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# Life Extension of Residue Hydrodesulfurization Catalyst by Intermittent Injection of Oil-Soluble Metal Precursors to Feed Oil

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A method to extend the life of a residue hydrodesulfurization (HDS) catalyst during use was devised by injecting oil-soluble metal precursors to the feed oil intermittently. The method is based on the idea that oil-soluble metal precursors are transformed to catalytically active particles and that conventional HDS catalysts capture most of them. The resulting catalyst possesses additional HDS activity. The scheme was experimentally verified with the commercial vacuum residue HDS catalyst and an atmospheric residual oil that contained 310 ppm of molybdenum naphthenate and 60 ppm of cobalt naphthenate. The catalyst, which was exposed to the metal-containing oil, captured most of the dispersed particles and its HDS activity was improved. The improved catalytic activity requires a less-severe temperature increase policy, which will extend the life of the catalyst further. A less-expensive molybdenum-containing organic compound, MOLYVAN L, was as effective as molybdenum naphthenate in improving HDS activity when used with cobalt naphthenate. The conversion improvement of the bigger molecule, asphaltene, by the catalyst that was exposed to dispersed catalysts suggests that the deposited metals were located primarily on the outer surface of the catalyst.

## Introduction

The worldwide regulation on sulfur levels of liquid fuel is getting stricter, and the demand for the cleaner and lighter oil fractions is increasing.<sup>1</sup> However, the overall average quality of crude oil is heavier and sourer, and this trend is expected to continue.<sup>2</sup> Thus, refiners have witnessed the increased capacity of hydrodesulfurization (HDS) processes, especially residue-HDS (RDS) processes. The catalyst used in the RDS reaction becomes deactivated, because of both severe reaction conditions and catalyst poisons in the feed oil. The RDS catalyst is known to be deactivated by coking in the initial period and by the deposition of metals (vanadium, nickel, and iron) from residual oil, resulting in its life being limited to approximately one year.<sup>3,4</sup>

Numerous efforts have been made either to improve the RDS catalyst to have a longer life or to regenerate the spent catalyst for reuse. For example, the maximum tramp-metal uptake capacity of new catalysts is increasing, and those catalysts show the high activity, even with the significant metal contamination.<sup>5</sup> On the

other hand, oxidative regeneration of spent RDS catalysts by removing coke could recover the activity of the regenerated catalyst. However, the degree of regeneration was limited only to a low extent when large amounts of metal were deposited to the catalyst.<sup>5</sup> Selectively removing deposited metals (vanadium and nickel) from spent catalysts by the acidic solution is a costly process, and it may alter the chemical and physical properties of the catalysts.<sup>6–8</sup> As an alternative to the regeneration of spent RDS catalysts, the following method of extending the life of conventional RDS catalysts was devised in this work.

Unsupported dispersed catalysts can be used to upgrade heavy feeds in procedures such as the M-coke process,<sup>9–16</sup> in the direct liquefaction of coal, and in co-

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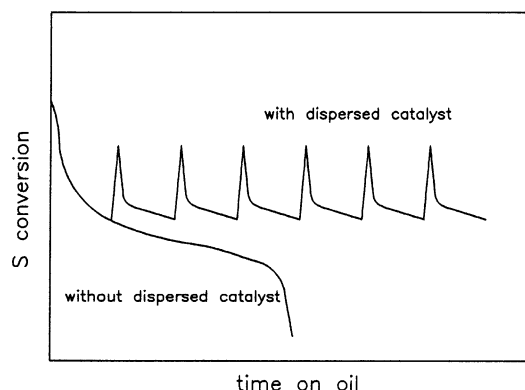
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**Figure 1.** Conceptual illustration of life-extension method of supported hydrosulfurization (HDS) catalysts by intermittent injection of dispersed catalysts in the feed oil.

