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The use of coal liquefaction catalysts for coal/oil coprocessing and heavy oil upgrading

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Abstract

The catalytic hydrogenation of heavy oil and mixed coal-heavy oil (coprocessing) systems has been the focus of a recent study at the Federal Energy Technology Center (FETC). The intent of this effort was to extend the use of coal liquefaction technologies to heavy oil upgrading and coprocessing systems. Specifically, new dispersed molybdenum-based catalysts developed at FETC and a novel silica-doped hydrous titanium oxide (HTO : Si)-supported NiMo catalyst developed at Sandia National Laboratories (SNL) were tested in these systems. The results indicate the potential of coal liquefaction catalysts for use in coprocessing and heavy oil upgrading. High conversions of coal–oil mixtures were observed with dispersed catalyst loadings as low as 100 ppm Mo. Similar results were observed in heavy oil systems. Also, the novel NiMo/HTO : Si catalyst was at least as effective as commercially-available supported catalysts (e.g. Amocat 1C) for conversion of high boiling point material to distillable products and aromatics removal. Published by Elsevier Science B.V.

Keywords: Coal liquefaction; Heavy oil upgrading; Coal–oil coprocessing

1. Introduction

Comparison of coal liquefaction, heavy oil upgrading, and coal–oil coprocessing systems reveals many similarities in the catalytic requirements for these systems. In this study, we define coal–oil coprocessing as the co-reaction of coal and petroleum-derived heavy oils or resids. Both hydrogenation and hydrogenolysis reactions are important for converting these heavy feedstocks to distillate products. Since similar reaction environments are encountered during heavy oil upgrading, coal liquefaction and coal–oil coprocessing, catalysts in these systems suffer from similar types of inhibitors and poisons. It is, therefore, logical to expect similar trends in catalyst activity for these systems.

The development of novel catalysts (in either dispersed or supported forms) with improved activity, selectivity, and life is of significant interest for coal liquefaction, heavy oil upgrading, and coal–oil coprocessing systems. Examples of novel supported catalysts include hydrous metal oxide (HMO)-supported NiMo catalysts developed at Sandia National Laboratories (SNL), which can be fabricated in either a bulk powder form or a coated form on an engineered

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substrate (e.g., extrudate, monolith, etc.) [1–4]. This study will compare these novel HMO-based NiMo catalysts to conventional alumina-supported NiMo catalysts for a variety of different model compound, hydrotreating, coal liquefaction, and coal–oil coprocessing conditions. This work will also evaluate the efficiency of different Mo-based dispersed and supported catalysts for model compound hydrogenation/hydrodesulfurization, oil or resid upgrading, coal liquefaction, and coal–oil coprocessing. In addition to comparing the reactivity of the different dispersed and supported catalysts, this study will also examine the inter-relationship between reaction pressure and catalyst concentration in dispersed catalyst systems. This overall work builds on several recent studies at the Federal Energy Technology Center (FETC) where the catalytic hydrogenation of coal and model solvents using dispersed or supported catalysts at different pressures has been evaluated [5,6].

2. Experimental

2.1. Materials

The aromatic hydrocarbons pyrene and dibenzothiophene (DBT) (Aldrich Chemicals, Milwaukee, WI) and 1-methylnaphthalene (1-MN) (Fisher Scientific, Fair Lawn, NJ) were used as model compounds for batch microautoclave experiments. Nitrogen impurities were removed from the as-received pyrene in order to ensure uniform hydrogenation activity results, while the 1-MN and DBT were used in the as-received form. Briefly, the pyrene purification procedure involved first dissolving the pyrene in toluene, passing the pyrene/toluene solution over a column of acidic alumina, and recrystallizing the pyrene from the solution. The as-received pyrene contained approximately 300 ppm nitrogen, while the cleaned pyrene contained 10–60 ppm nitrogen.

For examination of realistic feeds, the reactants used included Hondo resid (450°C$^+$ boiling point material from a vacuum distillation tower) and fluid catalytic cracking (FCC) product decant oil. The FCC decant oil was a distillate product from an FCC unit and contained 36 wt.% 450°C$^+$ boiling point material. Illinois no. 6 and Blind Canyon bituminous coals, with properties described previously [7,8], were used for direct coal liquefaction and coal–oil coprocessing experiments. A brief summary of each of these respective reactants and feedstocks is shown in Table 1.

2.2. Unsupported catalysts

The unsupported (dispersed) catalysts investigated in this study included aqueous ammonium heptamolybdate (AHM). [Aldrich Chemicals, Milwaukee, WI]. Under coal liquefaction process conditions, the aqueous AHM (12 wt.% solution) phase generates a high surface area (261 m^2/g) dispersed MoS_2 catalyst [7]. Molyvan-A, a molybdenum oxysulfide dithiocarbamate complex, and Molyvan-L, a molybdenum oxysulfide organophosphorodithiolate complex, were also used as dispersed catalyst additives in this study. (R.T. Vanderbilt Co., Buena Park, CA).

2.3. Supported catalysts

Four different supported catalysts were evaluated in this study, although evaluation of several of these catalysts was limited to selected reactions and processes (batch, semibatch, and continuous). Three of

Table 1
Characteristics of the various feeds used in catalyst testing

Feed	wt.% 450°C$^+$	Proton aromaticity[a]	wt.% S	wt.% N	wt.% Ash
FCC decant oil	36.2	36.5%	1.46	0.26	<0.01
Hondo resid	86.1	14.1%	5.44	0.08	0.2
Blind Canyon coal[b]	–	–	0.4	1.5	5.6
Illinois no. 6 coal[c]	–	–	3.1	0.9	10.7

[a] Determined by ^1H NMR spectroscopy.

[b] Also contains 4.7 wt.% H_2O.

[c] Also contains 4.2 wt.% H_2O.

these catalysts were commercially available NiMo/γ-Al_2O_3 catalysts (AKZO-NOBEL AO-60, Criterion 324, and Amocat 1C), while the fourth supported catalyst was experimental in nature, being synthesized as part of this study. This experimental material was a novel silica-doped hydrous titanium oxide (HTO : Si)-supported NiMo catalyst, prepared in both bulk powder and coated (on an Amocat γ-Al_2O_3 extrudate) forms, based on HMO technology developed at SNL. A summary of the composition of the various supported catalysts and the reactions and process conditions at which they were evaluated is given in Table 2.

