianco et al.[4] These processes have been studied extensively in the last 3 decades, due to their high flexibility in processing different quality feeds, effective mass transfer in the reactor, low pressure drop, and high H_2 utilization, which translates into lower coke and gas formation compared to fixed-bed hydroconversion processes.

The drawback of slurry-phase processes using unsupported catalysts is the uncertainty regarding catalyst recovery and reuse. Catalyst recovery and reuse is not an issue when using low cost metal catalysts such as Fe, but usually this is at the expense of producing low quality liquid and a substantial amount of low value coke. In processes using more expensive metals such as Mo, at metal concentrations above ~300 ppm in the feed, catalyst recovery and reuse is critical in making these processes economically viable.[3]

A significant number of studies have reported on the effect of catalyst precursor type, catalyst loading, H-donor compounds in the feed, and operating conditions on the hydroconversion reactions using fresh precursors in slurry-phase systems.[5−17] On the other hand, very few studies are available that address hydroconversion using recycled (both supported and unsupported) catalysts. Kouzu et al.[18] investigated the catalytic activity of a carbon-supported NiMoS catalyst in a batch autoclave and compared the catalyst activity to that of an alumina-supported catalyst in the hydroconversion of an atmospheric residue of a Middle Eastern crude at an initial H_2 pressure of 5 MPa and temperature 350−450 °C. The solid toluene-insoluble fraction was recovered from the first hydroconversion experiment and recycled. The authors showed that the activity of the carbon-supported catalyst remained almost constant when recycled twice, while the activity of the alumina-supported catalyst decreased in terms of suppression of toluene insoluble (coke) product. The carbon-supported catalyst had lower toluene insoluble yield in the first and second recycle compared to the experiment using fresh catalyst. The S content, N content, and selectivity toward different hydrocarbons in the products did not change significantly in the first and second recycle for the carbon-supported catalyst. Using alumina-supported catalyst, while the N content of liquid in the first and second recycle remained constant, the S content and coke yield increased linearly with recycle number. The authors did not report on catalyst deactivation since the catalyst was not recycled more than twice.

Dunn et al.[19] investigated the catalytic activity of two V and Ni-based carbonaceous solids with low (12 wt %) and high (50 wt %) metal loading in the hydroconversion of bitumen (Cold Lake atmospheric residue and gas oil to produce a product with the same API° and viscosity as Cold Lake bitumen). The solid with low (Ni+V) loading was recovered from an ExxonMobil

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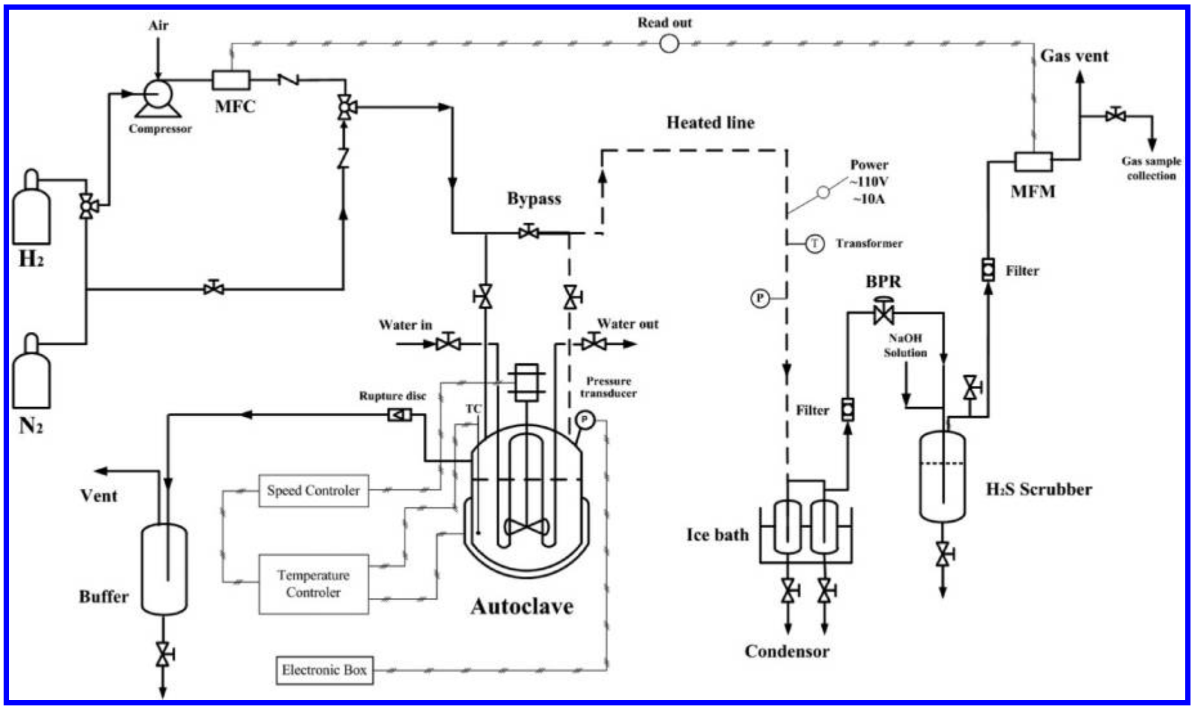

Figure 1. Schematic of semibatch slurry-phase heavy oil hydroconversion unit.

flexicoker (Venturi fines), while the solid with high metal content was a mild burnt Venturi fines mixed with the gasifier bed coke. A mixture of the solid ash and the feed oil were loaded in a semibatch reactor and heated at 365 °C for 20 min for in situ sulfidation of the vanadium and nickel oxides. Then the reactor was heated to 413 °C, and the reaction proceeded for 2 h. The solid catalyst was recovered by hot filtration of products under N_2 gas for recycle in a subsequent hydroconversion experiment. The study showed that the activity of the recycled catalyst was not the same as the activity of the catalyst used once-through. A 10% reduction in the API° of the liquid in the first recycle and marginal decrease thereafter was observed. Although the performance of the recycled catalyst in their studies yielded a hydroconverted product of decreased stability and lower API°, the overall reduction in product quality was small in comparison to that produced using fresh catalyst. To circumvent catalyst deactivation, the authors added 10 wt % fresh catalyst to the recycled solid, but product analysis of the hydroconversion experiments showed that the addition of fresh catalyst did not improve product quality. The authors also studied the effect of mild calcination of the recycled catalyst and showed that partial removal of contaminants from the catalyst increased the activity of the recycled catalyst but did not restore the activity to the level of the fresh sulfided solid.

Another relevant study was reported by Del Bianco et al.[20] Using an autoclave reactor operated at 410 °C, the authors investigated the recyclability of the asphaltene-catalyst mixture recovered from hydroconversion experiments. Using a high Mo concentration of 3000 ppm prepared from a molybdenum naphthenate precursor, the asphaltene-catalyst mixture from the first hydroconversion experiment was recycled 10 times. Although one of the first studies that detailed the recycling of dispersed catalysts, the reaction temperature (410 °C) was such that low conversion occurred (as is also the case for the results reported by Dunn et al.[19]). The results presented by Del Bianco et al., although very valuable for investigating the activity of recycled catalyst at low conversion, cannot be extrapolated to the high residue conversion conditions (high temperature of ~450 °C) relevant in commercial operations.