processing.<sup>17–19</sup> Oil-soluble metallic compounds, such as molybdenum naphthenate and cobalt naphthenate, are well-known to act as catalyst precursors for the HDS reaction.<sup>9,11,13,16</sup> Because they can be well-dispersed in the feed oil, maximum interaction of the oil and hydrogen with the transformed sulfide catalyst is easily achieved. However, those dispersed catalysts suffer from the problem of being disposable, because of the difficulty encountered when recovering them from the product oil. Recently, porous materials such as active carbon or silica–alumina were reported to capture catalytically active metal particles that have been generated from precursors.<sup>11,12,15</sup> The captured particles acted almost the same way as the conventional metal catalyst supported on the porous support material, indicating that in situ formation of the catalyst is possible when oil-soluble metal precursors and the porous support are simultaneously used in HDS of oils. Life extension of supported RDS catalysts was devised, based on the aforementioned results of in situ formation of the catalyst.

Figure 1 shows the concept of extending the life of RDS catalysts devised in this work. The conventional Ni-Mo/Al<sub>2</sub>O<sub>3</sub> HDS catalysts that are charged into the ordinary reactor lose their sulfur-removal activity gradually during their use. When a few hundred parts per million (ppm) of oil-soluble metal (molybdenum, cobalt) precursors are mixed with the feed oil and then introduced to the reactor for a short period, an immediate increase in the activity is expected, because the activity from the dispersed catalyst is added to the activity of the existing Ni-Mo/Al<sub>2</sub>O<sub>3</sub> HDS catalyst. After the introduction of the dispersed catalyst is terminated, the catalyst remaining in the reactor maintains an activity that is greater than the activity of the same catalyst that has not been exposed to the dispersed catalyst. The supported catalyst captures dispersed catalyst particles,

**Table 1.** Chemical Properties of Atmospheric Residual Feed Oil

property	value
elemental composition	
carbon	85.5 wt %
hydrogen	10.8 wt %
nitrogen	0.5 wt %
oxygen	0.3 wt %
sulfur	3.55 wt %
metal content	
vanadium	65 ppm
nickel	18 ppm
iron	3.0 ppm
asphaltene content	8.17 wt %

and the activity of the resulting catalyst becomes greater than that of the supported catalyst alone. The repeated introduction of dispersed catalysts keeps the activity of the catalyst above a certain level, requiring a smaller temperature increase policy to compensate the catalytic activity loss. It will result in longer life of the HDS catalyst.

In this work, the concept of the life extension of the RDS catalyst shown in Figure 1 was verified experimentally. The unique feature of this life-extension scheme is that it does not require any major change in the current HDS operational practices, such as the reactor, the catalyst, and the operating conditions. The only minor modification needed is the installation of a dispersed catalyst mixing apparatus in the feed stream. The operators can be assured that the reactor behavior after the change will not be very different from what they used to observe.

## Experimental Section

**Feed Oil.** The feed oil for the HDS experiment was the residual oil obtained from the atmospheric distillation unit of a Korean refinery. The chemical properties of the atmospheric residue (AR) are listed in Table 1. The analysis of the sulfur content was performed using an ANTEK 7000 sulfur/nitrogen analyzer (Antek Instruments, Inc.), and analyses of the carbon, hydrogen, and nitrogen contents were made using an elemental analyzer (Perkin–Elmer). The metal contents in the oil were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (Ultima C, Jobin–Yvon). The asphaltenes were defined as the pentane-insolubles and were measured by weighing the pentane-insoluble fractions collected from a 1- $\mu$ m-pore-size membrane filter.

**Catalysts.** The solid catalyst used in this study was the commercial catalyst used in the vacuum RDS (VRDS) unit. Both the new catalyst and the spent catalyst were used. The catalyst was the conventional Ni-Mo/Al<sub>2</sub>O<sub>3</sub>-type HDS catalyst (with 3.16 wt % nickel and 9.41 wt % molybdenum) in a cylindrical pellet form (0.13 cm in diameter and 0.3–0.5 cm in length). The spent catalyst is composed of 18.6 wt % vanadium that is accumulated from the feed oil, in addition to 14.1 wt % sulfur and 5 wt % carbon. The surface areas of the new catalyst and the spent catalyst were 164.4 and 36.2 m<sup>2</sup>/g, respectively. Cobalt naphthenate (Fluka, with 8 wt % cobalt) and molybdenum naphthenate (Shepherd Chemical Co., with 6.5 wt % molybdenum) were used as oil-soluble precursors of the dispersed catalyst. Metal naphthenates are fairly expensive (\$100–\$1000/kg; thus, the much-less-expensive molybdenum compound (MOLYVAN L, which is a sulfurized oxymolybdenum organophosphorodithioate, with 8 wt % molybdenum and a cost of ~\$15/kg, from R. T. Vanderbilt Co.) was also used. Cobalt naphthenate was used with the molybdenum compound, because the results of a previous study indicated that the combination of both compounds showed

