

THE USE OF COAL LIQUEFACTION CATALYSTS FOR COAL/OIL COPROCESSING AND HEAVY OIL UPGRADING

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INTRODUCTION

The catalytic hydrogenation of coal and model solvents using dispersed or supported catalysts at different pressures has been the focus of several recent studies at PETC. The effectiveness of these catalysts has been studied in coal liquefaction and coal-oil coprocessing. Coal-oil coprocessing involves the co-reaction of coal and petroleum-derived oil or resid. The results of these studies have indicated that both dispersed and supported catalysts are effective in these systems at elevated H₂ pressures (~2,500 psig). Attempts to reduce pressure indicated that a combination of catalyst concentration and solvent quality could be used to compensate for reductions in H₂ pressure [1].

Comparison of the coal and coprocessing systems reveals many similarities in the catalytic requirements for both systems. Both hydrogenation and hydrogenolysis activities are required and the reactive environments are similar. Also, the use of catalysts in the two systems shares problems with similar types of inhibitors and poisons. The logical extension of this is that it may be reasonable to expect similar trends in catalyst activity for both systems. In fact, many of the catalysts selected for coal liquefaction were selected based on their effectiveness in petroleum systems.

This study investigates the use of supported and dispersed coal liquefaction catalysts in coal-oil coprocessing and petroleum-only systems. The focus of the study was delineating the effects of coal concentration, pressure, and catalyst type.

EXPERIMENTAL

Materials - The reactants used include Hondo resid (vacuum tower bottoms) and fluid catalytic cracking (FCC) decant oil. The Hondo resid was an 850°F⁺ boiling material from a vacuum distillation tower. The FCC decant oil was a distillate product from an FCC unit and contained 36% 850°F⁺ boiling material. Illinois No. 6 and Blind Canyon bituminous coals were used. Several unsupported catalysts were investigated including aqueous ammonium heptamolybdate (AHM), preformed MoS₂ (surface area of 261 m²/g generated from aqueous AHM), Moly-Van-A, Moly-Van-L, sulfated iron oxide and FeOOH impregnated on coal [2]. Three different supported catalysts were evaluated, two commercial NiMo/γ-Al₂O₃ catalysts (Akzo AO-60 and Amocat 1C) and a novel HTO:Si-supported NiMo catalyst in coated form (on an Amocat γ-Al₂O₃ extrudate) based on hydrous metal oxide technology developed at Sandia National Laboratories.

The synthesis of ion exchangeable silica-doped hydrous titanium oxide (HTO:Si) supports and HTO:Si-supported NiMo catalysts in both bulk and coated forms has been discussed

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in detail elsewhere [3,4]. The synthesis procedure for the NiMo/HTO:Si-coated Amocat catalysts will be briefly described. Titanium isopropoxide and tetraethylorthosilicate were combined in a 5:1 molar ratio and then mixed with an ~10wt.% NaOH/methanol solution to give a soluble intermediate with a nominal Ti:Na molar ratio of 2. The Amocat blank γ - Al_2O_3 extrudate was soaked overnight in a large excess of the soluble intermediate, with the excess coating solution removed by vacuum filtration. Following vacuum drying at room temperature, Mo (target Mo loading was 10 wt.% in calcined form) was added to the HTO:Si-coated γ - Al_2O_3 extrudate via a two step acidification/anion exchange procedure using AHM. After room temperature vacuum drying and Mo analysis via atomic absorption spectrophotometry (AAS), 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 2h, the catalyst precursor was calcined in air at 500°C for 1h to provide the oxide precursor for on-line sulfiding. The final oxide precursor was found to contain 7.4 wt.% Mo and 2.4 wt.% Ni on a calcined basis. This catalyst was compared to a commercial Amocat 1C catalyst, containing 10.7 wt.% Mo and 2.4 wt.% Ni. Since the same support geometry, chemistry, and pore structure were used in both cases (Amocat blank γ - Al_2O_3 extrudate support), this allowed a relatively fair comparison between the NiMo/HTO:Si-coated catalyst and the Amocat 1C catalyst.

