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Development of a new hydrodemetallization catalyst for deep desulfurization of atmospheric residue and the effect of reaction temperature on catalyst deactivation

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Abstract

A new hydrodemetallization (HDM) catalyst with low catalytic activity was prepared to accomplish the hydrotreating of atmospheric residue (AR) under the deep desulfurization condition (sulfur content in product oil is below 0.3 wt.%). The combination of the HDM catalyst and the hydrodesulfurization (HDS) catalyst supported on an alumina with medium pore (11 nm) was applied to the hydrotreating of the AR to elucidate the effect of chemical composition of the HDM catalyst on the catalyst life. The operation, exceeding 6000 h, was accomplished over the combined catalyst system under the deep desulfurization conditions. The preferential decomposition of maltene as the heavy residue with high reactivity on the low active HDM catalyst resulted in the long catalyst life. The hydrotreating of atmospheric residue was carried out to elucidate the effect of the reaction temperature of the guard reactor on the life of HDM and HDS catalysts. When the guard reaction temperature was raised to 683 K, the catalyst was rapidly deactivated due to the deposition of coke on the catalysts. These results suggest that the separate decomposition of maltene and asphaltene is important for continuous hydrotreating of atmospheric residue.

Keywords: Residue hydrotreating; Hydrodemetallization catalyst; Catalyst deactivation; Asphaltene decomposition; Coke formation; Temperature effect

1. Introduction

It is known that the vacuum gas oil (VGO) produced by the hydrotreating (HT) process of heavy residue is supplied to an FCC process for the production of the raw material of gasoline. Since the decrease in sulfur content in the VGO is important to produce the low sulfur gasoline, the deep desulfurization of an atmospheric residue (AR) is carried out to prepare low sulfur VGO. The effective hydrotreating of heavy residue in the atmospheric residue should result in the production of low sulfur VGO. The heavy residue in atmospheric residue was divided into maltene and asphaltene, except for solid dry sludge. Maltene is the residue that dissolves in *n*-hexane while asphaltene dissolves in toluene but does not dissolve in n-hexane. The molecular weight of maltene is generally smaller than that of asphaltene and maltene is more reactive than asphaltene [1–3]. As a result, the maltene easily decomposed in the hydrotreating (HT) process. Sulfur, nitrogen and metals such as vanadium and nickel in a crude oil are concentrated in these residues. Especially, it is found that the asphaltene contains half of the metals and sulfur in the crude oil [4]. The main purpose of HT is to remove the metals and sulfur from the maltene and asphaltene.

An aliphatic chain in an asphaltene was cleaved over an HDM or HDS catalyst and resulted in an olefin and condensed aromatic ring at the reaction temperature [5]. The hydrocarbon in the ring was dehydrogenated and/or polymerized to a larger aromatic ring. Finally the large ring changed to carbon deposit [6]. The polymerization was accelerated by metals deposited on the catalyst. The authors found that when the HDS reaction of the residue with high aliphatic chain content and low sulfur content was carried

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out over a commercial HDS catalyst, the catalyst rapidly lost activity due to coke formation via the decomposition of asphaltene [7].

It has been reported that the deactivation of an HDM catalyst was caused by the deposition of metals on the pore mouth of the catalyst, because the metals mainly containing in porphyrines with a large molecular size could not penetrate into the pore of the HDM catalyst [8]. As a result, the residue with metals reacted at the pore mouth of the catalyst. On the other hand, since the molecular size of the residue with sulfur was smaller than that of pore size, the residue uniformly diffused in the pore converted to hydrogen sulfide and light fractions on the HDS catalyst. Furthermore, the coke produced from the oligomerization of the desulfurized hydrocarbon was also uniformly distributed in the pore of the catalysts. The difference in the reactivity of the residue with metals and sulfur was mainly attributed to the difference in molecular size of the residues. However, it was considered that the same distribution of metals and coke could be obtained from the difference in reactivity of the residue containing metals and sulfur. The HDS of AR separated from Kuwait crude oil (KW-AR) was carried out in a pilot scale reactor (3 m long and 500 cm^3) fixed with HDM catalyst (40 vol.%) and HDS catalyst (60 vol.%). The relationship between the coke distribution along the reactor length and time on stream was obtained after the HDS reaction operated under moderate reaction conditions. Early in the time on stream, most of the metals and sulfur were deposited on the HDM catalyst loaded at the upper part of the reactor. When the reaction was performed at severe conditions, high reaction temperature and high hydrogen pressure, the coke content on the HDM catalyst increased and rapid catalyst deactivation was observed [9]. These results indicate that both maltene with high reactivity and asphaltene with low reactivity simultaneously decomposed on the HDM catalyst under the severe reaction conditions. As the result, the deposition of coke was accelerated on the HDM catalyst. When the maltene could selectively decompose on an HDM catalyst with lower activity than the commercially obtained catalyst, the deposition of coke, which results in rapid catalyst deactivation, should be prevented.

