EVALUATION OF Mo CATALYST PRECURSORS FOR HYDROTREATING COAL DERIVED LIQUIDS

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Keywords: Coal liquefaction, molybdenum catalyst, activation

INTRODUCTION

Numerous studies have examined the use of dispersed catalysts for promoting the dissolution of coal and upgrading high-boiling and residual liquids.[1] Catalysts have been added in various forms, including oil soluble organometallics and carbonyls,[2,3,4] with industrial interest for application to a spectrum of residual feedstocks,[5] and demonstration in coal liquefaction at the pilot plant scale.[6] Dispersed catalysts offer certain advantages over supported catalysts for hydroprocessing such feedstocks. Because of their large molecular size, many of the feed constituents cannot access the internal pore structure of supported catalysts, and hence upgrading must proceed by an indirect process, probably involving H-transfer via lower molecular weight species. Another major deficiency of supported catalysts is their susceptibility to deactivation by reactions which cause the deposition of carbon and metals.

Dispersed catalysts can overcome the first of these obstacles and may be less susceptible to deactivation. At the same time, there are also difficulties in the utilization of dispersed catalysts. These include: attaining and maintaining adequate dispersion; and converting the precursor to the active phase. Moreover, the effective catalyst metals, such as Mo, are expensive and their application is only economically viable if they can be used at very low concentrations or efficiently recycled. In direct coal liquefaction, the presence of mineral matter and undissolved coal in the products of coal solubilization mean that a solids separation step is necessary and, inevitably, catalyst will be removed with the reject stream. However, in upgrading solids-free coal liquids and petroleum residua, there exists the potential to recycle nearly all of the catalyst with the unconverted residue. Hence, the catalyst inventory in the reactor can be maintained at a high concentration with only a low level of fresh catalyst addition. The success of such a process depends upon the ability to maintain catalyst activity during repeated recycles, and to avoid the substantial generation of solids or refractory liquid products that have to be removed in a drag stream, together with the catalyst.

With this concept in view, we have initiated a study of the effectiveness of dispersed Mo catalysts for hydroprocessing solids-free residual coal liquids that were obtained from the former Wilsonville Advanced Coal Liquefaction Research and Development Facility, while operating with Black Thunder subbituminous coal. In this work, comparisons are made between three different Mo-containing catalysts: a ground commercial NiMo supported catalyst, and two organometallics which, being oil-soluble, are expected to facilitate dispersion in the reactor feed. A series of experiments was made to examine the influence of presulfiding conditions on catalyst activity which was assessed by the extent of resid conversion and hydrogen consumption under a standard set of reaction conditions.

EXPERIMENTAL

Materials- The following reagents were used: high purity tetrahydrofuran (THF), Burdick & Jackson Brand from Baxter S/P; ultra high purity grade H_2 and a 7.93% H_2S/H_2 gas mixture, Air Products and Chemicals, Inc. A deashed resid (DAR) derived from Black Thunder mine coal processed at Wilsonville in Run 258A[7] was provided by CONSOL, Inc. This material was used as the hydrotreating feedstock. It contained 0.13% ash, and 76% 566°C+ (1050°F+) resid (af). Three hydrotreating catalyst precursors were evaluated: Molyvan L containing 8.1% Mo, RT Vanderbilt Co.; Mo naphthenate containing 6.1% Mo, ICN Biomedicals, Inc.; and AKZO AO-60, an alumina supported Ni/Mo catalyst, Hydrocarbon Technologies, Inc. In-house determinations of the Mo and Ni content of the AO-60 were 11.3 and 2.7 wt% respectively (dried sample), compared to 12.3 and 2.6% reported by the manufacturer. Because of the small quantities of catalyst used, an equal weight of 99% anhydrous hexadecane (Aldrich) was used to dilute the organometallic precursors to improve the precision of addition to the reactor.

Liquefaction Experiments- Catalytic hydrotreating experiments were conducted in microautoclaves; the methods and microautoclaves used have been described in detail elsewhere.[8] In a typical experiment, 3 grams of DAR and the appropriate amount of catalyst precursor (to give either 1000 ppmw Mo or Mo+Ni, total DAR feed basis) are added to the reactor. The reactor is sealed, purged with hydrogen, pressurized to 10.1 MPa total pressure (2% hydrogen sulfide, balance hydrogen) and leak tested. The reactor is heated by immersing it into a hot, fluidized sandbath. Real-time measurements of both the reaction temperature and pressure are recorded with a computer. For some experiments, a pretreating period was used where the reactor was heated at a lower temperature before going to the final reaction temperature. At the end of the reaction period, the cooled reactor is vented into a 10-liter gas collection cylinder at atmospheric pressure. The gas mixture is analyzed with a Carle Series AGC 400 Refinery Gas Chromatograph (Application 397-B). Vacuum distillations are performed on the remaining products using a modified ASTM D-1160 procedure to give a cutpoint of 566 °C. Material balances are based upon a forced catalyst balance with any loss and error being assigned to the yield of distillate product.