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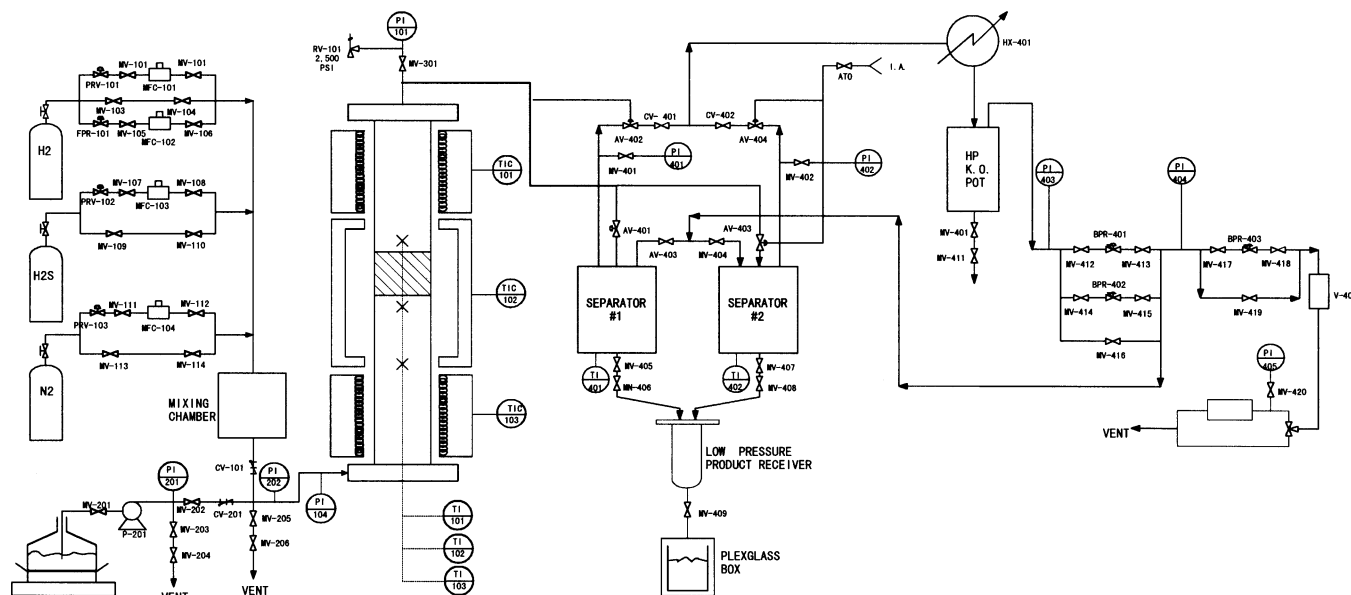
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**Figure 2.** Schematic diagram of the flow-through-type HDS test unit.

higher HDS activities than the molybdenum precursor alone.<sup>11</sup> Oil-soluble metallic compounds were dissolved in a certain amount of AR, which was preheated at 70 °C. The catalytically active forms of metals originated from metal naphthenates are sulfides ( $\text{MoS}_2$ ,  $\text{Co}_9\text{S}_8$ ).<sup>14,20,21</sup> Thus, twice the amount of elemental sulfur that is needed to transform both naphthenates to the corresponding sulfides was also added to the feed oil.