The preliminary runs were carried out to elucidate the effect of metal content in an HDM catalyst on the activities of HDS, HDM and asphaltene decomposition. A new HDM catalyst (CDS-DM1) with a small amount of effective metals was prepared for the deep desulfurization condition. Furthermore, vanadium was also impregnated on CDS-DM1, because vanadium sulfide has weak hydrodesulfurization activity. Although vanadium was supplied from the decomposition of the AR during the reaction, it was not presented at the beginning of the reaction. The hydrotreating of the heavy residue was performed over CDS-DM1 supported on an alumina with large pore (15 nm) followed by an HDS catalyst supported on an alumina with medium size of pore (11 nm).

It is reported that the reaction temperature of a guard reactor is used to be set up a tolerant temperature (highest temperature) of catalyst to decompose rapidly the maltene and asphaltene at the beginning of the hydrotreating. However, since the maltene and asphaltene simultaneously decomposed at the guard reactor, it is considered that the catalyst deactivation should be accelerated in this operation. The effect of operation conditions on the life of the HDM and HDS catalysts is examined by a couple of operations. Furthermore, the distribution of metal contents and coke content were measured in the guard reactor and main reactor after reaction to describe the difference in the catalyst deactivation with the temperature condition in the guard reactor.

2. Experimental

2.1. Chemical composition and properties of catalysts and properties of AR

The chemical composition and properties of the HDM catalyst (CDS-DM1) prepared for the present study and HDS catalyst (CDS-R2) are listed in Table 1. The chemical composition of a commercially obtained HDM catalyst as the reference is also listed in Table 1. The average pore size of the alumina support (Support C) for CDS-DM1 was 15 nm. The content of molybdenum and cobalt in CDS-DM1

Table 1
Properties of HDS and HDM catalyst

	Catalyst name (support)			
	CDS-R2 (A)	CDS-R7 (C)	CDS-DM1 (C)	Conventional HDM (unknown)[a]
Shape and size (mm)	Tri.1.15[b]	Tri.1.15	Tri.1.15	Cylind. 1.2–6
Pore diameter (nm)	10.4	14.0	14.0	20–100
MoO_3 content (wt.%)	12.0	12.0	3.3	7.0
CoO content (wt.%)	1.0	1.0	–	–
NiO content (wt.%)	1.5	1.5	0.7	1.4
V_2O_5 content (wt.%)	–	–	4.0	–

[a] Jpn. Petrol. Inst. (Ed.), Petroleum Refining Process, Kodansha, 1998, p. 46.
[b] Trilobe shape.

Table 2
Properties of atmospheric residue

	Crude oil name		
	Khafji AR (KH-AR)	Kuwait AR (KW-AR)	Arab. Heavy AR (AH-AR)
Specific gravity (g/cm^3)	0.979	0.956	0.990
S content (wt.%)	3.95	3.77	4.08
Ni + V content (ppm)	117	74	117
CCR content (wt.%)	13.0	13.2	15
ASP content (wt.%)	8.2	6.9	8.2

was lower than that in the reference HDM catalyst. Vanadium oxide was also supported on CDS-DM1. The pore size of the alumina support for CDS-R2 was 11 nm (Support A). The properties of the catalyst supports used in this study are listed in a previous paper [7].

The preliminary runs were carried out to examine the effect of molybdenum and cobalt content on HDM and HDS activity, molybdenum oxide (4.42 wt.%), cobalt oxide (3.12 wt.%) and molybdenum oxide (4.30 wt.%) + cobalt oxide (1.29 wt.%) were supported on the alumina (Support C) by an impregnation method.

The atmospheric residue obtained from Khafji crude (KH-AR) was used for the preliminary runs in the pilot plant scale fixed bed reactor. The atmospheric residue separated from Kuwait crude (KW-AR) was used for the hydrotreating reaction over the combined catalysts. The atmospheric residue from Arabian heavy crude (AH-AR) was used for the test runs performed at different temperature in the guard reactor. The properties of the atmospheric residues (AR) are listed in Table 2. The feature of the ARs used in the study was separated from a crude oil with heavy components and with a high sulfur content.

2.2. Hydrotreating reaction

2.2.1. Hydrotreating over a new HDM catalyst at deep HDS conditions

The experimental apparatus unit used for the present study is shown in Fig. 1. The detailed assembly of the fixed bed reactor was reported in a previous paper [6]. The unit composed the guard reactor (167 cm^3) and the main reactor (500 cm^3). It was considered that the former was the HDM reactor and the latter was the HDS reactor in a commercial HT plant.