In order to more fully characterize the reaction products, a high-temperature simulated distillation method has been developed. The SIMDIS apparatus (a Hewlett-Packard model 6890 gas chromatograph) and application software were developed by AC Analytical Controls, Inc. The method is designed to analyze hydrocarbons up to a boiling point of 750°C.

To select one of the catalysts for detailed parametric studies, a series of hydrotreating experiments was conducted at 440°C for 60 minutes. Each precursor was evaluated in a single run, in which it was used directly or was presulfided *in situ* at 375 °C for 30 minutes. A sample of the AO-60 was also sulfided *ex situ*. The presulfided AO-60, which had been delivered in its oxidic form, was prepared[8] *ex situ* by grinding the 1/16" extruded pellets, sizing to -100 mesh, air drying, and sulfiding in the microautoclave in the H_2S/H_2 gas mixture at 400°C. The dry, black powder was stored under dry N_2. Analysis of the sulfided material showed 1.9 mol S_{added} /mol of Mo, compared with the stoichiometric (including Ni) requirement of 2.3 mol S_{added}/ mol Mo. Sulfur addition rates reported in the literature typically range from 1.6 to 2.0 S/Mo, depending on pre- and post-treatment conditions.

From the test results, Molyvan L was selected for further activation studies. A parametric study was conducted in which a mixture of DAR and 1000 ppmw Mo as Molyvan L was presulfided for selected times and temperatures, followed by a hydrotreating reaction. Using 2% H_2S in hydrogen to sulfide the Mo, the influences of time (0, 5 and 30 minutes), temperature (300, 340, 375 and 440°C) and hydrotreat time (30 and 60 minutes) were examined. Estimates were also made of the activity of the dispersed catalyst after reaction, to assess its utility for recycle. Two different approaches were used to simulate recycled catalyst and resid combinations. In the first, an experiment was conducted using the DAR in reactions at 440°C for 60 minutes as the single-pass condition. Molyvan L, sufficient to give 1000 ppmw Mo, was added to only 10% of the DAR, and this mixture was reacted to simulate the first pass at an equivalent Mo concentration of 10,000 ppmw. The gases were collected, the reactor opened and the remaining 90% of the DAR was added and the second pass effected (labeled Method RM1). In a parallel study, the DAR was again reacted with Molyvan L at the 1000 ppmw Mo level in a first pass, only this time feeding 100% of the feedstock. The products were distilled to 566°C, and the residual fraction recovered. Fresh DAR and heavy distillate were then added to restore the reactor feed to 3 g for a second pass with the same 566°C+ composition as in the first pass (Method RM2). Because of losses in recovering the resid, the concentration of Mo in the second pass was 200 ppmw lower than the first pass, but the effect of conversion changes due to this lower concentration is less than can be estimated from the available data.

RESULTS AND DISCUSSION

As shown in Table 1, each of the Mo precursors improved resid conversion over that found (19%) without added catalyst, increasing conversion to 34-38%, either with or without the presulfiding procedure used. The one exception was the *in situ* presulfided AO-60 catalyst, which increased resid conversion to an average of 45%. Both organometallic precursors exhibited reasonably good activity, with resid conversion somewhat less than that found for the presulfided AO-60 catalyst, and with little apparent effect from the presulfiding step.

Based on a comparison of resid conversion and hydrogen consumption data, Molyvan L was selected for the parametric study, to evaluate the benefits of presulfiding in some detail. These results are presented in Figure 1 (30 and 60 minute conversion reactions). At lower presulfiding temperatures, it appears there is little effect of this pretreatment on catalyst activity, and it may even be adverse. The data, therefore, suggest that Molyvan L attains an active form within the first few minutes of the reaction under hydrotreating conditions. This finding is consistent with other research[9] using a dispersed Mo precursor at short reaction times. Based on these results, it was determined that presulfiding over the times and temperatures tested was not necessary to produce an active catalyst, and this step was omitted in subsequent work.

A plot of reaction time vs log (wt percent resid remaining) for three pairs of duplicate experiments is shown in Figure 2, where it is seen that the early portion of the reaction may be fairly well represented by first order kinetics with respect to the disappearance of resid. The reaction clearly slows in the 60 to 90 min period when presumably only the more refractory resid remains. The progressive reduction in rate is of interest from a presulfiding viewpoint since there is no suggestion that a more active Mo catalyst form was generated, either in combination with carbon, sulfur or other species, as the reaction steadily progressed, but lends further support to the suggestion that the active species was present fairly soon into the experiment.