**Test Unit and Procedures.** A schematic of the flow-through-type HDS activity test unit is shown in Figure 2. A cylindrical packed-bed reactor with an inside diameter of 1.3 cm and a length of 70 cm was used. Three grams of the new catalyst in a pelletized form, diluted with nonporous ceramic beads (16–30 mesh size), were charged into the reactor. The weight of the spent catalyst was twice that of the new catalyst per the same volume, because of the accumulated coke and metals. Thus, in the case of the spent catalyst, 6 g were charged into the reactor. The volume of the catalyst bed was 12  $\text{cm}^3$ . At both the inlet and the outlet of the reactor, stainless-steel sieve screens were installed to prevent the catalyst from escaping from the reactor. Nonporous ceramic beads filled the remaining reactor space in the catalyst bed, to facilitate both mixing of the feed oil and hydrogen and preheating of the reaction mixture. The reactor length was divided into three zones, and each zone was heated by the individual heating element (two heating tapes on both ends and one radiation-type heater in the middle). The temperature of the catalyst bed was measured by a thermocouple embedded into the bed.

The feed oil was stored in a jacketed vessel that was heated at 75 °C to ensure the fluidity. The vessel was mounted on a balance to measure the flow rate. The feed oil was supplied to the reactor by a metering pump (Milton Roy). High-pressure hydrogen supplied by a mass flow controller (MFC) (Brooks) was mixed with the feed oil before being introduced to the reactor.

The reaction pressure was maintained at 69 bar with three back-pressure regulators, which were located at the end of the gas stream. After the product mixture left the reactor, it went through one of the two gas–liquid separators. A small separator (capacity of 500  $\text{cm}^3$ ) was used for the purpose of sampling liquid product, and a larger separator (capacity of 1000  $\text{cm}^3$ ) was used to collect the liquid product during the nonsampling period. Four air-actuated valves were sequentially operated

**Table 2.** Typical Reaction Conditions

condition	value
reaction temperature	415 °C
pressure	69 bar
catalyst bed volume	12 $\text{cm}^3$
atmospheric residue (AR) flow rate	20 $\text{cm}^3/\text{h}$
liquid hourly space velocity, LHSV	1.67 $\text{h}^{-1}$
$\text{H}_2$ flow rate	10 L/h

to ensure the independent pressure control of each separator after emptying the liquid. The gas stream from the separator passed through a high-pressure knockout pot, to remove light hydrocarbons before going through the back-pressure regulator. A dry gas meter was installed at the exit of the back-pressure regulator, to measure the gas flow rate. A computer-controlled process logic controller (PLC) (Texas Instruments, Inc.) constantly monitored the temperature and the pressure of the reactor. After the temperature or the pressure exceeded the preset values, the PLC automatically cut off the power supplied both to the heaters and to the liquid pump. In addition, the signal to the MFC supplying the hydrogen was set to zero, to prevent overpressurization of the system. Thus, overnight unattended operation of the entire system was possible.

Before the start of the run, the catalyst was presulfided with a mixture stream of 10%  $\text{H}_2\text{S}$  and 90%  $\text{H}_2$  (100  $\text{cm}^3/\text{min}$ ) at 450 °C for 2 h. Table 2 lists the typical reaction conditions. The sulfur content of the product oil measured by a sulfur/nitrogen analyzer was used to calculate the sulfur conversion.

## Results and Discussion

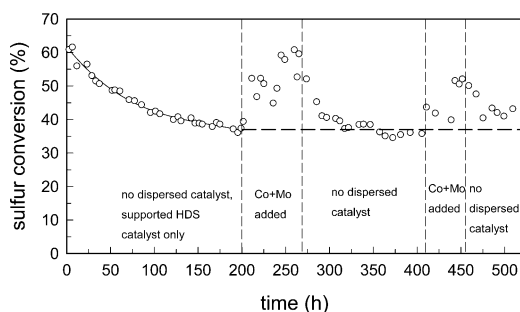
### Proof of the Concept Run with New Catalyst.