In the present study, the results of catalyst recycle under high residue conversion conditions in a semibatch, slurry-phase hydroconversion unit are presented. Catalyst recycle was simulated by recovering the solid coke-catalyst mixture from each hydroconversion experiment. After washing in toluene, drying, and crushing, the coke-catalyst mixture was added to the residue oil of a subsequent hydroconversion experiment without any further addition of catalyst to the reactor. The effect of initial catalyst concentration as well as catalyst precursor on the number of possible recycles before deactivation was investigated. The effect of solids loading in the reactor was also studied, and a preliminary analysis of the coke-catalyst mixture is presented. Finally, a possible mechanism of catalyst deactivation during hydroconversion is described.

2. EXPERIMENTAL SECTION

Two types of Mo precursors were used to prepare the MoS_2 reported herein. A Mo-octoate precursor, with 15.5 wt % Mo in molybdenum 2-ethylhexanoate, was provided by the Shepherd Chemical Company. The Mo-micelle precursor consisted of molybdenum(V) chloride ($MoCl_5$) (Sigma-Aldrich, 99%) dissolved in a water pool and dispersed in n-hexane (Acros Organics, 95%). Polyoxyethylene-4-lauryl-ether (PE4LE) (Sigma-Aldrich, 99%) was used as surfactant to stabilize the reversed micelle. The Mo-micelle precursor was reduced using a 2 M $LiBH_4$ solution to convert the metal salt to zerovalent Mo. Due to the highly hygroscopic nature of $MoCl_5$, no additional water was added when preparing the micelle. As an example, to prepare the Mo-micelle such that 600 ppm of Mo was present in 80 g of the residue oil, 6 mL of n-hexane and 1.92 mL of PE4LE were 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 with a light green color. The $MoCl_5$ was subsequently reduced by addition of excess $LiBH_4$ prior to addition of the precursor to the 80 g of residue oil. All the micelle preparation steps were done at ambient temperature. To prepare different concentrations of Mo in the residue oil, the amount of each chemical used for the Mo-micelle synthesis was adjusted. Details of the Mo-micelle precursor characterization have been reported previously.[21] Concentrations of 100, 300, and 600 ppm Mo in the residue oil using the Mo-micelle precursor were investigated as well as 600 and 1800 ppm Mo in the residue oil using the Mo-octoate precursor. Note that the active phase of the catalyst in the reactor was MoS_2, but all catalyst concentrations are reported as ppm of Mo in this study. For both precursors, the sulfidation of Mo was done in situ using the H_2S gas produced during the early stages of heat up of the reactor.

Figure 1 shows a schematic of the semibatch, slurry-phase reaction system used in this study, that included a stirred reactor of volume equal to 250 mL. Reaction conditions were selected to mimic high residue conversion conditions. A reaction temperature of 445 °C, a H_2 pressure of 13.8 MPa with continuous flow of 900 mL (STP)/min H_2, and a reaction time of 1 h were used for all the hydroconversion experiments (using both fresh and recycled catalyst) reported herein. The inlet H_2 gas flow and the exit gas were measured and monitored with a mass flow controller and mass flow meter, respectively. The total gas inlet and outlet volume was totalized using a Brooks Instrument 0154 flow controller for calculation of gas yield and H_2 uptake of each hydroconversion experiment. To capture the light hydrocarbons carried out of the reactor by the continuous H_2 flow, a double-stage (2 × 150 mL) cold separator placed in an ice bath was used in the high pressure zone (after the reactor and before the back-pressure regulator) to separate and collect C_{5+} hydrocarbons leaving the reactor in the exit gas. A H_2S scrubber using 400 mL of 1 N solution of NaOH was placed after the back-pressure regulator (BPR) to remove any H_2S gas from the exit gas stream. The gas leaving the reactor during the 1 h operation was collected in a Tedlar gas sampling bag for analysis.

For experiments in which fresh precursor was used, the reactor was loaded with the desired amount of catalyst together with 80 g of the residue oil. After sealing, the reactor was purged in a 300 mL (STP)/min flow of N_2 and then H_2, each for 5 min. Using a back-pressure regulator (26−1700 series high pressure back-pressure regulator from Tescom) installed after the condenser, the reaction system was pressurized with H_2 to a reaction pressure of 13.8 MPa for all experiments. The reactor was then heated to the desired reaction temperature (445 °C) and after 1 h, the reactor was rapidly cooled to ∼15 °C using an internal cooling coil and cold water as coolant. In a typical hydroconversion experiment, it took about 1 min to cool the reactor from 445 to 300 °C and 10 min to reach 50 °C. A sample temperature and pressure profile from a typical hydroconversion experiment for the heat-up and reaction period is presented in Figure 2. Before depressurizing the reactor, a gas sample was collected for analysis by GC. Solid and liquid products of the reaction were also recovered and separated using a Beckman Coulter Allegra 25R refrigerated centrifuge, operated at 12,000 rpm and 15 °C for 30 min. Random selections of the liquid samples recovered from the centrifuge were tested to ensure that the toluene-insoluble content of the liquid was less than 0.5 wt %. The recovered solid was mixed with the solid recovered from washing the reactor wall and internal fittings. The recovered solids were filtered and washed with toluene to remove toluene-soluble materials, followed by drying in a vacuum oven (5 inHg) at 120 °C for 3−4 h. The coke was defined as the toluene-insoluble solids recovered in each experiment. The continuously collected gas sample from the exit line as well as the gas sample collected from the reactor after completion of the experiment were analyzed by an HP 5890A gas chromatograph. Light gases (C_1−C_4) and their isomers were separated using a 5 m temperature programmed Porapak Q packed column and quantified with a flame ionization detector (FID).

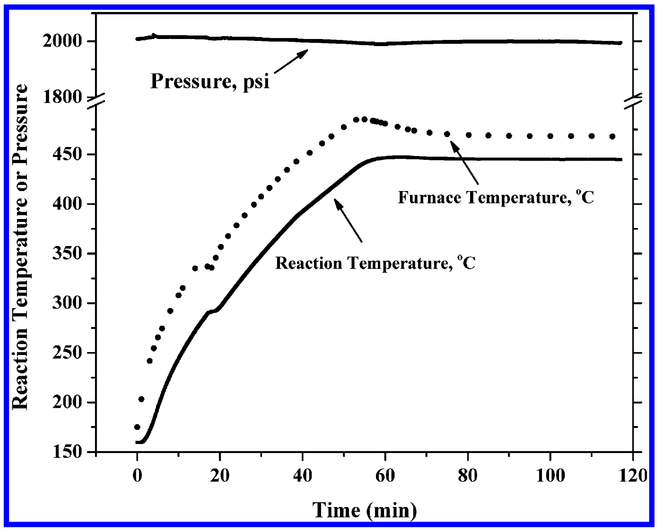

Figure 2. A sample temperature and pressure profile of a typical hydroconversion experiment.

The only difference in experimental procedure between the experiments in which the fresh precursor was used and those in which recycled catalyst was used was in the reactor loading. In the recycle experiments, the coke-catalyst mixture recovered from a previous experiment was used as the catalyst for a subsequent hydroconversion experiment without addition of any further fresh catalyst.

In all experiments, 80 g of Cold Lake vacuum residue (CLVR; provided by Imperial Oil) was used as feed. The properties of the CLVR are listed in Table 1. Gas yield was calculated as the gas (hydrocarbons) produced during the reaction divided by the CLVR feed weight. Coke and liquid yields were similarly defined as the weight of coke (after washing and drying) and liquid recovered after each hydroconversion experiment divided by the CLVR feed weight, respectively (wt % of feed). The coke yield calculation for the recycle experiments was based on the net weight of coke generated (total solid recovered after reaction − the weight of solid coke added to the reactor) divided by the weight of the CLVR feed.