Table 2 reports the results of the simulated recycle experiments with Molyvan L. Using data from an earlier experiment with 10,000 ppmw Mo loading to calculate the total resid feed to the second pass, a second pass resid conversion of 33.7% was calculated for Method RM1. This is the same as the single pass resid conversion (33.6%) determined earlier using all fresh feedstock (ie, no recycle). However, lower conversion (24.7% vs 33.7% in RM1) was found in Method RM2, that could have reflected reduced reactivity of the recycled residual fraction, which in this experiment comprises most of the second pass reactor feed and contains the recycled catalyst. Figure 3 is a plot of the total reactor pressure for the two passes of RM2, and their nearly equal pressure histories suggest that the Mo is similarly active in both passes. A pressure profile for the same reaction without added Mo is shown for reference, where the immediate pressure reduction evident in the previous experiment is absent.

To determine the effect of fresh catalyst addition to the recycled catalyst in between the first and second pass (similar to catalyst make-up in an operating plant) 100 ppmw fresh Mo was introduced between the two reaction steps (Method RM2'). This increased the total Mo concentration from 800 to 893 ppmw. Other procedures remained the same as with the previously described experiment. Resid conversion in the second pass for this experiment was almost restored to that obtained in a single pass. Previous work has shown that resid conversion is relatively insensitive to fresh Mo concentrations above about 500 ppmw. Consequently, it may also be supposed that the freshly added catalyst is more active than the recycled Mo. The apparent reduction in recycle activity may be due to the conditions used for catalyst and resid recovery. Thus there appears to be two reasons for the reduced second pass conversion in the RM2 experiment, namely reduced resid reactivity and reduced catalyst activity. Note that for each of the recycle experiments, hydrogen consumption is reduced below that of the single pass experiment, as is hydrocarbon gas make. Relatedly, SEM/EDS studies of the hydrotreating residues at high catalyst loading showed the Mo species were well distributed across the recovered residual fractions.

CONCLUSIONS

Similar hydrotreating activity was found for the two dispersed organometallic catalyst precursors studied, and presulfiding over the times and temperatures tested was not required for high catalytic activity. Simulated recycle experiments have shown that conversion is reduced, the causes of which are attributed to reduced activity of the recycled resid and lower catalytic activity of the recycled Mo. Both of these factors could be affected by the process steps required to recover the catalyst and resid, and are the subject of continuing investigation.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Department of Energy (no. DE-AC22-95PC95050), funded through a CONSOL, Inc subcontract, and the Commonwealth of Kentucky. We also thank Hydrocarbon Technologies, Inc. for providing the AKZO AO-60; the RT Vanderbilt Co. for supplying a sample of Molyvan L; Dr. Scott Carter of the CAER for his development work with the AC SIMDIS equipment; and Rebecca Cash of the CAER for her work in the laboratory.

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Table 1. Results of hydrotreating tests of catalyst precursors in deashed resid.

Catalyst precursor	Feed	none	Molyvan L	Molyvan L	Mo naphthenate	Mo naphthenate	AO-60	AO-60	AO-60 sulfided ex situ
Pretreat time @ °C	-	none	none	30 @ 375	none	30 @ 375	none	30 @ 375	none
Reaction time @ °C	-	60 @ 440	60 @ 440	60 @ 440	60 @ 440	60 @ 440	60 @ 440	60 @ 440	60 @ 440
Ni, ppmw feed	-	-	-	-	-	-	173	171	175
Mo, ppmw feed	-	-	1013	988	997	1010	817	803	825
Products, wt% maf feed									
Hydrocarbon gas, C_1-C_6+	-	6.2	6.0	6.2	9.4	6.0	9.4	7.2	5.7
$CO + CO_2$	-	0.3	0.1	0.4	0.9	0.2	1.1	0.3	0.1
566°C-	24.3	32.3	43.6	45.2	42.2	45.7	41.0	51.0	47.5
566°C+	75.7	61.2	50.3	48.2	47.5	48.1	48.5	41.5	46.7
Total	100	100	100	100	100	100	100	100	100
Resid conversion, wt % 566°C+	-	19.2	33.6	36.3	37.3	36.5	36.0	45.2	38.4
H_2 consumed, mg/ g maf feed	-	7	22	18	17	16	19	18	16

Note: 10.1MPa total pressure (cold, 2% H_2S in H_2 mixture) used for all hydrotreating tests.

Table 2. Evaluation of Molyvan L activity in simulated recycle.