Reactors - Three types of reactors were used in this study; microautoclave, 1-L semi-batch, and 1-L continuous. The microautoclave reactor is a 43 mL tubular reactor. The 1-L semi-batch reactor employs a flowing gas, batch slurry system (typically 400 g charge). The 1-L continuous reactor is a flowing gas/flowing slurry (typically 200-400 g/h of slurry). These reactor systems and the product work-up procedures used in these systems have been described previously [2]. An on-line sulfiding procedure was used for sulfiding the supported catalysts for 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 1h and 404°C for 1h. The various feed and process details for the different continuous run periods are described in Figure 1.

^1H NMR Spectroscopy - ^1H nuclear magnetic resonance (NMR) spectra of the 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) to the total integrated area according to an adaptation of the method of Brown and Ladner [5].

RESULTS

Microautoclave Tests - Several different unsupported catalysts and supported AO-60 catalyst were evaluated in a series of microautoclave tests. These catalysts included molybdenum and iron based catalysts. The results of these tests are presented in Table 1. An interesting result was that the unsupported Mo-based catalysts exhibited superior levels of coal conversion activity compared to the supported catalyst. From the catalysts compared in the coal liquefaction microautoclave tests, one unsupported catalyst and AO-60 were compared for Hondo resid upgrading (along with a no catalyst case). The conditions for these tests were similar to the conditions used for the coal liquefaction evaluations. With no catalyst present, 39 mmols of H_2 were consumed with Hondo resid. In the presence of Moly-Van-A, 109 mmols of H_2 were consumed compared to 60 mmols

for AO-60. Also, a comparison of the proton aromaticity of the products from the Moly-Van-A and no-catalyst tests indicate that the proton aromaticity was reduced from 14 to 11% in the presence of catalyst compared to no reduction in proton aromaticity with no catalyst. The proton aromaticity obtained with Moly-Van-A compared favorably to the proton aromaticity observed with supported catalysts (10-12%) in continuous tests at nominally similar conditions (see Table 3).

1-L Semi-Batch and Continuous Tests - The effect of pressure was investigated in a series of 1-L semi-batch tests. The results of these tests are shown in Table 2. As expected, improvements in conversion were observed with increasing pressure. Additional experiments (not shown) indicate that as pressure increases, catalyst activity is observed at lower catalyst concentrations. In fact, the difference between no catalyst and catalyst was insignificant at 500 psig for catalyst concentrations of 100 ppm, but as pressure increased, a significant difference was observed between the no catalyst and catalyst case.

Similar results were observed with increased pressures in the 1-L continuous reactor system as were observed in the semi-batch. Namely, the conversions increased with increasing pressure. These results are shown in Table 3. The unsupported catalyst appeared to outperform the supported catalysts with Hondo resid. However, with FCC decant oil only, lower levels of proton aromaticity were observed with supported catalysts than were observed with unsupported catalysts.

Comparison of Amocat 1C and NiMo/HTO:Si-Coated Amocat Catalysts - These two catalysts were compared in side-by-side tests in the continuous unit over a period of 10 days onstream. They were compared under oil-only conditions for Hondo resid and FCC decant oil, and in coal-oil coprocessing with Illinois No. 6. Heretofore the whole product liquids produced during the various run periods from the Amocat 1C and NiMo/HTO:Si-coated Amocat catalysts have been evaluated for aromaticity by ^1H NMR [5]. In the future, we are planning to evaluate differences between the performance of the two catalysts in terms of HDS, HDN, H:C ratio, and boiling point distribution of the different product liquids, in addition to coal/resid conversion. Figure 1 summarizes the changes in proton aromaticity of the whole product liquids produced by each catalyst within and between various run periods. Note that the proton aromaticity of both the FCC decant oil and the Hondo resid are included for reference (see zero time data points). 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, and both catalysts performed very similarly (especially with longer time on stream), reducing the proton aromaticity to 24%. Both catalysts also performed similarly in reducing the proton aromaticity of the pure Hondo resid 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 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. Similar results were obtained in earlier two stage (catalytic/catalytic) direct coal liquefaction tests with Illinois #6 coal, where a NiMo/HTO:Si-coated catalyst produced a higher yield of lower boiling point distillate material relative to Amocat 1C [6]. Also

