ACTIVITY OF SPENT CATALYSTS
IN THE HYDRODESULFURIZATION OF GAS OIL

SD Sumbogo Murti[1], **Hartiniati** [2]

1) Center for Energy Technology (B2TE)
2) Center for Energy Resources Development Technology (PTPSE)
Agency for the Assessment and Application of Technology (BPPT),
JL. MH Thamrin No 8 Jakarta Pusat 10340
E-mail: sd.sumbogo@bppt.go.id

ABSTRACT

Activities of spent catalysts were examined in hydrodesulfurization (HDS) of gas oil at $340^{o}C$ under 50 kg/cm^2 H$_2$. Two types of spent commercial catalyst (NiMo/Al$_2$O$_3$ dan CoMo/Al$_2$O$_3$) were used in single and two-stage of reaction configuration to show the inhibition effect of the by-product such as H$_2$S and NH$_3$. Hydrogen renewal between stages was attempted to show additional inhibition effects of the by-products such as H$_2$S and NH$_3$. Spent NiMo/Al$_2$O$_3$ dan CoMo/Al$_2$O$_3$ catalysts showed contrasting activities in HDS. HDS over spent CoMo/Al$_2$O$_3$ was much improved by H$_2$ refreshment. The effect of two-stage hydrodesulfurization was markedly reduced over the spent NiMo/Al$_2$O$_3$. Spent catalysts apparently lost their activity due to the carbon deposition, which covered the active sites more preferentially.

Keywords   : Spent catalyst, Hydrodesulfurization, Gas Oil

ABSTRAK

Aktivitas katalis bekas telah diuji dalam hydrodesulfurisasi (HDS) minyak diesel pada suhu 340 ^{o}C dan tekanan hydrogen 50 kg/cm^2. Dua macam katalis bekas yaitu NiMo/Al$_2$O$_3$ dan CoMo/Al$_2$O$_3$ dipakai dalam satu dan dua tahap konfigurasi reaksi untuk menunjukkan efek menghambat dari produk samping seperti H$_2$S dan NH$_3$. Penambahan gas hydrogen baru pada tahap kedua juga dimaksudkan untuk melihat tambahan efek menghambat yang ditimbulkan oleh H$_2$S dan NH$_3$. Katalis NiMo dan CoMo bekas menunjukkan aktivitas yang kontras dalam HDS. Aktivitas HDS dengan katalis CoMo bekas meningkat dengan penggantian H$_2$ baru. Pengaruh dari dua tahap HDS menurun banyak terhadap katalis NiMo bekas. Katalis bekas kehilangan aktivitasnya karena adanya deposisi karbon yang menyelimuti bagian aktif dari katalis tersebut.

Kata kunci   : Katalis bekas, Hidrodesulfurisasi, Minyak Diesel

1. INTRODUCTION

Burning of fossil energy especially coal and oil will damaged the environmental. The increasing concerns   on the environmental conditions requires the new approaches to decrease the sulfur content of diesel oil to less than 15 ppmS. Hydrodesulfurization of refractory sulfur species is the key task to achieve those tightened regulation. Such sulfur species were identified to be 4-methyl (4M), 4,6-dimethyl(4,6-DM) and 4,6,*x*-trimethyl (4,6,*x*-TM) dibenzothiophenes   (DBTs) [Girgis, MJ et al 1991 and Whitehurst et al 1998], which are of very low reactivity, apparently   because of steric and electronic hindrance

exerted by their methyl groups located in the neighborhood of the sulfur atom in the center ring [Ma, X et al 1996]. In addition, they suffer severe inhibition by H2S and NH3 produced from the HDS and HDN of reactive sulfur and nitrogen species and aromatic species, especially, at their very low concentration below 500 ppm, which imposes further difficulty on their deep desulfurization [Isoda T, 1994 and Kabe T, 2001]. Hence, removal of H2S, NH3 and nitrogen species prior to the HDS has been known as a very effective way to achieve the deep desulfurization [Shin, S, 2001 and Sumbogo Murti, SD 2003].

Catalyst deactivation is an important factor in petroleum industries, from both economic and technological points of view. Coke deposition on the catalyst is generally believed to be the primary cause of catalyst deactivation in hydrotreatment of gas oil [E. Furimsky 1993]. The loss of catalytic activity makes it necessary to raise the reaction temperature to maintain the same level of conversion, although, the operation must be finally terminated for the replacement of the catalyst. Sintering and activity loss during the coke oxidation complicate the regeneration of the supported catalyst. In general, research on the HDS has been performed on fresh catalysts. However, the initial catalytic activity must be reduced due to vigorous deactivation observed in the practical HDS plant. Such observation stimulated us to examine the spent catalyst, because the practical HDS is run over the"spent" catalyst.