The life-extension concept shown in Figure 1 was simulated with 3 g of a new VRDS catalyst charged in the reactor, and the result is shown in Figure 3. During the initial 200 h of RDS reaction with the AR feed oil, the catalyst became deactivated and the sulfur-removal activity of the new catalyst decreased from an initial sulfur conversion of 60% to 37%. After 200 h of the reaction, the feed was switched to the oil that contained 310 ppm molybdenum and 60 ppm cobalt, both in the naphthenate form (the concentration was based on the weight of the metal only). Immediately after the change of the feed oil, the sulfur conversion jumped to 52% and

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**Figure 3.** Change in sulfur removal activity of new Ni-Mo/ $\text{Al}_2\text{O}_3$  commercial catalyst during and after the introduction of 370 ppm of a combination of molybdenum naphthenate and cobalt naphthenate mixed with atmospheric residue (AR) feed oil (415 °C, 69 bar).

then gradually increased to 61%. This was due to the additional sulfur-removal activity of the dispersed catalyst.

After 60 h of the dispersed catalyst injection period, the feed was changed back to the oil that did not contain any molybdenum naphthenate or cobalt naphthenate. In this period (a reaction time of 270–410 h), the activity of the catalyst was slowly decreased to show 36% of the sulfur conversion, which is approximately the same as the activity just before the introduction of dispersed catalysts. For the reference, the conversion curve for the zero deactivation case was also shown (as a dashed line). If it is assumed that the catalyst continued to deactivate without exposure to the dispersed catalyst, the conversion curve should be located below the dashed line shown in Figure 3. In that case, the activity of the catalyst with the experience of dispersed catalyst could be regarded higher than that of the inexperienced catalyst. Even in comparison with the zero deactivation case, the injection of dispersed catalysts to the feed oil at least prevented further deactivation of the HDS catalyst, as was illustrated conceptually in Figure 1.

After ~50 h of the second introduction of the dispersed catalyst (reaction time of 410–455 h), the resultant catalyst in the reactor showed 42% of the sulfur conversion. This activity was higher than that of the catalysts with a single exposure (36%) or no exposure (37%) to the dispersed catalysts. This is the anticipated result, because the HDS catalyst that was exposed to dispersed catalysts twice has a greater amount of captured metals than that with the single exposure. Thus, the activity improvement was more evident with the doubly exposed catalyst.

During the introduction of 310 ppm of molybdenum and 60 ppm of cobalt in the feed oil, the product oil contained 18 ppm of molybdenum and 8 ppm of cobalt, indicating that the solid HDS catalyst in the reactor captured most of the dispersed metal catalysts. Thus, the catalyst within the reactor possessed additional sulfur-removing activity, because of the captured metal catalysts.

There are two possibilities of dispersed catalysts being anchored to the supported catalyst. The first possibility is that metal naphthenates are decomposed and transformed to sulfides on the surface of the supported catalyst and then the sulfides are deposited on the surface. The second possibility is that a transformation

of metal naphthenates occurs in the fluid phase and that sulfides form small particles with some carbon. The porous supported catalyst then captures fine particles of a sulfide–carbon complex. The first case can occur when the metallic precursors are so stable that they can reach the pores of the supported catalyst without being converted to sulfides. The transformation of metallic precursors to metal sulfide proceeds on the surface of the supported catalyst and then the sulfides are deposited on it. Nickel and vanadium complexes contained in the heavy oil are deposited in the pores of the HDS catalyst in that way. We can call this process an in situ impregnation.