Method	RM1	RM2	RM2'
Rxn temp., First pass Second pass	440 440	440 440	440 440
Run time, First pass Second pass	60 60	60 60	60 60
Fresh Mo, ppm feed	-	-	100
Recycle Mo, ppm feed	1006	800	793
Products, wt% maf feed			
Hydrocarbon gas, C_1-C_6+	4.4	4.6	5.0
$CO + CO_2$	0.1	0.1	0.1
566 °C-	47.0	38.3	43.9
566 °C+	48.5	57.0	51.0
Total	100	100	100
Second-pass resid conversion, wt % 566 °C+	33.7	24.7	32.7
H_2 consumed, mg/ g maf feed	15	12	14

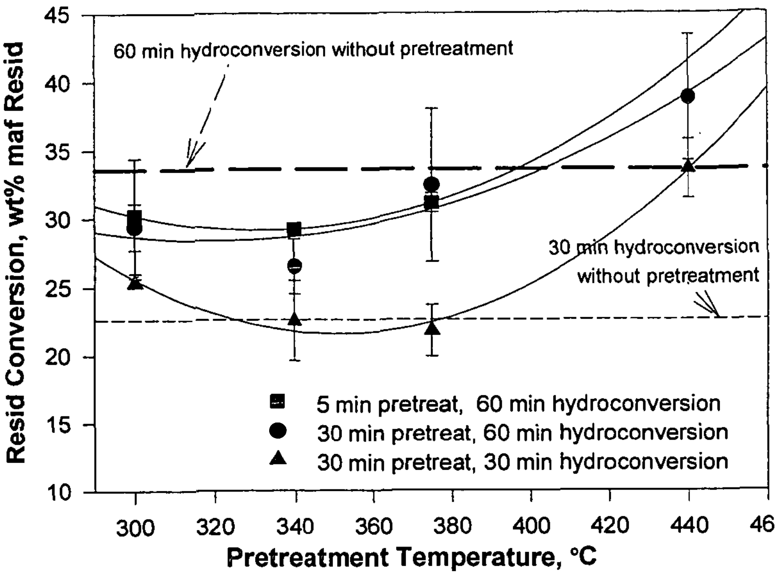

Figure 1. Effect of pretreatment time and temperature on 566°C+ resid conversion in 30 and 60 minute reactions of a deashed resid with 1000 ppmw Mo in Molyvan L, at 440°C.

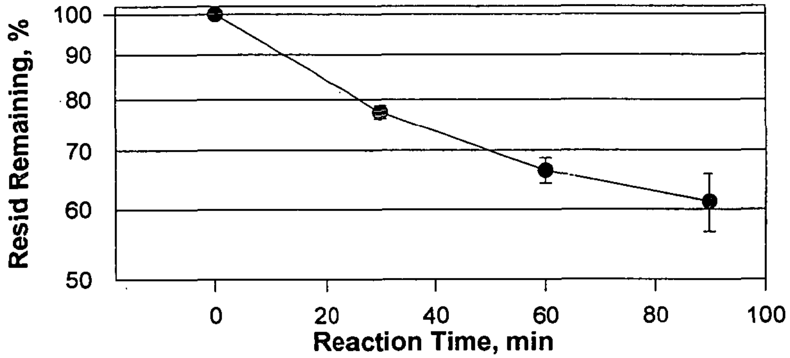

Figure 2. Disappearance of 566°C+ resid vs reaction time, hydrotreating deashed resid with 1000 ppmw Mo in Molyvan L at 440°C, without pretreatment.

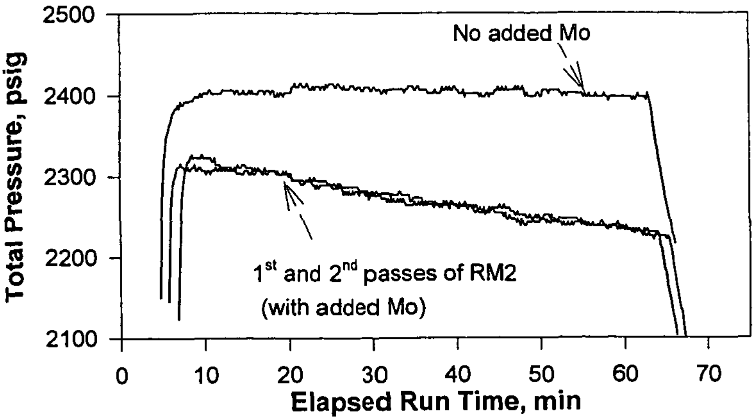

Figure 3. Impact of fresh and recycled Mo on total pressure in 60 min reactions at 440°C.