Table 1. Properties of Cold Lake Vacuum Residue Used As Feed

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 atom 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
ash, wt %		1.4
molecular weight		765
specific gravity		1.04

The distribution of the different hydrocarbon cuts in the liquid product was determined by high temperature simulated distillation (HTSD) using the ASTM D7169 methodology. The residue in this study was defined as all products having boiling points above 524 °C. Residue conversion was determined by comparison of the residue content of the feed and the residue content of the products (residue content of liquid as well as generated coke). Toluene insoluble organic residue (TIOR) conversion was defined as

$$TIOR\ conversion\% = \frac{(W_{R,F} - (W_{R,L} + W_c))}{W_{R,F}} \times 100 \qquad (1)$$

where $W_{R,F}$ is the weight of residue in the feed, $W_{R,L}$ is the weight of residue in the liquid product, and W_C is the net weight of solid coke generated in the experiment.

To measure the asphaltene content (n-C_5 asphaltene) of the feed and liquid product, 2 g of sample was dissolved in ~2 mL of toluene. Asphaltenes were subsequently precipitated by introducing an excess amount (80 mL) of n-C_5 to the solution. After filtering the slurry with a 0.22 μm membrane filter and washing with excess n-C_5, solid asphaltene was dried overnight in an oven at 120 °C. Asphaltene conversion was then calculated by comparison of the mass of asphaltene in the feed and the mass of asphaltene in the liquid product in each recycle experiment as follows

$$Asphaltene\ conversion\% = \frac{(W_F \times C_{A,F} - W_L \times C_{A,L})}{W_F \times C_{A,F}} \times 100 \qquad (2)$$

where W_F and W_L are the weights of the feed and liquid product, respectively, and $C_{A,F}$ and $C_{A,L}$ are asphaltene concentrations in the feed and liquid product.

H_2 uptake was measured by comparison of the weight of H_2 fed to the reactor and the weight of H_2 recovered at the exit during the 1 h reaction period. The H_2 concentration in the exit gas flow was calculated by difference based on the measured hydrocarbon concentrations in the exit gas. The H_2 uptake was expressed in grams of H_2 per 100 g of feed.

For the catalyst recycle experiments, the coke-catalyst mixture recovered from a hydroconversion experiment was mixed with about 50 mL of toluene at room temperature and shaken on a rotary shaker overnight. The slurry was then placed in an ultrasonic shaker for 15 min and filtered using a 0.22 μm membrane filter. The solid was subsequently washed with fresh toluene to remove any oil-soluble compounds from the coke. The filtered coke samples were dried under 5 inHg vacuum at 120 °C for 4 h. The dried coke samples were then ground to a fine powder using an agate pestle and mortar and used as the recycle catalyst. SEM analysis of the coke prior to recycling (Figure 3) showed uniform particles with a size distribution from 1 to 30 μm.

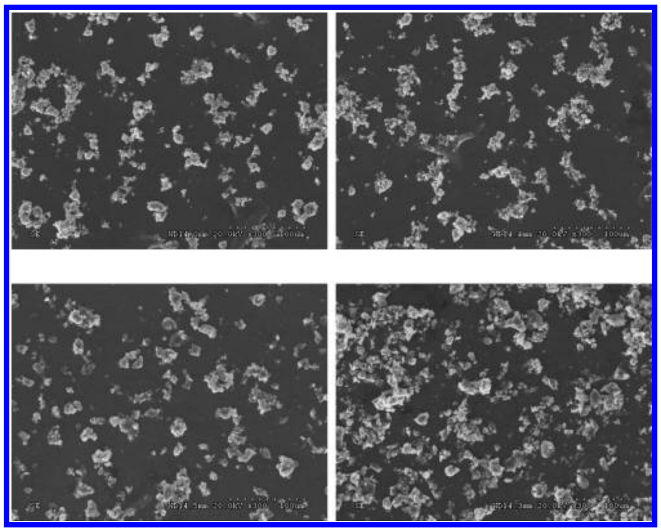

Figure 3. SEM micrograph of 4 different coke samples prior to recycling.

Great care was taken ensure that no coke-catalyst mixture was lost during the recovery from the reactor, washing, filtration, drying, and grinding steps. Except for a few milligrams of the coke sample used for characterization, the rest of the coke-catalyst mixture was used as the catalyst in the next hydroconversion reaction.

In the recycle experiments, the coke-catalyst mixture (prepared as described above) added to the reactor was mixed with the residue oil overnight (for at least 8 h) at 12.4 MPa of N_2 gas and 160 °C. The reactor was depressurized the next day, purged, and then pressurized with H_2 gas to the reaction pressure of 13.8 MPa to start the hydroconversion reaction using the recycled catalyst.

Solid product (coke) was characterized by X-ray diffraction (XRD) after each recycle step. The XRD patterns of the recovered coke were obtained with a Rigaku Multiflex diffractometer using Cu Kα radiation (λ = 1.5406 Å, 40 kV, and 20 mA), a scan range of 2θ from 10° to 90° with a step size of 0.04°, and a scan rate of 2°/min.

The errors associated with the experimental measurements in the semibatch reactor are summarized in Table 2 and Table 3. Table 2 reports the measured data from a series of repeated recycle experiments using 300 ppm Mo in the form of the Mo-micelle precursor and shows good repeatability of the recycle experiments. Table 3 reports the standard errors of the measured values estimated from a series of 10 repeated experiments conducted at 3 different sets of operating conditions. In addition we report the C and H recovery percentage from these 10 experiments.

3. RESULTS AND DISCUSSION

3.1. Activity of Recycled Catalyst. Previous work has shown that more than 90% of the catalyst initially added to the reactor was present in the solid product (coke) recovered after the hydroconversion reaction.[21] Characterization of the coke-catalyst mixture showed that the metal particles in the coke-catalyst mixture were both sulfided and well-dispersed within the coke matrix.[21]

To investigate the effect of initial catalyst concentration on the number of catalyst recycles before catalyst deactivation was observed, both Mo-micelle and Mo-octoate precursors were used to provide a range of Mo concentrations. The activity of the recycled catalyst was assessed in terms of H_2 uptake, coke suppression, residue and asphaltene conversion and selectivity of the catalyst toward different hydrocarbon cuts in the liquid products. Mo concentrations of 100, 300, and 600 ppm using the Mo-micelle precursor and 600 and 1800 ppm using the Mo-octoate precursor were investigated. Figure 4 shows the coke yield versus the number of recycles in this series of experiments measured at 445 °C, 13.8 MPa H_2, and 1 h reaction time.

Figure 4 shows that with 100 ppm Mo derived from the Mo-micelle precursor, the hydroconversion of CLVR had a coke yield of 4.8 wt %. In the first recycle of the coke-catalyst mixture recovered from this experiment, the coke yield increased to 13 wt %, a clear indication of rapid catalyst deactivation. An increase in the initial Mo concentration to 300 ppm, using the same Mo-micelle precursor, decreased the coke yield to 1.9 wt % compared to the experiment with 100 ppm Mo. The recovered coke, when recycled, had a coke yield of 2.5 wt %, but this rapidly increased to 11.4 wt % in the second recycle, indicating catalyst deactivation after the first recycle. Figure 4 also shows that with 600 ppm Mo using both Mo-micelle and Mo-octoate precursors, a significant increase in the number of recycles was possible before a loss in the catalyst activity and increased coke yield was observed. With 600 ppm Mo derived from the Mo-micelle and Mo-octoate precursors, the coke-catalyst mixture was recycled 4- and 3-times, respectively, while the catalyst maintained its activity in terms of coke suppression. After the fourth recycle, both catalysts were deactivated, and the coke yield increased to more than 8 wt %.