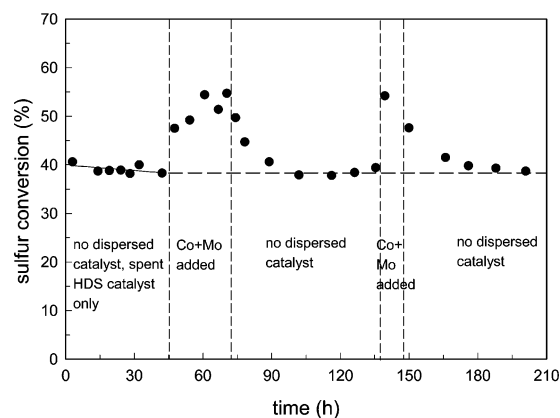
Although we cannot rule out the first possibility in our case, several literature studies have suggested that the transformation of molybdenum naphthenate to the sulfide–carbon complex occurred in the fluid phase.<sup>13,14,16,20,21</sup> Rueda et al. observed that the solid generated from molybdenum naphthenate and sulfiding reagents ( $\text{CS}_2$  or elemental sulfur) in an organic solvent (hexadecane or methylnaphthalene) at 350 °C was the mixture of carbonaceous species and  $\text{MoS}_2$ .<sup>20,21</sup> The solids had BET areas ranging from 240  $\text{m}^2/\text{g}$  to 500  $\text{m}^2/\text{g}$ . The carbonaceous phase accounted for 6–8 wt % of the total solid, and its condensed aromatic nature originated from the decomposed naphthenic salt. The carbonaceous phase prevents sintering of the fine particles of  $\text{MoS}_2$ . In the M-coke process,<sup>16</sup> micrometer-sized catalyst particles are comprised of a metal sulfide component combined with a carbonaceous component.

The transformation reaction of molybdenum naphthenate is known to be very fast, even at temperatures as low as 360 °C.<sup>14</sup> Considering the relatively high reaction temperature (415 °C) and the low liquid hourly space velocity (LHSV) of our case, most of the molybdenum naphthenate and cobalt naphthenate must be transformed to the sulfide–carbon complex before arriving at the pores of the HDS catalysts. Thus, the second case, which involved the formation of the working catalyst in the form of fine particles of  $\text{MoS}_2$  and  $\text{Co}_9\text{S}_8$ , with the carbonaceous species mostly coming from the naphthenate salt, followed by the capture of particles by the HDS catalyst, seemed to occur predominantly in our case.

The result shown in Figure 3 clearly proved that our concept of extending the life of HDS catalysts is possible by the repeated injection of small amounts of oil-soluble metal catalysts to the feed oil.

In real practices, a guard bed that is installed at the exit of the solid catalyst bed can capture the remaining dispersed catalysts in the product oil. Inexpensive materials such as active carbon or porous alumina can be used in the guard bed.<sup>11</sup> After the concentration of the metal captured by the guard bed has reached a certain level, the guard bed may also act as the additional HDS catalyst bed, giving an improved sulfur conversion.

**Spent Catalyst.** The same procedure of the life extension was applied to 6 g of the spent VRDS catalyst that had been in service for one year in a commercial HDS reactor. Although the spent catalyst had been used for a year, it still possessed some HDS activity, and the initial sulfur conversion was 41% (Figure 4). As expected, the spent catalyst showed a low degree of

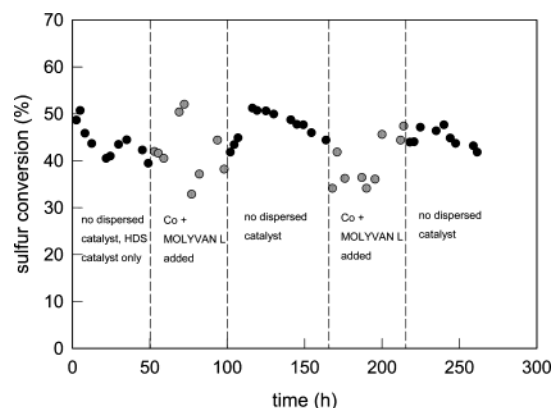


**Figure 4.** Improvement in the sulfur-removal activity of a spent Ni-Mo/Al<sub>2</sub>O<sub>3</sub> commercial catalyst with the introduction of 370 ppm of a combination of molybdenum naphthenate and cobalt naphthenate mixed with AR feed oil (415 °C, 69 bar).

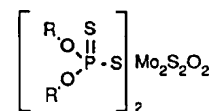
deactivation during the initial 44 h with the AR feed oil, and the sulfur conversion decreased to 38%. After the feed oil was switched to the oil that contained 310 ppm of molybdenum naphthenate and 60 ppm of cobalt naphthenate, the sulfur conversion jumped to 55%. After the feed was switched back to the oil that was free of the dispersed catalyst, the activity of the spent catalyst was decreased to 38% sulfur conversion. The spent catalyst, after being exposed to dispersed catalysts twice, exhibited a sulfur conversion of ~39%, which was almost the same as the initial activity of the spent catalyst, indicating that the intermittent injection of oil-soluble catalysts prevented the further deactivation (the dashed line in Figure 4). Enhancement of the activity of the spent catalyst was not as significant as that of the new catalyst, partly because of the shorter injection period of dispersed catalysts. The result in Figure 4 indicates that life extension is also possible with the spent catalyst that was almost at the end stage of its life.