The synthesis of ion exchangeable HTO : Si supports and HTO : Si-supported NiMo catalysts in both bulk and coated forms has been discussed in detail elsewhere [1–4]. The synthesis procedure for the bulk NiMo/HTO : Si and the NiMo/HTO : Si-coated Amocat catalysts will be briefly described herein. Titanium isopropoxide and tetraethylorthosilicate were combined in a 5 : 1 molar ratio and then mixed with a 10 wt.% NaOH/methanol solution to give a soluble intermediate with a nominal Ti : Na molar ratio of 2. In the case of the bulk HTO : Si-supported NiMo catalysts, the soluble intermediate was hydrolyzed using an acetone–water solution, resulting in the precipitation of an amorphous silica-doped sodium titanate ion exchanger material. For coated catalyst preparation, the Amocat blank γ-Al_2O_3 extrudate was soaked overnight in a large excess of the soluble intermediate, followed by vacuum filtration to remove the excess coating solution. Both the bulk or coated forms of the silica-doped sodium titanate were then vacuum dried at room temperature, followed by Mo (target Mo loading was 10 wt.% in calcined form) addition via a two step acidification/anion exchange procedure using AHM.

After room temperature vacuum drying and Mo analysis via atomic absorption spectrophotometry, Ni was added (moles Ni/[moles Ni+moles Mo]=0.35) via incipient wetness impregnation using nickel (II) nitrate. After drying in air at 100°C for 2 h, the catalyst precursor was calcined in air at 500°C for 1 h to provide the oxide precursor for the final sulfided catalyst. The composition of the final oxide precursors for the NiMo/HTO : Si catalysts in both bulk and coated forms is shown in Table 2. These catalysts were compared to a commercial Amocat 1C catalyst in model compound reaction studies and/or continuous testing. Since the same support geometry, chemistry, and pore structure were used for the Amocat 1C and the NiMo/HTO : Si-coated Amocat catalysts (Amocat blank γ-Al_2O_3 extrudate support), this allowed a relatively fair comparison between these two materials.

2.4. Reactors and test conditions

Three types of reactors were used in this study: microautoclave, 1 L semibatch, and 1 L continuous. Since the reactor systems and the product work-up procedures used in each system have been described in detail previously [2,5,6], only brief explanations will be provided herein.

Batch microautoclave experiments were conducted both at FETC and SNL. The FETC microautoclave reactor consisted of a 42 ml tubular reaction vessel equipped with an internal thermocouple and pressure

Table 2
Summary of supported catalyst compositions and test matrix

Catalyst	wt.% Mo	wt.% Ni	wt.% other	Reactions studied
C-324	13.2	2.7	3.2 wt.% P	1-MN (batch[a])
AO-60	12.3	2.6	–	1-MN, coal, Hondo (all batch[a])
Amocat 1C	10.7	2.4	–	Pyrene and DBT HDS (batch[a]) and continuous[b]
NiMo/HTO : Si-coated Amocat	8.4[c]	2.8[c]	–	Pyrene and DBT HDS (batch[a]) and continuous[b]
Bulk NiMo/HTO : Si	9.6[c]	3.2[c]	–	Pyrene and DBT HDS (batch[a])

[a] Batch microautoclave reactors.
[b] 1 L continuous unit.
[c] Compositions determined by atomic absorption spectrophotometry.
Note: supported catalysts were not evaluated in semibatch reactor tests.

transducer, which was used to perform individual sets of 1-MN hydrogenation, Blind Canyon coal liquefaction, and Hondo resid upgrading experiments using either dispersed or supported catalysts. Following charging of the microautoclave reactor with specific reactants and catalysts (or catalyst precursors), the reactor was pressurized to 400–1200 psig H_2 at ambient temperature, and attached to a rocker arm (180 cycles/min). All reactions were then performed by plunging the pressurized reactor into a preheated fluidized sand bath, where it was held for 0.5 h at 425°C. Temperature and pressure data were recorded every 10 s. Following the reaction, the reactor was quenched to ambient temperature by a combination of water and air cooling. Typical times required for reactor heating and cooling were less than 5 min. Following cooling, the reactor was vented and the gas collected for analysis.

For all of the batch microautoclave reaction studies, dispersed catalyst precursors (Molyvan-A, Molyvan-L, or AHM) were charged with the respective feed materials, with the expectation that the final sulfided catalyst state was achieved at reaction conditions via in situ sulfidation. In contrast, the supported catalysts were presulfided and charged in fine powder form with the respective feed materials. For the 1-MN hydrogenation experiments, 6.6 g of 1-MN and enough catalyst to yield 1000 ppm of Mo (relative to 1-MN) were placed in the microautoclave reactor. A range of reaction pressures (400–1200 psig H_2) were used for these experiments. For the Blind Canyon coal liquefaction experiments, 3.3 g of Blind Canyon bituminous coal, 6.6 g of 1-MN solvent, and enough catalyst to yield 1000 ppm of Mo (relative to coal) were placed in the microautoclave reactor, which was charged to a pressure of 1000 psig H_2. For the Hondo resid upgrading experiments, 6.6 g of Hondo resid and enough catalyst to yield 1000 ppm of Mo (relative to Hondo resid) were placed in the microautoclave reactor, which was charged to a pressure of 1000 psig H_2.