In the present study, spent NiMo and CoMo on alumina catalysts were evaluated in the hydrodesulfurization of straight run and its nitrogen species free gas oils, interm of gross and molecular-based desulfurization behaviors. The activities and characteristics of spent catalysts in HDS and HDN were compared to those of their virgin ones to clarify the influences of long run operation on the catalytic performances in the deep HDS.

2. EXPERIMENTAL

2.1. Gas Oil Samples

Some representative properties of straight run gas oil are summarized in Table 1. Commercial NiMo/Al2O3 and CoMo/Al2O3 catalysts were provided by an European catalyst vendor after their test runs of a middle east gas oil for about 8000 h. The commercial catalysts carried 2–5% w/w of NiO, 21–27% w/w of MoO3 on alumina and 18–24% w/w of MoO3, 3–6% w/w of CoO on alumina; which the surface area were 175 and 191m2/g for virgin NiMo and CoMo catalysts, respectively. The catalyst was presulfided prior to the reaction by H2S (5 vol.%)/H2 flow at 360°C for 2 h.

2.2. Hydrotreatment

Hydrotreatment of gas oils was performed in a 100 ml autoclave-type reactor equipped with a sampling port. Gas oil (10 g) was hydrotreated at 340°C under 50 kg/m2 H2 (initial hydrogen pressure at room temperature), over 1 g of presulfided catalyst by single

and two-stage reaction configurations, as illustrated in Fig. 1. The heating time to the reaction temperature was always 40 min.

Table 1. Composition of gas oils

Gas Oil	
Carbon (wt %)	85.95
Hydrogen (wt%)	12.30
Sulfur (wt%0	1.64
Nitrogen (ppm n)	300

The stirring speed was 1000 rpm to prevent any mass-transfer problems. The reaction times for the single stage reaction were 30 and 60 min after the reaction temperature was achieved, while the two-stage reaction consisted of two 30 min reactions.

In the two-stage reaction scheme, the reactor was cooled down rapidly to room temperature within 5 min after the first stage reaction. The second stage was operated after refreshing the reaction atmosphere with fresh H_2 (50 kg/cm2) at room temperature.
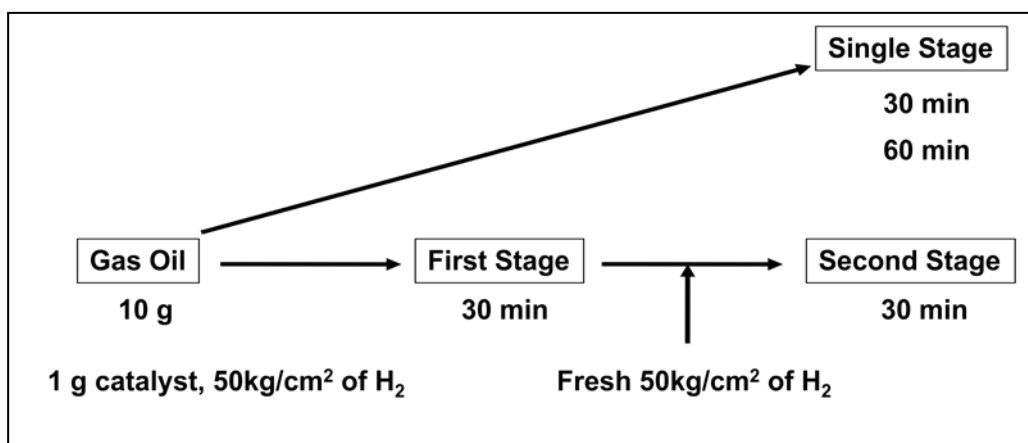

Fig. 1. Hydrotreatment conFiguration

2.3. Analysis of Hydrotreated Product

Carbon, sulfur and nitrogen species in the gas oil were analyzed by gas chromatography with an atomic emission detector (GC-AED). A Hewlett-Packard gas chromatograph (HP6890) coupled with an atomic emission detector (G2350A) was used in this study. The GC-AED has been known as a very powerful technique to analyze the element of interest [Sumbogo Murti SD, 2002].

2.4. *Characterization of Catalyst*

Deposited carbon in catalysts was analyzed by laser Raman scattering spectroscopy (NEC, NRS-2000B, 514.5 nm, 0.3 W) at 1200–1800 cm−1.

3. RESULT

3.1. HDS of Total Sulfur

Table 2 shows the remaining sulfur level after HDS. Relatively, reactive sulfur species (benzothiophenes, BTs) were easily removed by 30 min HDS even over spent NiMo and CoMo catalysts, giving total sulfur contents of 5733 and 3525 ppm, respectively. However, major refractory sulfur species (dibenzothiophenes, DBTs) still remained after 60 min of reaction, their sulfur levels being 1439 and 943 ppm, respectively, over spent NiMo catalyst. Two-stage reaction configuration by refreshing reaction atmosphere with fresh H2 enhanced the HDS over both spent catalysts, leaving 1090 and 489 ppm, respectively.
HDS activities of spent NiMo and CoMo catalysts to reduce total sulfur content in the gas oil were much lower than those of the virgin ones under the same conditions as compared in Table 2.