**Life Extension with MOLYVAN L and Cobalt Naphthenate.** As an alternative to expensive molybdenum naphthenate, the less-expensive molybdenum-containing compound MOLYVAN L (with 8 wt % molybdenum) was used as the oil-soluble catalyst with cobalt naphthenate. MOLYVAN L has also been used as a catalyst for direct coal liquefaction.<sup>17</sup> The total concentration of metals in the AR feed oil was 370 ppm: 310 ppm was molybdenum and 60 ppm was cobalt. Again, the HDS reaction was started with the new VRDS catalyst and the AR feed oil without the dispersed catalyst. After 50 h of the reaction, the sulfur conversion of the new VRDS catalyst decreased from 50% to 40% (Figure 5). At that point, the feed was changed to the oil that contained MOLYVAN L and cobalt naphthenate. In contrast to the molybdenum naphthenate case, the sudden increase in the sulfur conversion activity due to MOLYVAN L was not observed. However, the activity of the HDS catalyst after experiencing 50 h of MOLYVAN L and cobalt naphthenate increased to the level of the 50% sulfur conversion, indicating that MOLYVAN L was also converted to the catalytically active form and then captured by the HDS catalyst.

During the second period of switching the feed oil that contained MOLYVAN L and cobalt naphthenate (after



**Figure 5.** Change in sulfur-removal activity of new Ni-Mo/Al<sub>2</sub>O<sub>3</sub> commercial catalyst during and after the introduction of 310 ppm of MOLYVAN L and 60 ppm of cobalt naphthenate mixed with AR feed oil (415 °C, 69 bar).

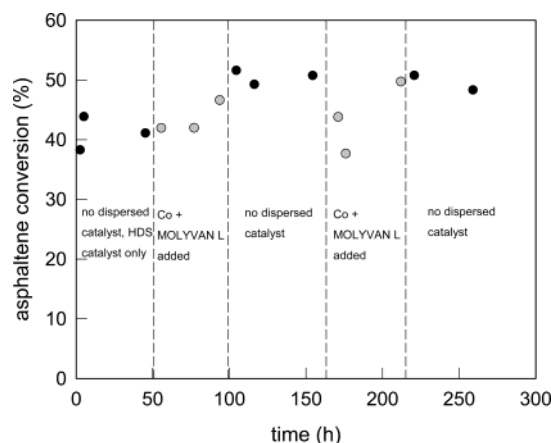


**Figure 6.** Molecular structure of MOLYVAN L.

165–217 h of reaction time), an increase in the sulfur conversion activity was not observed either. The sulfur conversion activity of the HDS catalyst after being exposed to MOLYVAN L and cobalt naphthenate twice, was maintained at 43%–40%, which is higher than that of the VRDS catalyst that was not exposed to the dispersed catalyst (40%). Thus, the less-expensive MOLYVAN L was determined to be as effective as molybdenum naphthenate in extending the life of VRDS catalysts.

The reason for the different behavior of MOLYVAN L from molybdenum naphthenate is not clear. Metal naphthenates are derived from naphthenic acids. The structure of naphthenic acids is that of a highly alkylated cyclopentane. In the meanwhile, MOLYVAN L (which is sulfurized oxymolybdenum organophosphorodithioate) has the molecular structure shown in Figure 6. It is presumed that MOLYVAN L has more difficulty in transforming to a catalytic active species such as MoS<sub>2</sub> than molybdenum naphthenate does, because the transformation involves the removal of both oxygen and organophosphorodithioate groups. Slower transformation of MOLYVAN L to MoS<sub>2</sub> might be one of the reasons for the initially low conversion during the period of injecting MOLYVAN L and cobalt naphthenate and then the increased conversion in the later period of feeding the oil without dispersed catalysts. MOLYVAN L has six S atoms per two Mo atoms. Two extra S atoms will be removed as H<sub>2</sub>S after MOLYVAN L is transformed to MoS<sub>2</sub>. We mixed twice the amount of elemental sulfur that is needed to transform MOLYVAN L and cobalt naphthenate to the corresponding sulfides in the feed, to be consistent with other runs with added molybdenum naphthenate. However, most of elemental sulfur in this case might not be used for sulfide transformation. This could result in the lower sulfur conversion during the MOLYVAN L injection period.