Batch microautoclave experiments were also conducted at SNL using several of the various supported catalysts evaluated in this work (Amocat 1C, bulk NiMo/HTO : Si, and NiMo/HTO : Si-coated Amocat catalysts). Testing was performed with the bulk NiMo/HTO : Si catalyst so that the possible partitioning of the active NiMo phase between the two potential support materials (γ-Al_2O_3 and the HTO : Si) in the case of the NiMo/HTO : Si-coated Amocat catalyst and its subsequent effect on catalyst activity could be evaluated. These model compound experiments included both pyrene hydrogenation and DBT hydrodesulfurization (HDS) reactions. To activate these supported catalysts prior to testing, both calcination and sulfidation treatments were used. However, since the Amocat 1C catalyst was received in a calcined form, it was simply sulfided in extrudate form at 420°C for 2 h in 10% H_2S/H_2, ground and sieved to -200 mesh, and tested. The bulk NiMo/HTO : Si catalysts were pelletized, crushed and sieved to $-10/+20$ mesh, calcined at 500°C for 1 h, sulfided at 420°C for 2 h in 10% H_2S/H_2, ground and sieved to -200 mesh, and tested. The NiMo/HTO : Si-coated Amocat catalyst was calcined and sulfided as above but in extrudate form, then ground and sieved to -200 mesh, and tested. For pyrene hydrogenation experiments, pyrene (0.1 g), hexadecane (1 g), and sulfided catalyst (0.010 g) were loaded into a stainless steel microautoclave reactor (4.2 ml volume) that was cold pressurized to 500 psig H_2. For DBT HDS experiments, DBT (0.1 g), hexadecane (1 g), and sulfided catalyst (0.050 g) were loaded into a stainless steel microautoclave reactor (4.2 ml volume) that was cold pressurized to 1200 psig H_2. These microautoclave reactors were also equipped with a temperature and pressure measurement capability similar to that previously described. After attachment to a rocker arm (140 cycles/min), the reactors were plunged into a preheated sand bath at the desired reaction temperature (300°C for pyrene hydrogenation and 350°C for DBT HDS) and held for 10 min at temperature. Due to the small reactor size, the sample heat-up and cool-down times were extremely short (<2 min). Following reactor cooling to ambient temperature, the reactor was vented and the product liquid collected for analysis.

The 1 L semibatch autoclave reactor employed a flowing gas, batch slurry system (typically 400 g charge), with only the aqueous AHM dispersed catalyst precursor used for these studies. The feed used in these tests was FCC decant Oil with either a 0, 5, or 10 wt.% Illinois no. 6 coal addition, with the H_2 pressure being varied from 500 to 2500 psig. The test conditions were 30 min reaction time, 435°C reaction temperature (40 min nominal heat-up time), and

100 ppm Mo (relative to total feed) catalyst addition (added as a 12 wt.% aqueous AHM solution). Again, it was assumed that the feed compositions and reactions were sufficient to ensure conversion to the final dispersed MoS_2 catalyst. Following the reaction, the reactor was cooled to ambient temperature (30 min nominal cool-down time), the reactor was depressurized, and the products were removed.

The 1 L continuous reactor was a flowing gas/flowing slurry (typically 200–400 g/h of slurry) unit, and consisted of a once-through system with no provision for recycle. Two types of experiments were performed in this reactor system. First, various concentrations of aqueous AHM (0–500 ppm Mo relative to total feed) were evaluated as a dispersed catalyst for upgrading of either a 90 wt.% FCC decant oil+10 wt.% Illinois no. 6 coal mixture (H_2 pressure=500 psig) or a 90 wt.% Hondo resid+10 wt.% Illinois no. 6 coal mixture (H_2 pressure=1500 psig) at a reaction temperature of 425°C with a 30 min residence time. An in-line prereactor with a residence time of 0.33 h was used to activate the dispersed catalyst precursor (aqueous AHM) at 275°C in 3% H_2S in H_2. The overall continuous test unit configuration for dispersed catalyst testing is very similar to that described previously [6]. Second, two supported catalysts (Amocat 1C and NiMo/HTO : Si-coated Amocat catalysts) were compared in side-by-side tests in a similar 1 L continuous unit over a period of 10 days on stream. They were compared under oil-only conditions for both FCC decant oil and Hondo resid, and in simulated first stage direct coal liquefaction (FCC decant oil+coal) and coal-resid coprocessing (Hondo resid+coal), both of which used Illinois no. 6 coal. After loading 35 g of the calcined supported catalysts in extrudate form into an annular basket, an on-line sulfiding procedure was used for sulfiding the supported catalysts in the continuous reactor system. After an initial He purge at 177°C, a flow rate of 2.5 scfh 3% H_2S in H_2 and a nominal ramp rate of 2°C/min was used, with set points of 288°C for 1 h and 404°C for 1 h. The processing and feed conditions used for the various run periods for the continuous testing of the supported catalysts are summarized in Table 3. An annular catalyst basket configuration in conjunction with a central agitator (1000 rpm) was used for all of these tests, with a gas (3% H_2S in H_2) flow rate of 5 scfh, a total pressure of 2500 psig, and a slurry feed rate of 146 g/h (2.1 h residence time and weight hourly space velocity (WHSV)=1.25 g coal/h (g cat)).

2.5. *Product characterization – batch microautoclave experiments*

The degree of 1-MN hydrogenation, Blind Canyon coal liquefaction, and Hondo resid upgrading was monitored by the consumption of H_2 from the gas phase. At the completion of each run, product gases were collected and analyzed by gas chromatography (GC) according to a previously published method [9]. The gaseous H_2, C_1–C_4 hydrocarbons, and vaporized solvent were corrected for non-ideal behavior, and the amount of H_2 present was then calculated from the estimated amounts of H_2 in the liquid phase and the gaseous H_2 at each individual temperature–pressure measurement. Liquid–vapor equilibrium data for H_2 and solvent at the temperatures and pressures of the test were taken from the work of Sokolov and Polyakov [10] and Yao, et al. [11]. The values obtained were then used to calculate the amount of H_2 consumed as a function of time. The total H_2 consumption and gas yields were also calculated. Previous work has shown a good correlation between the degree of 1-MN hydrogenation monitored by various analytical methods, including gas analysis (hydrogen consumption),

Table 3
Summary of feed and process conditions used in continuous unit tests

Run period	Feed	Purpose	Temperature (°C)	Time (h)
1	FCC decant oil	Hydrotreating	400	100
2	FCC decant oil	Hydrotreating	425	32
3	70:30 wt.% FCC : coal	First stage liquefaction	425	32
4	Hondo	Hydrotreating	425	36
5	90 : 10 wt.% hondo : coal	First stage coprocessing	425	32

gas chromatography/mass spectrometry (GC/MS), low voltage, high resolution mass spectrometry (LVHRMS), and nuclear magnetic resonance (NMR) spectroscopy [5].