consistent with these results is the fact that higher model compound hydrogenation activities have been observed for TiO₂- or HTO:Si-supported NiMo catalysts (in either bulk or coated forms) than alumina-supported NiMo catalysts [3,7]. The data for the last run period (90 wt.% Hondo resid + 10 wt.% Illinois No. 6 coal) with the NiMo/HTO:Si-coated catalyst is especially interesting since the proton aromaticity is lower for this product liquid than for pure Hondo resid (run period 4). These improved results with the NiMo/HTO:Si-coated catalyst in the case of the feeds containing Illinois No. 6 coal indicate an important result with potential for coal/resid coprocessing applications.

CONCLUSIONS

Unsupported catalysts exhibited activities at least as high as supported catalysts for coal/oil coprocessing and oil upgrading applications. Further, it appears that similar trends with respect to pressure and catalyst formulations were observed for oil upgrading and coprocessing. These results support the potential for coal liquefaction catalysts for coprocessing and oil upgrading.

The NiMo/HTO:Si-coated catalyst compared favorably to Amocat 1C for oil upgrading and coal-oil coprocessing. In fact, at more demanding feed conditions the NiMo/HTO:Si-coated catalyst seemed to outperform the Amocat 1C. These observations were based on ¹H NMR analyses of whole liquid products from the tests. Further analyses of the products from these tests are pending.

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Figure 1. Comparison of Catalyst Performance: Amocat 1C vs. NiMo/HTO:Si-Coated Amocat