Previous studies[22] showed that Mo-micelle and Mo-octoate precursors, when added to the reactor in the form of fresh precursors, have very similar activity in terms of coke suppression, residue conversion, hydrogen uptake, and liquid yield. The differences in performance of these two precursors in the fourth recycle experiment is believed to be due to differences in the chemical and morphological properties of

Table 2. Comparison of Repeated Recycle Experiments Using 300 ppm Mo in the Form of Mo-Micelle Precursor

		fresh experiment		1st recycle		2nd recycle	
		1	2	1	2	1	2
feed, g		80.23	80.22	80.67	79.85	79.94	79.25
H_2 uptake (wt %)		2.05	1.99	2.42	1.98	1.62	2.01
H_2S yield (wt %)		1.58	1.29	1.43	1.47	1.03	1.14
gas yield (wt %)		3.51	4.98	6.08	4.90	7.88	6.40
liquid yield (wt %)		88.48	87.48	83.77	89.84	73.64	79.22
wt%	<204 °C	24.92	24.17	28.02	N/A	33.67	28.99
	204 °C−348 °C	34.55	35.48	36.64	N/A	37.92	37.56
	348 °C−524 °C	26.85	26.87	25.44	N/A	19.53	21.44
	524 °C+	13.68	13.48	9.90	N/A	8.88	12.01
coke yield (wt %)		1.95	1.81	2.52	2.87	11.45	8.11
mass recovery (wt %)		93.11	93.18	92.47	96.83	93.48	93.87
asphaltene (wt %)		60.96	65.14	59.38	53.28	62.20	55.87
TIOR conversion (wt %)		81.22	81.82	85.55	N/A	75.96	76.45

Table 3. Experimental Repeatability in Hydroconversion Experiments[a]

parameter		std error as a % of the mean
H_2 uptake, error		±2.90%
gas yield, error		±8.81%
liquid yield, error		±1.04%
wt%	<204 °C	±3.88%
	204 °C−348 °C	±1.54%
	348 °C−524 °C	±1.22%
	524 °C+	±4.79%
coke yield, error		±5.38%
TIOR conversion, error		±1.38%
		mean value ± STD DEV[b]
mass recovery (wt %)		93.63 ± 0.71
carbon recovery (wt %)		94.36 ± 2.02
hydrogen recovery (wt %)		95.54 ± 4.06

[a]Values are calculated based on 10 different repeat experiments using different catalyst concentrations and precursors. [b]STD DEV: Standard deviation.

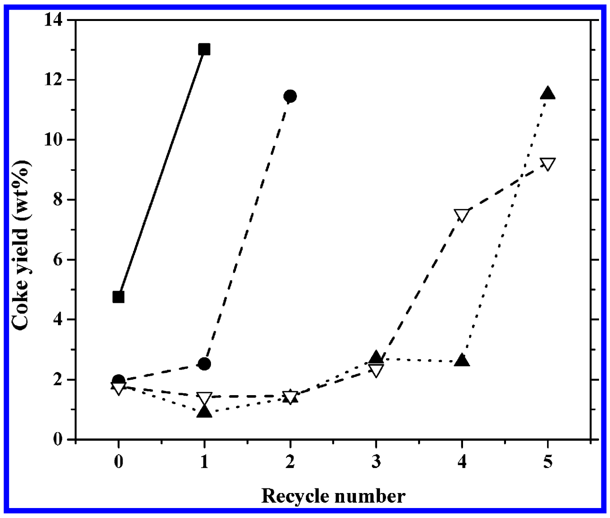

Figure 4. Coke yield versus recycle number from experiments using different catalyst precursors and Mo concentrations: 100 ppm Mo using Mo-micelle precursor (■), 300 ppm Mo using Mo-micelle precursor (●), 600 ppm Mo using Mo-micelle precursor (▲), and 600 ppm Mo using Mo-octoate precursor (▽).

the generated coke. The properties of the generated coke during recycle are described and discussed in more detail in a subsequent publication.[23]

One effect that should be noted in Figure 4 is that in the experiments with high catalyst concentrations (600 ppm Mo using Mo-micelle and Mo-octoate), the coke yield reached a minimum in the first recycle. This is probably because with a high initial catalyst concentration, a substantial amount of catalyst is available for H transfer to the free radicals generated during thermal cracking. Consequently, coke formation is suppressed, and coke yields similar to the coke yield from experiments using the fresh precursor are observed. Previous studies[20] have shown that the asphaltene (which is the main precursor of toluene insoluble coke) recovered from the liquid product of a hydroconversion reaction can be further cracked when recycled. Similarly, a portion of the toluene insoluble coke, which consists of both reactive amorphous coke and more refractory, calcined coke, may react and crack during recycle. The coke yield from the recycle experiments was calculated from the total mass of coke recovered after the hydroconversion reaction minus the mass of coke added to the reactor before the recycle experiment. If the recycled catalyst is very active and generation of new coke in the first recycle is the same as the coke generated with fresh catalyst precursor, the consumption of the recycled coke in the recycle experiment will result in a reduced coke yield. As the number of recycles increases, consumption of the recycled coke continues, but higher rates of coke formation due to the gradual deactivation of the catalyst increases the coke yield.

The H_2 uptake in hydroconversion is an important indicator of catalyst hydrogenation activity. Upgrading of heavy-oil and residue starts with a thermally driven C−C bond cleavage (when no catalyst with strong acidic sites is available).[24] Subsequently, H_2 transfer from the gas phase to the thermally produced free radicals and olefins stabilizes and hydrogenates the cracked compounds. The transfer of H_2, only a small portion of which is direct H_2 transfer to highly reactive free radicals, prevents polymerization and condensation reactions of large molecules and poly aromatic hydrocarbons (PAH)[24] yielding toluene insolubles. In the presence of excess free radical and olefinic compounds (which are generated during cracking and β-scission reactions), H_2 consumption is expected to be proportional to the extent of coke suppression achieved during hydroconversion. Figure 5 shows the changes in the H_2 uptake from different recycle experiments in which different

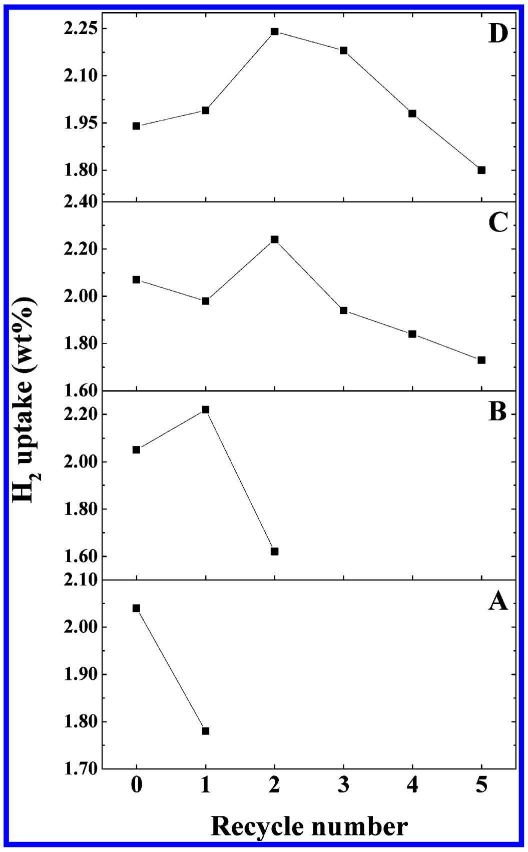

Figure 5. H$_2$ uptake versus the recycle number in recycle experiments starting with different Mo concentrations using Mo-micelle and Mo-octoate precursors: 100 ppm Mo using Mo-micelle (**A**), 300 ppm Mo using Mo-micelle (**B**), 600 ppm Mo using Mo-micelle (**C**), and 600 ppm Mo using Mo-octoate (**D**).

initial Mo concentrations and Mo precursors were used. In all cases, H$_2$ uptake showed a noticeable decrease with recycle number. With 100 ppm Mo using the Mo-micelle precursor initially, the decrease occurred in the first recycle. For experiments with 300 and 600 ppm Mo using Mo-micelle or Mo-octoate precursors initially, the decrease occurred on the second and fifth recycle, respectively. H$_2$ uptake using the recycled catalysts at Mo concentrations of 300 and 600 ppm showed a maximum. The maximum is possibly because in the first or second recycle the catalyst remains active, whereas cracking of the recycled coke produces significantly more molecules with unsaturated bonds and free radicals which are a potential source of H$_2$ consumption.