In addition to monitoring H_2 consumption via gas analysis (as described above), coal conversions (on a moisture/catalyst/ash free basis) were calculated using standard THF and heptane extraction techniques previously described [5,12].

For the pyrene hydrogenation and DBT HDS batch microautoclave experiments conducted at SNL [2], the liquid products were removed from the reactor by rinsing in toluene. Following the addition of an internal standard (2-methylnaphthalene), the product solutions were brought to a known volume and analyzed by GC. Pyrene hydrogenation and DBT HDS activity were expressed in terms of a first order rate constant for conversion of pyrene to 4,5-dihydropyrene [2,13] and the disappearance of sulfur containing species (DBT and tetrahydrodibenzothiophene), respectively.

2.6. *Product characterization – semibatch and continuous unit experiments*

Proton nuclear magnetic resonance (^1H NMR) spectra of selected microautoclave batch (Hondo resid upgrading) and continuous product liquid samples were recorded in deuterated dichloromethane solutions on a Varian VXR-300 NMR spectrometer equipped with a 5 mm broadband probe. Proton aromaticities were calculated as the ratio of the integrated area of aromatic protons (5.5–9.0 ppm chemical shift) to the total integrated area, according to an adaptation of the method of Brown and Ladner [14].

True boiling point distillation was used to fractionate the whole product liquids from the semibatch and continuous tests into 450°C$^+$ and −450°C cuts. Conversion of the high boiling point (450°C$^+$) material was then calculated relative to the boiling point distribution of the respective feed material.

The product liquid samples from the various run periods for the continuous tests were also analyzed for sulfur (S) and nitrogen (N) content relative to the respective feed material using an Antek 7000 S/N analyzer (Antek Industrial Instruments, Houston, TX). Activities are reported as percent S or N removed from the feed.

3. Results and discussion

3.1. *Microautoclave tests*

The effectiveness of several different supported and dispersed catalysts was evaluated in a series of microautoclave tests employing various combinations of 1-MN, coal, and Hondo resid. For all of these tests, the catalysts were fairly compared by adding the appropriate amount of dispersed or supported catalyst to yield a constant Mo loading. Note that for the different types of experiments, different Mo loading targets were used. The results from microautoclave runs with only 1-MN in the feed are presented in Fig. 1 for various supported NiMo catalysts (filled symbols) relative to several dispersed Mo catalysts (open symbols). The fact that at these reaction conditions the thermal conversion was negligible and the catalytic hydrogenation of 1-MN was not equilibrium-limited allows a fair comparison of catalyst activity [5]. Hydrogen consumption, which can be correlated with the degree of 1-MN hydrogenation to tetralin compounds [5], is generally higher for the supported NiMo catalysts than for the dispersed Mo catalysts. The hydrogen consumption values correspond to ~50%, as opposed to ~30% conversion of 1-MN to hydro-

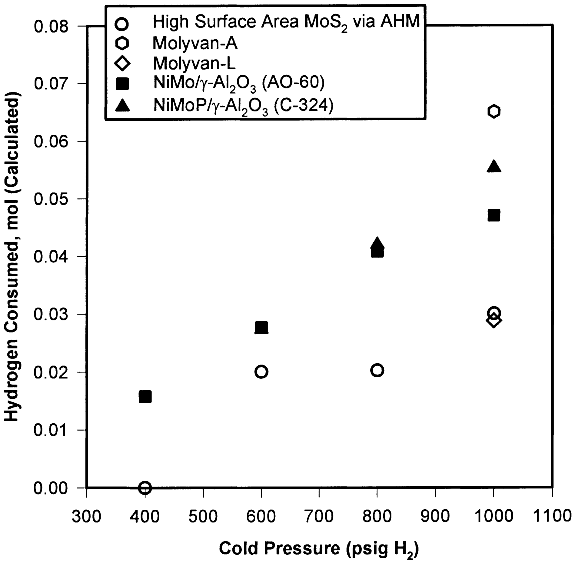

Fig. 1. Effect of catalyst type and H_2 pressure on batch 1-MN hydrogenation results.

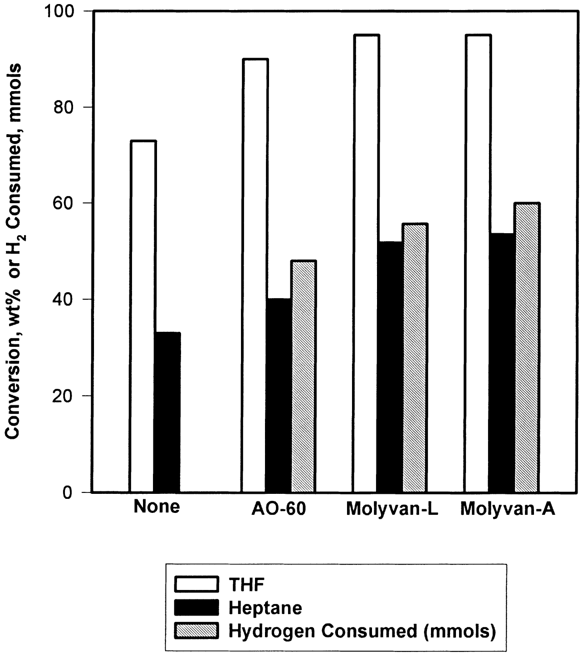

Fig. 2. Effect of catalyst type on coal conversion for Blind Canyon coal liquefaction tests (reaction conditions: batch mode, 425°C, 0.5 h, 1000 ppm Mo, and 1000 psig H_2).

genated products for the supported NiMo and dispersed Mo catalysts tested at 1000 psig H_2, respectively. The promoting effects of Ni in supported-MoS_2 catalysts for a wide range of hydrotreating reactions are well documented [15–17]. The lone exception to the above trend is the high activity observed for the dispersed Molyvan-A catalyst relative to the various supported NiMo catalysts.