Table 2. HDS extent of gas oils over virgin and spent catalysts[a]

Reaction	Single stage		Two-stage
Time	30 min	60 min	60 min
NiMo Virgin	2245	901	394
Spent	5733	1439	1090
CoMo virgin	1177	421	333
Spent	3525	943	489

a) Values are the remaining of total sulfur content (ppm)

3.2. HDS of Refractory Sulfur Species

The reactivities of refractory sulfur species (DBTs) in HDS over spent and virgin NiMo and CoMo catalysts are summarized in Table 3. The single stage of 60 min HDS left 798 and 455 ppm of refractory sulfur species over spent NiMo and CoMo catalysts, respectively. The two-stage reaction enhanced the HDS markedly over spent CoMo, leaving 270 ppm and enhanced it slightly over spent NiMo, leaving 692 ppm.

Table 3. HDS reactivity of refractory sulfur species[a)]

Reaction	Single stage		Two-stage
Time	30 min	60 min	60 min
NiMo Virgin	2116	889	194
Spent	2303	798	692
CoMo virgin	691	264	229
Spent	1432	455	270

a) Values are the remaining of sulfur species (ppm)

It must be noted that HDS activity of spent catalysts decreased more against refractory sulfur species. Two-stage reaction enhanced the HDS over both spent NiMo and CoMo catalysts up to 94 and 95% conversion, respectively

3.3. HDS of 4,6-DMDBT and 4-E,-6-MDBT

Among the refractory sulfur species, 4,6-dimethyldibenzothiophene (4,6-DMDBT) and 4-ethyl-6-methyl dibenzothiophene (4-*E*,6-MDBT) have been regarded to be the most refractory and survived in the last stage of HDS. The reactivities of these species in HDS are summarized in Table 4. 4,6-DMDBT over the spent NiMo catalyst exhibited much the same reactivity as that over the virgin one in the single stage reaction.

Table 4. HDS reactivity of refractory sulfur species[a)]

	Single stage		Two-stage
Reaction Time	30min	6 min	60 min
4,6-DMDBT			
NiMo Virgin	123	77	33
Spent	121	76	71
CoMo virgin	69	48	45
Spent	113	80	62
4-E,6-MDBT			
NiMo Virgin	59	33	16
Spent	59	39	32
CoMo virgin	28	20	20
Spent	46	33	24

a) Values are the remaining of sulfur species (ppm)

In contrast, refreshment of reaction atmosphere by fresh H2 in two-stage reaction enhanced the HDS of refractory sulfur species over the virgin NiMo much more than that over spent one. The HDS of 4-*E*,6-MDBT was found to show the almost same trend as that of HDS of 4,6-DMDBT, as summarized in Table 4.

3.4. Raman spectroscopy of spent catalysts

Fig. 2 shows the Raman spectra of the spent catalysts. Two peaks were observed at 1590 and 1350 cm−1 on Raman spectra of spent CoMo and NiMo catalysts. Both spectra appeared very similar in the shape and position of the carbon peaks, although, the spent CoMo gave a slightly higher intensity of the 1350 cm−1 peak, indicating less extent of graphitization [T. Jawhari, 1995]. Virgin NiMo showed a very small peak at 1590 cm−1, which appeared from the carbon impurity incorporated during the catalyst preparation, while virgin CoMo did not show any peak ascribable to carbon.
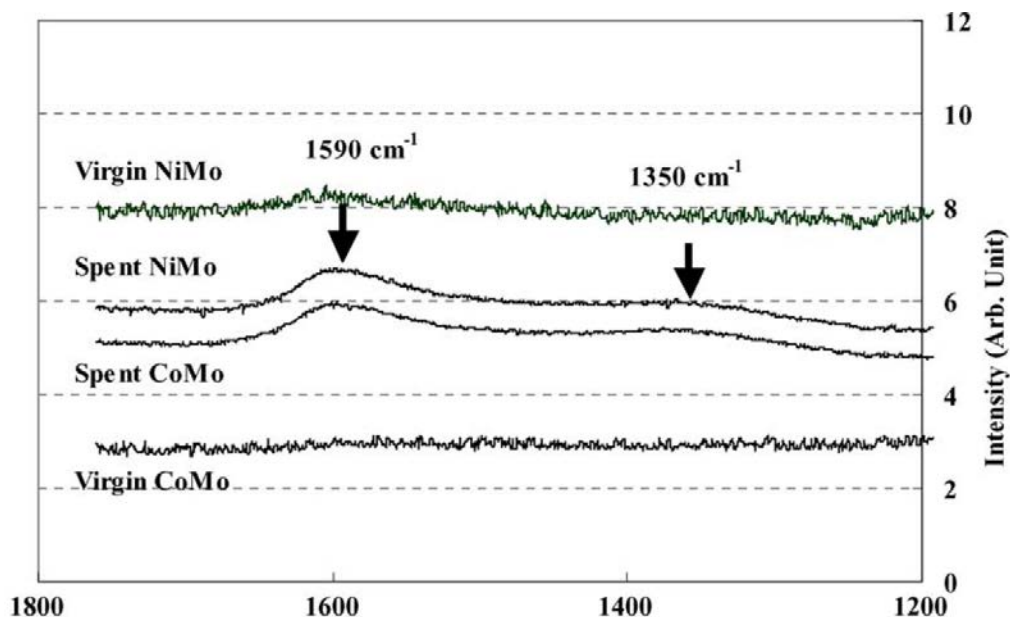