Figure 6 shows the correlation between the coke yield and H$_2$ uptake for all the recycle experiments done in the present study. Clearly an increase in H$_2$ uptake is correlated with a decrease in coke yield. Hydrogen uptakes higher than a certain value in the experiments of this study (~2.1 wt %, shown by the vertical line in the Figure 6) appear not to have very much effect on coke suppression (data points shown in the circle in Figure 6). Generally higher H$_2$ consumption is an indication of increased coke suppression provided there are sufficient cracked molecules in the reactor that need to be hydrogenated. However, if the cracking rate is not very high (such as at low temperature or with low carbon content of the feed oil) while the rate of hydrogenation is high due to excess catalyst in the reactor, then H$_2$ is used for hydrogenation that increases the H/C atom ratio of the liquid and solid products. Also, excessive

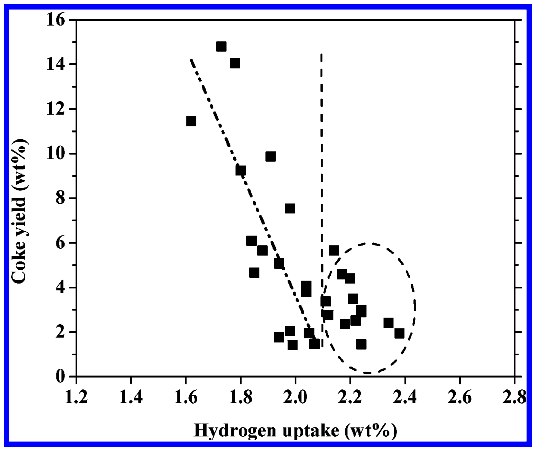

Figure 6. Coke yield versus H$_2$ uptake in the recycle experiments.

hydrogenation of the liquid in the reactor reduces asphaltene stability, which eventually causes more coke formation. Under these conditions, an increase in H$_2$ uptake has little effect on the extent of coke suppression.[10,22,25]

In the TIOR conversion calculation (eq 1), the generated coke is considered as part of the residue product of the reaction, based on its high boiling point (above 524 °C). TIOR conversions from the recycle experiments using Mo-micelle and Mo-octoate as catalyst precursors are shown in Figure 7.

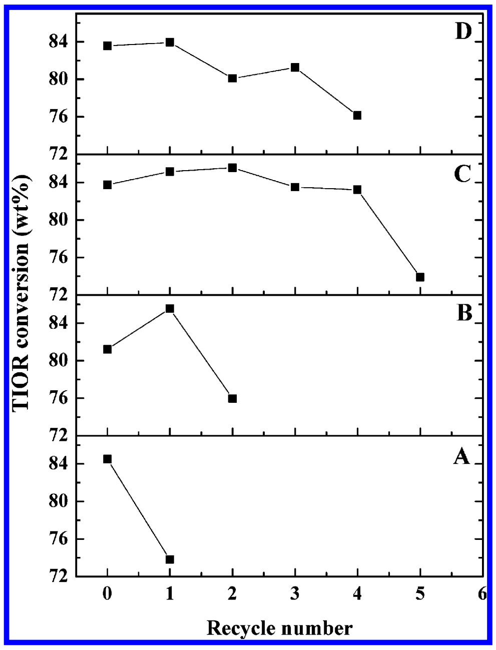

Figure 7. TIOR conversions in different recycle experiments starting with different Mo concentrations and precursors: (A) 100 ppm Mo using Mo-micelle precursor, (B) 300 ppm Mo using Mo-micelle precursor, (C) 600 ppm Mo using Mo-micelle precursor, and (D) 600 ppm Mo using Mo-octoate precursor.

Consistent with the coke yields presented in Figure 4, a significant decrease in TIOR conversion was observed at the point that the catalyst deactivated (the last recycle experiment for each Mo concentration). The TIOR conversions at different Mo concentrations using fresh precursor (first data points with recycle number zero) are all in the range of 81−85 wt %. The high level of TIOR conversion in the first experiment was maintained during recycling provided the catalyst was still active. With a Mo concentration of 100 ppm (Mo-micelle precursor), the TIOR conversion decreased to 74 wt % in the first recycle (coke yield from this experiment also increased as presented in Figure 4). The deactivation was observed after 2 and 4 recycle experiments with 300 ppm and 600 ppm Mo in the form of Mo-micelle, respectively. Recycle experiments using the Mo-micelle precursor had a slightly higher TIOR conversion compared to the recycle experiments using the Mo-octoate precursor. Comparing the TIOR conversion data presented in Figure 7 with the coke yield data shown in Figure 4, it can be concluded that catalyst deactivation decreased the TIOR conversion significantly. The decrease in TIOR conversion was because of the substantial amount of coke generated in the experiments in which the catalyst was deactivated.

Figure 8-A, Figure 8-B, Figure 8-C, and Figure 8-D present the naphtha (<204 °C boiling point), light gas oil (204 - 348 °C boiling point), heavy gas oil (348−524 °C boiling point), and residue (>524 °C) yields in the liquid products from the recycle experiments with Mo concentrations of 100, 300, and 600 ppm using the Mo-micelle precursor and 600 ppm using the Mo-octoate precursors. Starting with 100 ppm Mo using the Mo-micelle precursor (Figure 8-A), selectivity toward different hydrocarbon products did not change very much in the recycle experiment. This is possibly because the experiment in which 100 ppm Mo using Mo-micelle precursor was used had a high (~5 wt %) coke yield and catalyst concentration was not high enough to suppress coking. At higher initial Mo concentration (300 and 600 ppm), the coke yield of the first experiment (experiment in which fresh precursor was added to the reactor) was significantly lower than the coke yield of the experiment in which the catalyst was deactivated (last experiment of each recycle series). This significant change in the coke yield had a clearer and more visible impact on the selectivity change of the hydroconversion reaction toward different hydrocarbon cuts in the liquid products. With an increase in the number of recycles, the yield of fractions heavier than naphtha (light gas oil, heavy gas oil, and residue) decreased in the liquid products. This shift is especially noticeable in the last experiment of the recycle series with a Mo concentration of 600 ppm using both Mo-micelle (Figure 8-C) and Mo-octoate (Figure 8-D) precursors. The decrease is accompanied by a shift toward lighter products (the yield of naphtha increased) due to a high coke yield (Figure 4) and carbon rejection in the hydroconversion reactor when the catalyst is deactivated in the last recycle experiment. The results are in agreement with previous work where a less active catalyst precursor resulted in high coke yield and produced lighter liquid product than the experiment in which less coke was produced.[21] Similarly, Del Bianco et al.[20] investigated recycling of Mo-based dispersed catalysts in a slurry-phase batch reactor. Unlike the present study, they used very mild hydroconversion conditions (410 °C) and an initial Mo concentration of 3000 ppm. Furthermore, instead of recycling the solid coke-catalyst, they recycled the n-C_5 asphaltene-catalyst mixture but reported a similar trend with a decreased heavy gas oil and residue fraction of the liquid product with increased recycling.