The results from microautoclave runs in which Blind Canyon coal and 1-MN were employed in the feed are shown in Fig. 2. An interesting result was that the dispersed catalysts (Molyvan-A and Molyvan-L) exhibited superior coal conversion and H_2 consumption compared to the supported catalyst (AO-60). It has previously been observed that solvent (1-MN) hydrogenation is significantly decreased in the presence of coal, with the largest decreases in solvent hydrogenation capacity associated with supported NiMo catalysts (e.g., AO-60) [5]. Extending these efforts to pure Hondo resid upgrading (no coal or 1-MN added) showed that a similar trend in catalyst activity is observed, as illustrated in Fig. 3. Once again, the dispersed catalysts displayed the same or higher H_2 consumption than the supported catalyst. With no catalyst present, 39 mmol of H_2 were consumed; in the presence of Molyvan-A, 109 mmol of H_2 were consumed, and 60 mmol of H_2 were consumed with the supported catalyst (AO-60). The other unsupported catalyst, Molyvan-L, showed a level of hydrogen consumed only slightly higher than the AO-60 catalyst. In this case, the striking difference in catalyst activity results between the Molyvan-A and Molyvan-L catalysts is similar to the trend observed in Fig. 1 for the 1-MN hydrogenation results.

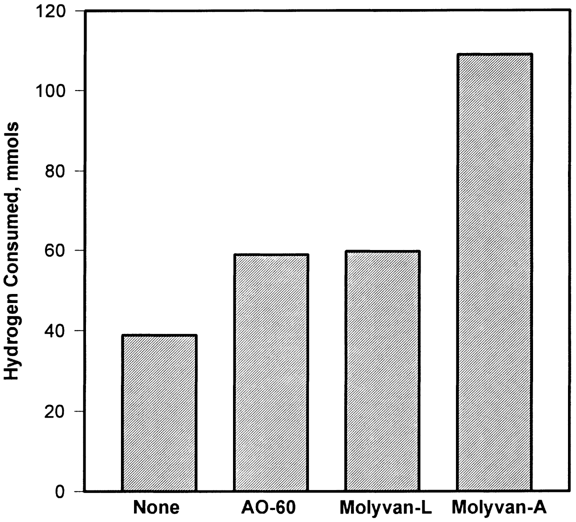

Fig. 3. Effect of catalyst type on Hondo resid upgrading (reaction conditions: batch mode, 425°C, 0.5 h, 1000 ppm Mo, and 1000 psig H_2).

One possible explanation for the improvement of activity of the dispersed catalysts (relative to the supported catalysts) in systems with coal or Hondo present in the feed may be the absence of diffusional limitations typically observed in supported catalysts that restrict the diffusion of the large coal or Hondo resid molecules. When the dispersed catalysts are employed, the active sites may be more easily accessible to these large asphaltene molecules. In the case of the 1-MN hydrogenation model reaction, the relatively small 1-MN molecules have no difficulty in accessing the active sites on either the dispersed or supported catalysts. The generally higher activity of the supported catalysts for this reaction is, therefore, indicative of a more active supported sulfided NiMo phase than in the case of a dispersed MoS_2 phase.

However, the combination of diffusional limitations and the presence of poisons or inhibitors in realistic coal or heavy oil feeds severely limits the activity and life of supported catalysts in these applications. In spite of their generally lower activity in model compound tests, it may be advantageous to employ dispersed catalysts for use in the hydroprocessing of heavy feeds due to their increased active site accessibility relative to supported catalysts. Further work is necessary to understand the significant differences in activity observed for the Molyvan-A and Molyvan-L catalysts in the various test reactions. These differences could be due to the fact that the final dispersed MoS_2 catalysts produced by in situ sulfidation could have been significantly affected by the different feed compositions and reaction conditions used in these respective tests.

3.2. 1 L semibatch and continuous tests

The 1 L semibatch tests were performed using only the aqueous AHM dispersed catalyst. For these tests, improvements in the distillate yield (conversion to −450°C boiling point material) were observed with increasing H_2 pressure as expected. In addition, catalyst activity was more pronounced at higher pressures. With 10% coal (see Table 4) at 500 psig, no improvement in conversion is observed when 100 ppm dispersed catalyst was added, but at 2500 psig, a significantly higher conversion of 450°C^+ material occurred when catalyst was present.

Table 4
Effect of pressure on FCC decant oil hydrotreating and coal-oil coprocessing (FCC decant oil and illinois no. 6 coal) in 1 L semibatch tests with unsupported catalysts (reaction conditions: 435°C, 0.5 h, 100 ppm Mo (added as aqueous AHM))

wt.% coal concentration	H_2 pressure (psig)	% 450°C^+ conversion
0	1500	0
0	2500	29
5	500	0
5	1500	6
5	2500	19
10	500	11 (12)[a]
10	1500	27
10	2500	48 (18)[a]

[a] Data for same run conditions with no catalyst addition shown in parentheses.

Table 5
Effect of catalyst concentration at reduced pressures using aqueous AHM in 1 L continuous tests (reaction conditions: 425°C, 30 min residence time, FCC decant oil or Hondo resid+10% illinois no. 6 coal in feed)

Feed	H_2 pressure (psig)	Mo concentration (ppm)	% 450°C^+ conversion
FCC decant oil	500	0	0
FCC decant oil	500	100	12
FCC decant oil	500	500	18
Hondo resid	1500	100	47
Hondo resid	1500	500	61

Increasing the concentration of the dispersed catalyst was also found to improve conversion of 450°C^+ material in the 1 L continuous reactor system, as shown in Table 5. When FCC decant oil was employed as the feed at 500 psig H_2, the conversion to distillable products increased from 0 to 12 to 18% as the catalyst concentration was increased from 0 to 100 to 500 ppm Mo. Similarly, when pure Hondo resid was used in the feed at 1500 psig, conversion increased from 47 to 61% when catalyst concentration was increased from 100 to 500 ppm Mo.

The results from the semibatch and continuous unit experiments with the dispersed catalysts demonstrate that one can compensate for reduced pressure in heavy oil upgrading and coal–oil coprocessing reactions by employing higher catalyst concentrations. As more catalyst is added, the available H_2 is more effectively utilized. Reducing the pressure requirements of a commercial upgrading or coprocessing reactor could significantly lower construction and operating costs.