The concentration of asphaltene was also measured during the HDS reaction run of Figure 5, and the conversion results are shown in Figure 7. The figure



**Figure 7.** Improvement of asphaltene conversion activity of new Ni-Mo/Al<sub>2</sub>O<sub>3</sub> commercial catalyst with the introduction of 310 ppm of MOLYVAN L and 60 ppm of cobalt naphthenate mixed with AR feed oil (415 °C, 69 bar).

shows that the conversion of asphaltene increased after the catalyst experienced the mixture of MOLYVAN L and cobalt naphthenate. The location of the captured metal sulfide particles can be speculated from the result of the asphaltene conversion. The molecular weight of asphaltene is in the range of 500–5000.<sup>22</sup> The reaction of those large molecules occurs mostly on the outer surface or pore mouths of the HDS catalyst. The increased conversion of the asphaltene by the catalyst that was exposed to oil-soluble metal catalysts in the feed oil indicates that most of the captured metals were positioned at the outside of the pores. If metals from the dispersed catalysts were deposited inside of the pores of the HDS catalyst, very little increase in the conversion of asphaltene would be observed. Thus, the most of captured metal sulfides should be deposited at the outside of the HDS catalyst particles. The interaction between the HDS catalyst and the metal sulfide-carbon complex could mostly be of a physical nature, as was indicated by the possible location of captured particles.

This finding is very important, in that the blockage of the catalyst pores due to the deposition of metals from dispersed catalysts might not occur. Otherwise, blockage of the pores would lead to accelerated deactivation. Energy-dispersive X-ray (EDX) mapping results of the activated carbon granules that are exposed to the molybdenum naphthenate and cobalt naphthenate,

showing that the metals were evenly deposited on the surface of the carbon, supports our hypothesis.<sup>11</sup>

**Advantages of the Life-Extension Scheme.** The main advantage of this method is that the life extension is accomplished with minimal changes in the existing process, including the catalyst. Only the installation of the dispersed catalyst mixing apparatus in the feed stream is needed. The degree of the catalytic activity improvement can be controlled by the concentration, duration, and frequency of injection of the metal precursors. After the life-extension method is applied, the usage of the temperature increase policy to compensate the loss of the catalyst activity will be small or none, because the activity can be improved or maintained over a long period of time. Thus, the deactivation due to the higher-temperature operation is prevented, resulting in longer life of the catalyst. The net effects of the catalyst life extension are fewer purchases of new catalysts and minimum loss during the shutdown period for the catalyst recharge. The spent catalysts thus obtained are richer in metals, which are more economical for metal reclamation.

### Conclusion

A method of extending the life of the residue hydrodesulfurization (RDS) catalyst by the intermittent injection of oil-soluble metal precursors to the feed oil was verified experimentally with the commercial vacuum residue hydrodesulfurization (VRDS) catalyst and the atmospheric residual oil that contains 310 ppm of molybdenum naphthenate and 60 ppm of cobalt naphthenate. The catalyst that had been exposed to the feed oil that contained dispersed metal catalysts captured most of metal sulfide-carbon complex particles, and its HDS activity was enhanced. The less-expensive molybdenum-containing organic compound MOLYVAN L was as effective as molybdenum naphthenate in improving hydrodesulfurization activity when used with cobalt naphthenate. The improvement of the asphaltene conversion of the catalyst, after being exposed to dispersed catalysts, indicates that the location of the deposited metals is primarily on the outer surface of the catalyst.

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