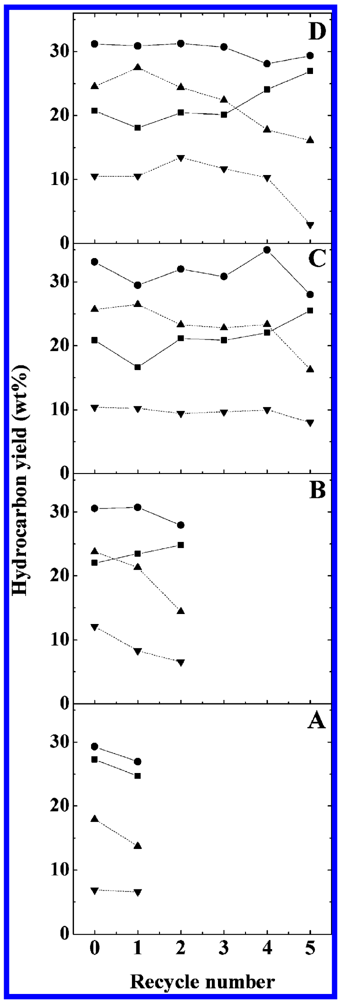

Figure 8. Selectivity change toward different hydrocarbon cuts in the recycle experiments starting with 100 ppm Mo using Mo-micelle precursor (A), 300 ppm Mo using Mo-micelle precursor (B), 600 ppm Mo using Mo-micelle precursor (C), and 600 ppm Mo using Mo-octoate precursor (D). (■) < 204 °C, (●) 204−348 °C, (▲) 348−524 °C, and (▼) > 524 °C.

Transformation of asphaltene molecules is known to be the main mechanism of coke (toluene insoluble hydrocarbons) formation during hydroconversion. The transformation occurs through the formation of a mesophase, an aromatic rich liquid phase, and liquid−liquid phase separation in the hydroconversion reactor.[1,24,26] It is also known that this transformation is irreversible and fast,[25] but it can be partially prevented if an active hydrogenation catalyst is present in the hydroconversion reactor to suppress the polymerization of the polyaromatic cores of the asphaltenes. Hydrogenation results in the production of hydrocarbons with fewer aromatic rings in their structure and prevents mesophase formation and liquid−liquid phase separation. Figure 9 shows the asphaltene conversion measured during catalyst recycle experiments. Similar to the coke yield from these experiments (Figure 4), when the catalyst deactivated (the last experiment in each recycle series), the asphaltene conversion decreased noticeably. The decrease is due to a low rate of H_2 transfer to the liquid for conversion of the asphaltene molecules into lighter liquid products. This mechanism is also supported by the high asphaltene conversion level from experiments in which fresh precursors were used (recycle number zero) when the initial Mo concentration increased from 100 ppm to 300 ppm and 600 ppm. The effect of catalyst concentration on the asphaltene conversion is much clearer when asphaltene conversion in a thermal experiment (in which no catalyst was used; the open

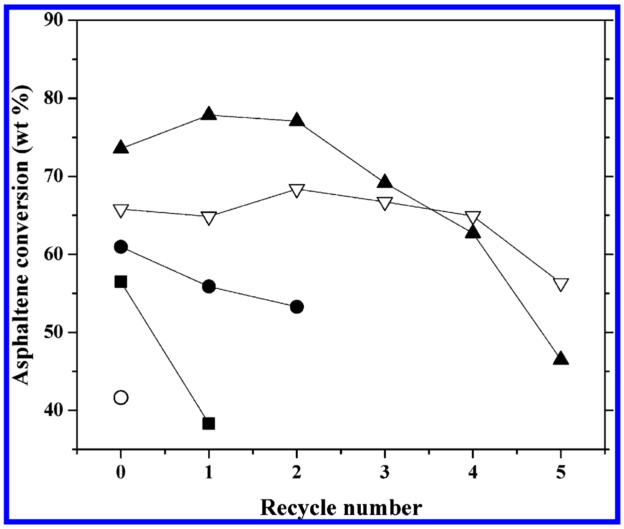

Figure 9. Asphaltene conversion in recycle experiments using different initial catalyst concentrations and precursors: 100 ppm Mo using Mo-micelle precursor (■), 300 ppm Mo using Mo-micelle precursor (●), 600 ppm Mo using Mo-micelle precursor (▲), 600 ppm Mo using Mo-octoate precursor (∇), and a thermal experiment (○).

circle data point in Figure 9) is compared with the asphaltene conversions of any of the catalytic experiments.

The asphaltene conversion data for 600 ppm Mo, using the Mo-micelle and Mo-octoate precursors, shown in Figure 9, suggest that the Mo-micelle precursor had a higher asphaltene conversion compared to the Mo-octoate precursor, and this trend is reversed when the number of recycles is greater than 3. However, taking into account the error associated with the asphaltene conversion data of these experiments (73.55 ± 9.39 wt % and 65.80 ± 7.05 wt % respectively for experiments using 600 ppm Mo in the form of fresh Mo-micelle and Mo-octoate precursors measured in 8 different repeat experiments) we conclude that there is minimal difference in the asphaltene conversion between the two precursors.

3.2. Significance of Solid Loading. In all of the recycle experiments reported herein, the coke-catalyst mixture recovered from the hydroconversion experiment was washed, dried, and ground to a powder and then used as the catalyst for the subsequent hydroconversion experiment. In this way, catalyst recycle was simulated and the activity of the recycled catalyst determined. The coke yield from the hydroconversion experiments with recycle catalyst was calculated based on the net amount of coke produced in the hydroconversion experiment. To ensure that all the Mo catalyst initially added to the reactor was used in the subsequent recycle experiments, all of the solid coke-catalyst recovered from the hydroconversion experiment was used in the next recycle hydroconversion experiment. Consequently, as the number of recycle experiments increased, the solids loading in the reactor increased. Figure 10 compares the amount of coke added to the reactor, to that generated and the total coke in the reactor after recycling for a series of recycle experiments, starting with 600 ppm Mo using the Mo-micelle precursor.

In all the recycle experiments, the maximum initial solids loading in the reactor was <7.5 wt %. To investigate any potential solids loading effect on the coke yield of the recycle experiments, several experiments with variable amounts of coke added to the reactor along with 600 ppm Mo using the Mo-octoate precursor were conducted. In this series of experiments the coke added to the reactor originated from a thermal hydroconversion experiment in which no catalyst was used. The standard washing, drying, and grinding procedure was performed on these coke samples prior to recycling. Figure 11 shows the coke yield versus solid coke loading in the reactor for these experiments. With an increase in solids loading up to 7.5 wt %, the coke yield decreased linearly. However, when the solids loading was increased further to 10 and 12.5 wt %, the coke yield from the hydroconversion experiment increased rapidly. The linear decrease in coke yield with increased solids loading is due to cracking of the added coke, a portion of which yielded liquid or gas. Assuming a constant generation of coke in the reactor for all of the experiments (600 ppm Mo was used in these experiments) and assuming that a portion of the added coke cracks under hydroconversion conditions, a linear decrease in coke yield with coke loading would be expected.