3.3. Comparison of supported catalysts – model compound test results

Testing of the NiMo/HTO : Si-coated Amocat catalyst in continuous operations was justified by promising results obtained relative to conventional catalysts (e.g., Amocat 1C) for model compound reactions such as pyrene hydrogenation and DBT HDS. A summary of the model compound test results is shown in Table 6.

The results shown in Table 6 demonstrate that both bulk and coated NiMo/HTO : Si catalysts are more active for pyrene hydrogenation than conventional catalysts, such as Amocat 1C, on both a catalyst weight basis and an active metals basis. The fact that

Table 6
Model compound test results for the Amocat 1C, bulk NiMo/HTO : Si, and NiMo/HTO : Si-coated Amocat catalysts

Catalyst[a]	Model reaction	k ((g catalyst)$^{-1}$ min^{-1})	k ((g TAM)$^{-1}$ min^{-1})[b]
Amocat 1C	Pyrene hydrogenation[c]	9.3	71.0
Amocat 1C	DBT HDS[d]	0.023	0.17
NiMo/HTO : Si-coated Amocat	Pyrene hydrogenation[c]	10.8	100.9
NiMo/HTO : Si-coated Amocat	DBT HDS[d]	0.019	0.19
Bulk NiMo/HTO : Si	Pyrene hydrogenation[c]	12.2	95.4
Bulk NiMo/HTO : Si	DBT HDS[d]	0.025	0.20

[a] For catalyst compositions, see Table 2.
[b] TAM denotes total active metals present in the catalyst (Mo and Ni).
[c] Pyrene hydrogenation test conditions: 300°C, 500 psig H_2, 10 min, batch mode, pseudo-first order reversible kinetics.
[d] DBT HDS test conditions: 350°C, 1200 psig H_2, 10 min, batch mode, pseudo-first order irreversible kinetics.

the pyrene hydrogenation activity of these HTO : Si-based catalysts on a catalyst weight basis is superior to that of the commercial catalysts even though they contain a lower amount of active metals perhaps indicates an important role of the HTO : Si support or the catalyst preparation procedure (anion exchange) [18]. Different results were observed in the case of the DBT HDS tests. In this case, the bulk NiMo/HTO : Si catalyst offered only a marginal improvement in activity relative to the Amocat 1C on either a catalyst weight basis or an active metals basis. The NiMo/HTO : Si-coated Amocat catalyst, although more active for DBT HDS than the Amocat 1C catalyst on an active metals basis, was less active on a catalyst weight basis. These results indicate the lack of a significant beneficial effect of the HTO : Si support for DBT HDS relative to pyrene hydrogenation [18]. The overall model compound results, therefore, predicted a potential for improved hydrogenation activity but lower hydrodesulfurization activity for the NiMo/HTO : Si-coated Amocat catalyst relative to the Amocat 1C catalyst.

3.4. *Comparison of supported catalysts – continuous unit results*

The Amocat 1C and NiMo/HTO : Si-coated Amocat catalysts were compared in side-by-side tests in the continuous unit over a period of 10 days on stream. Results for solvent (FCC decant oil or Hondo resid) only hydrotreating for the two catalysts will be compared first in terms of heteroatom (S and N) removal. These results will be followed by a comparison of catalyst performance in the conversion of high boiling point (450°C$^+$) material and aromatics over all run periods in the continuous test (see Table 3). These FCC decant oil or Hondo resid hydrotreating results are of course not directly comparable to those obtained for the dispersed AHM catalyst (see Table 5) since the continuous unit operational parameters were significantly different for dispersed and supported catalyst testing.

3.4.1. *Sulfur conversion*

Fig. 4 shows the relative sulfur conversions resulting from hydrotreatment of the FCC decant oil during

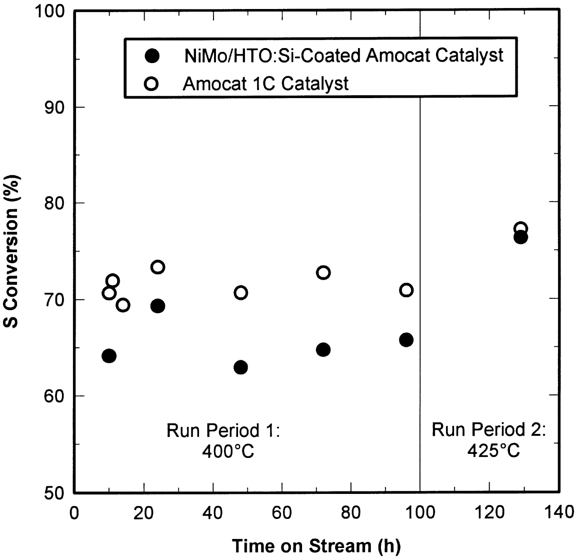

Fig. 4. Continuous hydrotreating of FCC decant oil-S conversion for different supported catalysts.

run periods 1 and 2 for the two different catalysts. For the initial run period, FCC decant oil hydrotreating at 400°C, catalyst line-out was demonstrated for both the Amocat 1C and NiMo/HTO : Si-coated Amocat catalysts, with the Amocat 1C catalyst showing a consistently higher S removal activity. This result is likely explained by the higher Mo content of the Amocat 1C catalyst, and is consistent with model compound (DBT HDS) test results with similar catalysts (see Table 6). However, at the higher temperature condition used for run period 2, the two catalysts performed very similarly in terms of S conversion. The performance of the NiMo/HTO : Si-coated Amocat catalyst was also inferior to that of the Amocat 1C catalyst in terms of S conversion (68.7% as opposed to 78.2% S removal) during the Hondo resid hydrotreating phase (run period 4) of the continuous test (data not shown in Fig. 4).