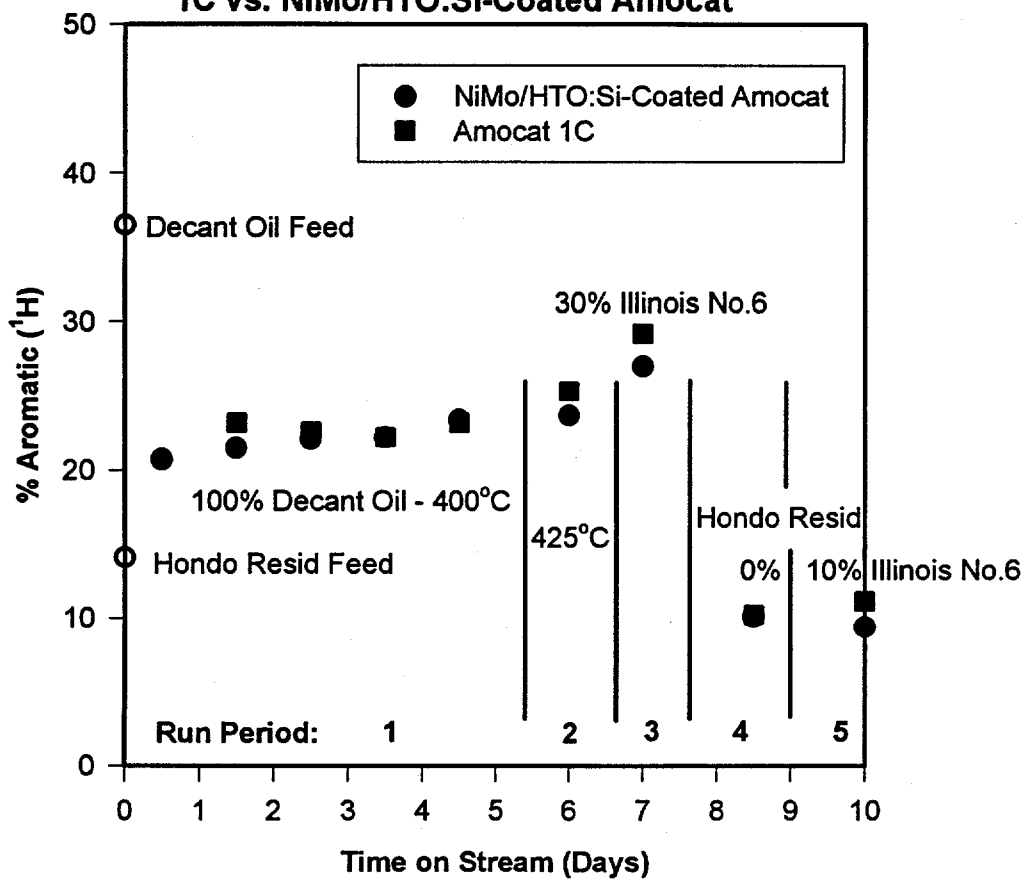


Table 1. Comparison of Catalysts in Microautoclave Tests, 425°C, 0.5 h, 1000 psig (cold), 2:1 1-methylnaphthalene to Blind Canyon or 100% Hondo resid and 1000 ppm Mo or Fe

Catalyst	THF Conversion (%)	Heptane Conversion (%)	H ₂ Consumption (mmols)
MoS ₂ (powder) ¹	93	49	50
Moly-Van-A ¹	95	50	56
Moly-Van-L ¹	95	51	60
Impregnated FeOOH ¹	87	41	45
Sulfated Iron Oxide ¹	87	39	44
AO-60 ¹	90	40	48
None ²	n/a	n/a	39
Moly-Van-A ²	n/a	n/a	109
AO-60 ²	n/a	n/a	60

¹ 2:1 1-methylnaphthalene to Blind Canyon

² Hondo Resid

Table 2. Effect of Pressure on Coal/Oil Coprocessing and Oil Upgrading in 1-L Semi-Batch Tests with Unsupported Catalysts, 435°C, 0.5 h, 100 ppm Mo (added as aqueous AHM), FCC Decant Oil and Illinois No. 6 Coal (when used)

Oil Type	Coal Concentration (wt.%)	Pressure (psig)	850°F ⁺ Conversion (%)
FCC	0	1500	0
FCC	0	2500	29
FCC	5	500	0
FCC	5	1500	6
FCC	5	2500	19
FCC	10	500	11/12 ¹
FCC	10	1500	27
FCC	10	2500	48/18 ¹

¹ No catalyst data presented for comparison.

Table 3. Effect of Pressure, Coal Concentration, or Catalyst Type in 1-L Continuous Tests Using Supported or Unsupported Catalysts, 425°C, 0.5 h (residence time), FCC Decant Oil or Hondo Resid, and Illinois No. 6 Coal (when used)

Oil Type	Catalyst	Coal Concentration (wt.%)	Pressure (psig)	Product Proton Aromaticity/ 850°F ⁺ Conversion (if available)
FCC	AHM	0	1500	40
FCC	AHM	0	2000	39/17
FCC	AHM	0	2500	39/24
FCC	AHM	5	2500	28/39
FCC	AHM	10	2500	29/24
FCC	AHM	30	2500	35/25
FCC	NiMo/HTO:Si-coated Amocat	0	2500	24
FCC	NiMo/HTO:Si-coated Amocat	30	2500	27
Hondo	AHM	0	2000	9
Hondo	AHM	0	2500	8
Hondo	AHM	5	2000	13
Hondo	AHM	5	2500	8
Hondo	AHM	30	2000	11
Hondo	AHM	30	2500	10
Hondo	AO-60	0	2500	12
Hondo	Amocat 1C	0	2500	10
Hondo	NiMo/HTO:Si-coated Amocat	0	2500	11
Hondo	AO-60	5	2500	10
Hondo	Amocat 1C	5	2500	11
Hondo	NiMo/HTO:Si-coated Amocat	5	2500	8