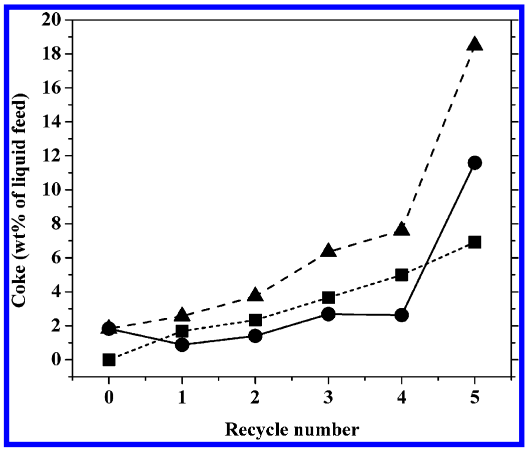

Figure 10. Coke added (■), generated (●), and total coke in the reactor (▲) in a series of recycle experiments starting with 600 ppm Mo added to the reactor using Mo-micelle precursor.

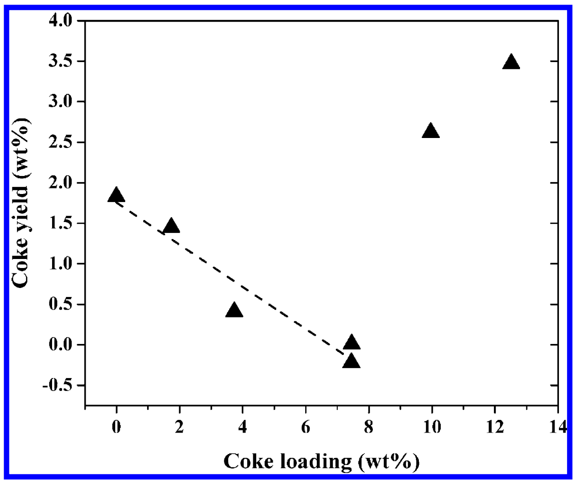

Figure 11. Coke yield versus solid loading in the reactor using thermal coke and 600 ppm Mo added to the reactor in the form of Mo-octoate. Straight line shows linear decrease of the coke yield with solid loading in the reactor at solid loading range of zero to 7.75 wt % of coke in the feed.

Another very important observation from this series of experiments was the net zero coke yield when 7.5 wt % of coke was added to the reactor with 600 ppm Mo using the Mo-octoate precursor (Figure 11). This observation, the validity of which was confirmed by repeated experiments (presented in Figure 11), suggests that the coke generated during hydroconversion equals the amount of solid coke that is converted to liquid or gas at a coke loading of 7.5 wt %. This observation can be explained based on the concept of the presence of two types of coke in the recovered solid, one of which has an amorphous structure and is soluble in quinolone and the other which is more calcined and graphitic in nature. The graphitic portion will have a high resistance to cracking when recycled, while the amorphous coke can be easily cracked. The amorphous portion of the recovered coke is most likely responsible for the decreased coke yield observed in the experiments when the solid loading in the reactor increased. Note that a coke yield of 1.9 wt % was obtained with 600 ppm Mo added to the reactor in the form of Mo-octoate (Figure 4). If one assumes a consistent amount of coke converted to gas or liquid by cracking of the added coke in the recycle experiment, an approximate calculation suggests that ∼25 wt % of the added coke (originally from a thermal experiment) was converted to liquid and gas. The results presented in Figure 11 are also consistent with the results presented for coke recycle starting with 600 ppm Mo added to the reactor in the form of both Mo-micelle and Mo-octoate precursors (Figure 4 and Figure 10). The coke yield (from the first recycle of the coke-catalyst mixture) was lower than the coke yield from the experiment in which fresh precursor was used. This observation can now be explained based on the findings from the solid loading hydroconversion experiments. Since in the first recycle experiment, recycle coke cracked and the coke generation was low due to a highly active and available catalyst, the net coke yield from the first recycle experiment was lower than the coke yield of the experiment in which no coke was added to the reactor and fresh precursor was used.

The proposed mechanism of coke consumption in the first recycle, although observed in other experiments (Figure 4), was confirmed by using pure graphite (graphite is much less susceptible to cracking compared to the coke generated by CLVR hydroconversion) instead of the thermal coke. In this experiment, pure graphite (7.5 wt %) along with 600 ppm of Mo using the Mo-octoate precursor were added to the residue oil, and the hydroconversion reaction was carried out under the same conditions as before. The graphite resulted in an increased coke yield to ∼4 wt % compared to the average coke yield of −0.1 wt % (average of two experiments) using the thermal coke. This is because the graphite does not crack to any great extent compared to the coke from CLVR hydroconversion.

The results presented in Figure 11 suggest that continuous recycle of catalyst in hydroconversion experiments with zero net coke yield is feasible. However, as discussed in Section 3.3, coke aging changes the chemical properties of the coke, making it more graphitic and hence less susceptible to cracking. This results in less and less cracking of the recycled coke as the number of recycles increases, and, consequently, an increase in the net coke yield would eventually occur.

When the solid loading was increased to 10 or 12.5 wt % in the reactor, the coke yield increased significantly to above 3 wt % (Figure 11). Although no supporting experimental data are available, it is believed that this increase was a consequence of highly disturbed hydrodynamics in the reactor due to the very high solids loading.

3.3. Catalyst Deactivation.

The data presented in Figure 4 showed that the initial Mo concentration in the reactor had an effect on the number of recycles before deactivation was observed and that this number increased as the initial catalyst concentration increased. With an increase in the initial catalyst concentration, more catalyst is available at the surface and pores of the recycled catalyst-coke mixture. Hence hydrogenation reactions and transfer of H to unsaturated bonds and free radicals produced during cracking occurs which eventually stabilizes the highly reactive chemical species in the reactor. Starting with a very low catalyst concentration (for example, 100 ppm Mo), the catalyst concentration in the recovered coke-catalyst mixture was very low, due to the low initial Mo concentration and a relatively high coke yield. Consequently, very few active sites would be available on the surface of the coke or within the pores with large enough diameter for macromolecules present in the feed to diffuse and react with H_2. When the initial catalyst concentration in the reactor increased, although part of the catalyst was totally covered with coke and therefore would not be available for hydrogenation reactions, there remains sufficient catalyst to participate in hydrogenation reactions and transfer H to free radicals and olefins and thereby suppress coke formation.

According to the above, there would be an optimum Mo concentration in the recovered coke-catalyst mixture. Mo concentrations above the optimum level would be in excess having the same performance in terms of coke suppression. On the other hand, when the Mo concentration in the coke-catalyst mixture drops below the optimum, the catalyst activity would drop due to a lack of active sites for hydrogenation. To confirm this mechanism, the coke yield from all recycle experiments versus the Mo concentration in the coke-catalyst mixture was plotted as shown in Figure 12. The Mo concentration of the coke was calculated by dividing the mass of Mo added to the reactor by the total mass of coke recovered at each recycling step. Since in each recycle experiment some coke was generated, the weight of coke continuously increased as the number of recycles increased (Figure 10). This yields a continuous decrease of Mo concentration in the coke-catalyst mixture as the number of recycles increases.