Fig. 2. Raman Spectra of Virgin and Spent Catalysts

3.5. *Elemental Analyses of Spent Catalysts*

Table 5 summarizes the elemental analyses of the spent catalysts. C, H, N analyses indicated that spent NiMo catalysts carried more carbon, larger C/H ratio and more nitrogen contents than those of the spent CoMo catalyst.

The NiMo catalyst adsorbs more nitrogen-containing species and promotes the carbonization of adsorbed aromatic species into the carbon on the surface. High acidity appeared responsible for the quantity and quality of deposited carbon.

Table 5. Elemental analyses of spent catalysts

	Spent NiMo	Spent CoMo
Carbon (wt%)	3.59	2.79
Hydrogen (wt%)	2.43	2.34
Nitrogen (wt%)	0.21	0.14

4. DISCUSSION

As indicated in the introduction, many practical HDS plant is operated with catalysts that lost their initial high activity. It is very important to differentiate the loss of activity on the reactive and refractory sulfur species. In general, the active sites for HDS of reactive and refractory sulfur species have been believed to be different from each other. Hence, the deactivation pattern for each site must be different.

The present study, attempted to evaluate the performance of the spent NiMo and CoMo catalysts for the HDS of gas oil by comparing their catalyst activities with those of the virgin ones. Gas refreshment to remove the gas-phase inhibitors prior to HDS was examined to provide the practical means to achieve the target with spent catalysts. Spent catalysts lost their activity due to the carbon deposition, which may cover the active sites of both sulfides and alumina support. The amount and quality of the deposited carbon must be influenced by catalyst properties and operating conditions. The spent NiMo catalyst carried more carbon and nitrogen according to elemental analyses. The carbon on the spent NiMo catalyst showed larger C/H ratio and higher intensity ratio of 1590/1350 cm−1 on Raman spectra than that on the spent CoMo. The carbon deposition decreased more severely the acidity of the NiMo catalyst, which was certainly characteristic to the particular catalyst. Such carbon is suggested to be present more preferably on the support of the higher acidity. The deposited carbon to reduce the activity of the direct HDS must also cover some of the active sulfides.

The spent catalyst lost all kinds of activities to variable extents. More loss was observed with refractory sulfur species.

The second stage with pure H2 free from H2S and NH3 restored the activity of the spent catalysts to some extent. Such hydrogen renewal must be favorable for both hydrogenation of refractory sulfur species and the direct desulfurization.

5. CONCLUSION

a. Spent catalysts apparently lost their activity due to the carbon deposition, which covered the active sites more preferentially.
b. Two-stage reaction enhanced the HDS over both spent NiMo and CoMo catalysts.

REFERENCES

D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.

E. Furimsky, F.E. Massoth, Catal. Today 17 (1993) 537.

M.J. Girgis, B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.

S. Shin, H. Yang, K. Sakanishi, I. Mochida, D. Grudoski, J. Shinn, Appl. Catal. A 206 (2001) 101.

S.D. Sumbogo Murti, H. Yang, K.-H. Choi, Y. Korai, I. Mochida, Appl. Catal. A 252 (2003) 331.

S.D. Sumbogo Murti, K. Sakanishi, O. Okuma, Y. Korai, I. Mochida, Fuel 81 (2002) 2241.

T. Isoda, X. Ma, I. Mochida, Preprint Am. Chem. Soc. Div. Petrol.Chem. 39 (1994) 584.

T. Jawhari, A. Roid, J. Casado, Carbon 33 (1995) 1561.

T. Kabe, Y. Aoyama, D. Wang, A. Ishihara, W. Qian, Q. Zhang, Appl. Catal. A 209 (2001) 237.

X. Ma, K. Sakanishi, I. Mochida, Ind. Eng. Chem. Res. 35 (1996) 2487.