3.4.2. Nitrogen conversion

The results for nitrogen removal from hydrotreatment of the FCC decant oil during run periods 1 and 2 are shown in Fig. 5, in the same format as that presented in Fig. 4. In contrast to the results obtained for sulfur conversion, the NiMo/HTO : Si-coated Amocat catalyst was found to outperform the Amocat 1C catalyst on a consistent basis in terms of N removal during hydrotreatment at 400°C. However, an even more significant advantage in N conversion was observed during run period 2 (FCC decant oil hydrotreating at 425°C). The combined nitrogen and sulfur removal results suggest that the NiMo/HTO : Si-coated Amocat catalyst performs slightly better in terms of overall heteroatom removal from the FCC decant oil feed at higher temperature (425°C) than the Amocat 1C catalyst. However, this apparent advantage in performance at high temperature did not carry over to the Hondo resid hydrotreating phase (run period 4) of the continuous test. The NiMo/HTO : Si-coated Amocat catalyst was inferior to the Amocat 1C catalyst in terms of N conversion (4.5% as opposed to 11.7% N removal) during the hydrotreatment of Hondo resid (data not shown in Fig. 5).

3.4.3. Conversion of 450°C$^+$ material

The results for conversion of the 450°C$^+$ fraction in the feed to −450°C material in the product liquid are summarized in Fig. 6, and show several interesting trends. The Amocat 1C catalyst demonstrated superior performance relative to the NiMo/HTO : Si-coated Amocat catalyst in terms of conversion of the high

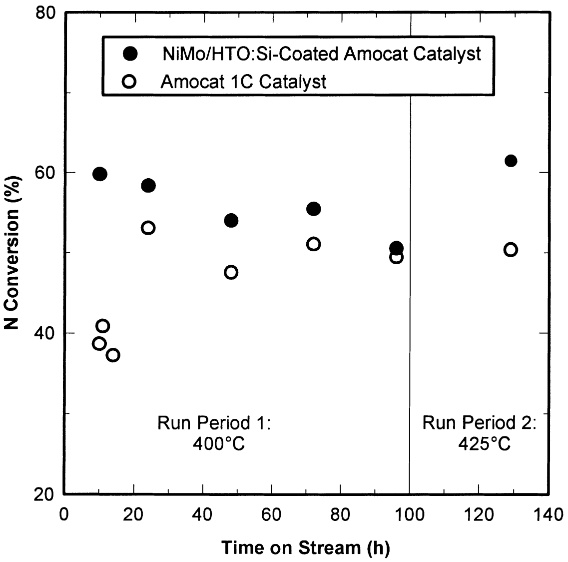

Fig. 5. Continuous hydrotreating of FCC decant oil-N conversion for different supported catalysts.

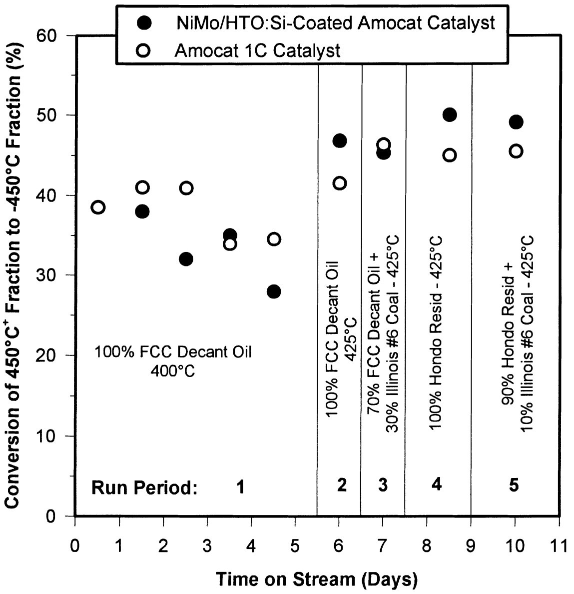

Fig. 6. Effect of catalyst type on conversion of high boiling point (450°C$^+$) material during continuous testing.

boiling point fraction during FCC decant oil hydrotreating at 400°C (run period 1). However, similar to the S and N removal results, the NiMo/HTO : Si-coated Amocat catalyst showed significant improvement for FCC decant oil hydrotreating at higher temperature (425°C), outperforming the Amocat 1C catalyst. In fact, for all run periods performed at high temperature (425°C) except for run period 3, the NiMo/HTO : Si-coated Amocat catalyst outperformed the Amocat 1C catalyst in terms of conversion of high boiling point material. The trends observed for the distillation-based conversion results were consistent with conversions based on heptane solubility of the whole product liquids relative to the respective feed material.

Run period 3 was an attempt to replicate the first stage coal liquefaction conditions (coal, temperature, pressure, and catalyst) used in a previous test of a similar NiMo/HTO : Si-coated Amocat catalyst in continuous two stage (catalytic/catalytic) direct coal liquefaction pilot plant at Amoco [19], although different solvents were used in these cases (FCC decant oil vs. Wilsonville run 257 solvent). In this previous work, the NiMo/HTO : Si-coated Amocat catalyst produced a higher yield of lower boiling point distillate material relative to Amocat 1C. However, in this study, the results for run period 3 showed similar performance for both catalysts. This new result may, therefore, indicate that the promising results observed previously at Amoco are explained by a higher second stage or hydrotreating activity of the NiMo/HTO : Si-coated Amocat catalyst relative to the Amocat 1C catalyst, although the role of the different solvents used in these two tests cannot be completely discounted. Another important result is that the NiMo/HTO : Si-coated Amocat catalyst outperformed the Amocat 1C catalyst in both run periods involving the Hondo resid. Although less efficient in terms of heteroatom removal in the case of the Hondo resid hydrotreating, this catalyst was more efficient in terms of converting high boiling point material. We have no current explanation for the significant difference in catalyst performance for these two processes.

3.4.4. Changes in proton aromaticity

The changes in proton aromaticity of the whole product liquids produced by each catalyst within and between various run periods are summarized in Fig. 7.