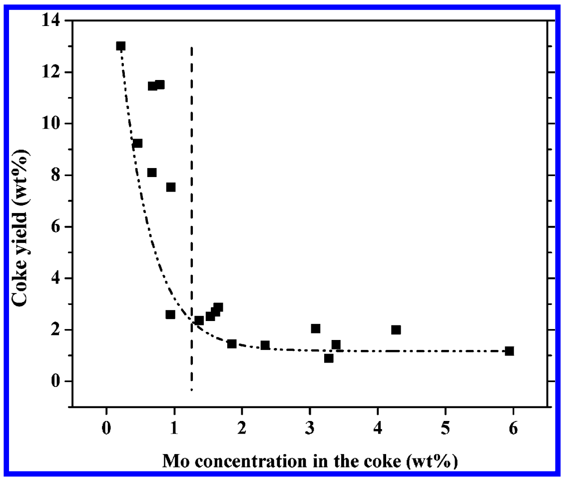

Figure 12. Coke yield versus Mo concentration in the coke-catalyst mixture used as catalyst in different recycle experiments using different initial concentrations of Mo added to the reactor in the form of Mo-micelle and Mo-octoate precursors. Vertical line shows the Mo concentration in the coke above which the coke yield will not change with Mo concentration in the recycled coke.

As shown in Figure 12, at low concentrations of Mo in the recycle coke, the coke yield decreased significantly with an increase in Mo concentration. When the recycled coke-catalyst mixture had a Mo concentration of ∼1.2 wt % and higher (shown by the vertical line in Figure 12), the coke yield remained low (1.5−2.5 wt %). Hence a Mo concentration of more than 1.2 wt % in the coke provides excess hydrogenation capability in the reactor. On the other hand, when the Mo concentration dropped below 1 wt %, the coke yield increased significantly, probably due to a lack of active sites for hydrogenation.

Based on the results presented in Figure 12, the question arises as to whether or not Mo concentration is the only variable affecting the recycled catalyst activity. If so, then increasing the Mo concentration in the feed would increase the number of recycles before catalyst deactivation would be observed. Hence, a series of recycle experiments using 1800 ppm Mo derived from Mo-octoate as the catalyst precursor were completed, and the results are shown in Figure 13. With 1800 ppm Mo, the catalyst was recycled 4 times without significant loss in activity in terms of coke suppression, but, surprisingly, the catalyst deactivated in the fifth recycle (coke yield ∼6 wt %). This was while some of the coke-catalyst mixture with lower Mo concentrations in the coke in comparison to the Mo concentration of coke recovered from the fifth recycle of 1800 ppm Mo using Mo-octoate precursor (with ∼2.5 wt % of Mo in the coke sample) had far lower coke yield (data points shown in the square in Figure 13). Although these coke samples had Mo in the coke, they were recovered from experiments in which the number of recycles was low (first, second, and/or third recycle). Hence, although the initial catalyst concentration affects the number of possible recycles, coke aging also appears to decrease the recycled catalyst-coke activity. Coke aging during several recycle experiments could change the morphology and chemical properties of the coke. These changes reduce the likelihood that the coke will crack and be consumed (transformed into liquid or gas phase) during recycle. Furthermore a change in morphology can potentially increase the resistance to diffusion of macromolecules into the coke pores to reach the catalyst hydrogenation sites and may also result in encapsulation of the MoS_2.

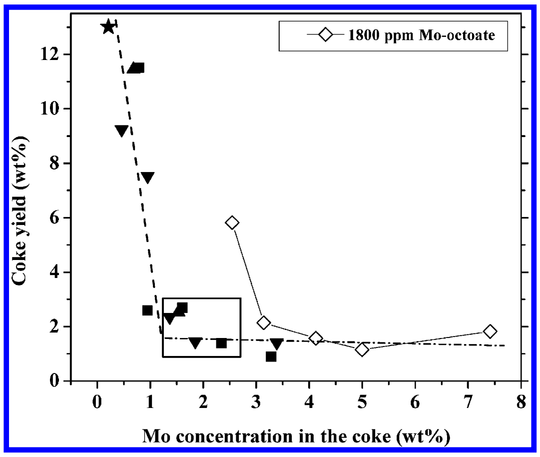

Figure 13. Coke yield versus Mo concentration in the coke-catalyst mixture used as catalyst in several series of recycle experiments using different initial concentrations of Mo added to the reactor in the form of Mo-micelle and Mo-octoate precursors.

Figure 14 shows the XRD diffractograms of coke samples recovered after each hydroconversion experiment and before recycle. There are several features in Figure 14 which give very useful insight toward identifying the deactivation mechanism of the recycled catalyst. Two peaks at 59° and 33° are assigned to the (110) and (100) crystal planes of MoS_2. As seen in Figure 14, the peak intensities decreased as the number of recycles increased because increased recycle increased the total amount of coke in the reactor (Figure 10), and this decreased the Mo concentration and consequently the MoS_2 concentration in the coke sample. A noticeable feature of the MoS_2 XRD peaks is that they are broad. This is an indication that during recycling there was no significant MoS_2 crystal size change or agglomeration of MoS_2. The absence of the (002) reflection of the MoS_2 at 14° is also an indication of highly dispersed MoS_2 with few layers.[27]

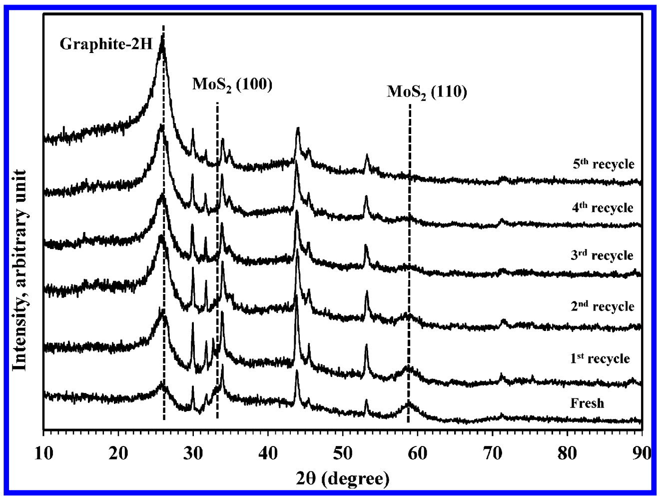

Figure 14. XRD diffractogram of coke samples recovered after different hydroconversion experiments in a series of recycle experiments using initial Mo concentration of 1800 ppm added to the reactor in the form of Mo-octoate precursor.

All the peaks that are not labeled in Figure 14 were assigned to Ni, V, and Fe sulfides. These peaks had almost the same intensity as the number of recycles increased since the metal sulfides originated from the residue oil and their concentration would be constant in the recovered coke from different experiments.

Another important observation from Figure 14 is the change in the shape of the peak at ∼26° assigned to graphite. This peak is an indication of the presence of graphitic carbon in the coke samples. As shown in Figure 14, the peak becomes larger and sharper as the number of recycles increased. This indicates that the recovered coke becomes more graphitic with increased recycling at high pressure and temperature. This transformation makes the coke less susceptible to cracking and dissociation under reaction conditions and, consequently, will result in more MoS_2 trapped in the highly stable matrices of the graphitic coke.

4. CONCLUSIONS

The coke-catalyst mixture recovered from hydroconversion experiments using CLVR was successfully recycled several times in subsequent hydroconversion experiments. Results from the recycle experiments showed that with a high initial Mo concentration in the feed (>600 ppm), the recovered coke-catalyst mixture could be recycled ≥4 times. The concentration of Mo, as well as the coke morphology, were identified as the main factors that determined the potential for catalyst recycle in the hydroconversion of CLVR. Experiments done to investigate the effect of solid loading in the reactor showed that for the range of operating conditions investigated, solid loading did not have a significant effect on the measured catalyst activity. However at high solid loading (>8 wt %), a significant decrease in efficiency of the MoS_2 catalyst for coke suppression was observed.

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Notes

The authors declare no competing financial interest.

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