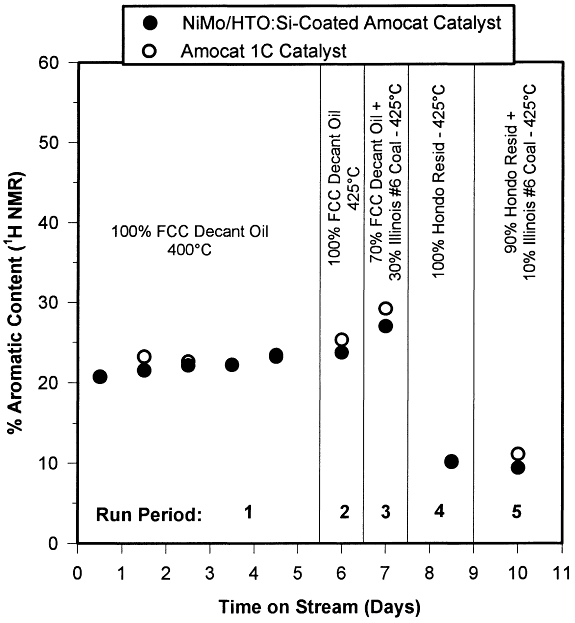

Fig. 7. Effect of catalyst type on aromatics content of product liquids from continuous testing.

For the initial run period, FCC decant oil hydrotreating at 400°C, both catalysts performed very similar (especially with longer time on stream), reducing the proton aromaticity from 36.5 (see Table 1) to 24%. Both catalysts also performed similar in reducing the proton aromaticity of the pure Hondo resid (14.1%, see Table 1) at 425°C in run period 4. However, at more demanding feed (addition of coal to either the FCC decant oil or the Hondo resid) and processing (higher temperature) conditions, the NiMo/HTO : Si-coated Amocat catalyst slightly outperformed the Amocat 1C catalyst. Although the differences in proton aromaticity were small, they appear to be consistent for these different feed/process conditions. Estimated error for the proton aromaticity values was ±1%. Also consistent with these results is the fact that higher model compound hydrogenation activities have been observed for TiO_2- or HTO : Si-supported NiMo catalysts (either bulk or coated forms) than alumina-supported NiMo catalysts (see Table 6) [4,18].

For the batch microautoclave tests with Hondo resid and dispersed catalysts, no change in proton aromaticity was observed without catalyst addition. The aromatic proton content of the product liquid samples obtained from continuous Hondo resid upgrading (run period 4) for these two supported catalysts (~10%) was very similar to that observed for the Molyvan-A dispersed catalyst (11%) during batch microautoclave testing with Hondo resid. Although this is an interesting result, the low aromatics content of the Hondo resid feed (14.1%), the different operational parameters of the continuous and batch units as well as possible thermodynamic limitations make a comparison of the hydrogenation ability of these different dispersed and supported catalysts difficult.

Several general conclusions can be made regarding the model compound and continuous testing results for the two supported catalysts. The NiMo/HTO : Si-coated Amocat catalyst showed superior hydrogenation performance for both a model reaction (pyrene hydrogenation) and the removal of aromatics in the high temperature hydrotreating of more realistic feeds such as FCC decant oil, coal+FCC decant oil, and Hondo resid+coal. For S removal, the NiMo/HTO : Si-coated Amocat catalyst was generally inferior to the Amocat 1C catalyst for both a model reaction (DBT HDS) and hydrotreating of FCC decant oil or Hondo resid. The performance of the NiMo/HTO : Si-coated Amocat catalyst for N removal from the FCC decant oil feed was superior to the Amocat 1C catalyst, especially at higher temperature (425°C), although the Amocat 1C material was a better catalyst for N removal from the Hondo resid feed. For conversion of high boiling point ($450°C^+$) material, the NiMo/HTO : Si-coated Amocat catalyst was superior to the Amocat 1C for nearly all of the different feeds hydrotreated at high temperature (425°C).

The overall results for the NiMo/HTO : Si-coated Amocat catalyst compare favorably with or are superior to those obtained for the Amocat 1C catalyst. This is somewhat surprising given the lower active metal (Ni and Mo) loadings present in the NiMo/HTO : Si-coated Amocat catalyst relative to Amocat 1C. These results are consistent with previous work [2–4,18], suggesting higher dispersions of the active MoS_2 phase, more efficient use of the active metals, and/or beneficial interactions between the MoS_2 phase and the HTO : Si support that lead to increased catalyst activity. The results for the NiMo/HTO : Si-coated Amocat catalyst are especially promising, given the significant cost savings for raw materials and processing relative to bulk NiMo/HTO : Si catalysts and the increased potential for synergistic effects between the HTO : Si and γ-Al_2O_3 supports.

4. Conclusions

The objective of this study was to apply coal liquefaction technology to the problem of heavy oil upgrading and coal–oil coprocessing, particularly with respect to supported and dispersed liquefaction catalysts. This objective was achieved and a number of conclusions can be drawn from this work.

The results from a series of microautoclave experiments demonstrated that whereas supported catalysts were superior to dispersed catalysts for the hydrogenation of 1-MN, dispersed catalysts were superior for the conversion of coal and petroleum resids. One possible reason for this is that the active sites in the dispersed catalysts are more accessible to the larger coal and petroleum resid molecules than the active sites in the supported catalysts.

The results from a series of semibatch experiments with dispersed catalyst demonstrated, not surprisingly, that conversion of coal and petroleum resids increases with increasing H_2 pressure. At low pressures, no benefit to coal and resid conversion was observed when a dispersed catalyst was used, but at higher pressures, the presence of catalyst imparted a substantial increase in conversion.

The results from a series of continuous unit experiments demonstrated that the loss of conversion of coal and petroleum resids caused by reduction of H_2 pressure can be compensated for by an increase in catalyst concentration. Higher catalyst concentrations permit the more effective utilization of available hydrogen in the system by the coal and resids.

Finally, supported catalysts were also studied in a series of continuous unit experiments. A novel NiMo/HTO : Si-coated Amocat catalyst prepared at Sandia National Laboratories, was shown to perform as well as or better than a commercial Amocat 1C catalyst for the conversion of coal and petroleum resids to distillable material and for the hydrogenation of aromatics. Under certain conditions (higher temperature) with certain feeds (FCC decant oil) the NiMo/HTO : Si-coated Amocat catalyst was also more effective than Amocat 1C at heteroatom (S and N) removal.

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