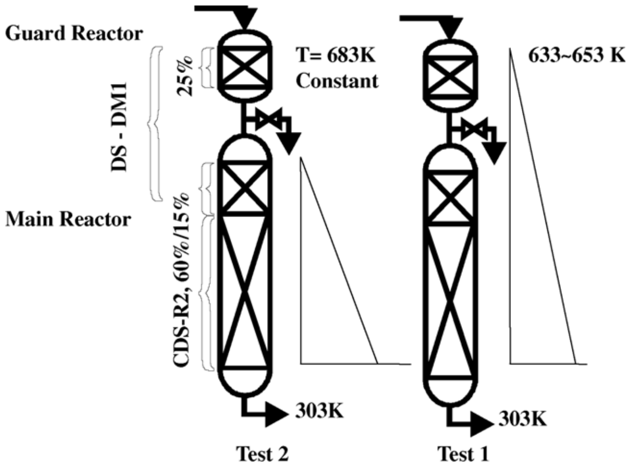

Fig. 1. Reactor assembles and temperature profile in reactors.

Table 3
Experimental conditions for preliminary run

Feed oil	Khafji atmospheric residue
Reaction temperature	653–693 K
LHSV	0.5 h^{-1}
Reaction pressure	15.0 MPa
H_2/N_2 ratio of feed gas	90/10 mol/mol
H_2/oil ratio	700 N m^3/m^3

The preliminary runs to determine the chemical composition of the HDM catalyst were carried out in the main reactor. The catalyst, 500 cm^3, was loaded in the main reactor. The experimental conditions for the preliminary runs are summarized in Table 3. The relationship between the sulfur content, asphaltene content, and metal content in the product oil and reaction temperature was examined for the reaction.

The HDM catalyst, 167 cm^3, was loaded in the guard reactor and 100 cm^3 of the HDM catalyst and 400 cm^3 of the HDS catalyst were loaded in the main reactor. As a result, the volume ratio of the HDM catalyst and HDS catalyst is 40 versus 60 as shown in Fig. 1. The temperature profile in the reactor unit is shown in Fig. 1; that is, the reaction temperature was gradually increased above 30 K from the inlet of the guard reactor to the outlet of main reactor. Since HDM and HDS are exothermic reactions, the temperature gradient was given in the pilot reactor to simulate a commercial HDM or HDS reactor [7]. The operation conditions for the combined catalyst system are listed in Table 4. In this operation, the sulfur content in the product oil was 0.1 wt.% at 4200 h from the beginning of the run and

Table 4
Experimental conditions for combined catalyst system

Feed oil	Kuwait atmospheric residue
Reaction temperature	WAT (633–693 K)
LHSV	0.16 h^{-1}
Reaction pressure	15.0 MPa
H_2/N_2 ratio of feed gas	90/10 mol/mol
H_2/oil ratio	800 N m^3/m^3
Sulfur in product	0.1–0.2 wt.%

Table 5
Operation conditions for guard reactor and guard + main reactor

Operation condition	Guard reactor	Guard + main reactor
Catalyst	CDS-DM1 (225 cm^3)	CDS-DM1 (100 cm^3) + CDSR2 (400 cm^3)
Feed oil	Arab. Heavy AR	Arav. Heavy AR
LHSV	2.0 h^{-1}	0.5 h^{-1}
Reaction pressure	15 MPa	15 MPa
H_2/N_2 ratio	90/10 mol/mol	90/10 mol/mol
H_2/oil ratio	–	700 N m^3/m^3

0.2 wt.% after 4200 h of operation time. The reaction temperature was specified to be the weight average temperature (WAT) in the operation.

2.2.2. Hydrotreating at different guard reactor temperatures

The temperature for the guard reactor was controlled in two ways: the first shown as *Test 1* in Fig. 1 was the same as the combined catalyst system previously written. In the second operation, shown as *Test 2* in Fig. 1, the temperature in the guard reactor was constant at 683 K and the temperature in main reactor was controlled from the inlet to outlet for 30 K gradient. The first row in Table 5 summarizes the reaction conditions for the guard and main reactors. On the other hand, the second row in the table lists the conditions for the guard reactor. In the operation, the sulfur content in the product oil was 0.6 wt.%.

After the reaction, the reactors were cut into several parts along the longitudinal direction. The used catalyst was collected from the parts of the reactor. The sulfur content, coke content and metal content deposited on each part of the catalyst were obtained by the following method: a prescribed weight of catalyst was loaded in a thermo-balance cell. The catalyst was heated in an air atmosphere for 5 h. The effluent gas from the thermo-balance was introduced into a SO_2 meter. The sulfur content was calculated from the sulfur concentration and the weight of the used catalyst. The coke content was determined by the balance of weight loss in the thermo-balance and sulfur content. The treated catalyst in the thermo-balance was immersed in *aqua regia* to dissolve all metals including the effective metals. The diluted solution was fed into the cell of an atomic adsorption spectrometer.

3. Results and discussion

3.1. Preliminary experiments for a new HDM catalyst preparation

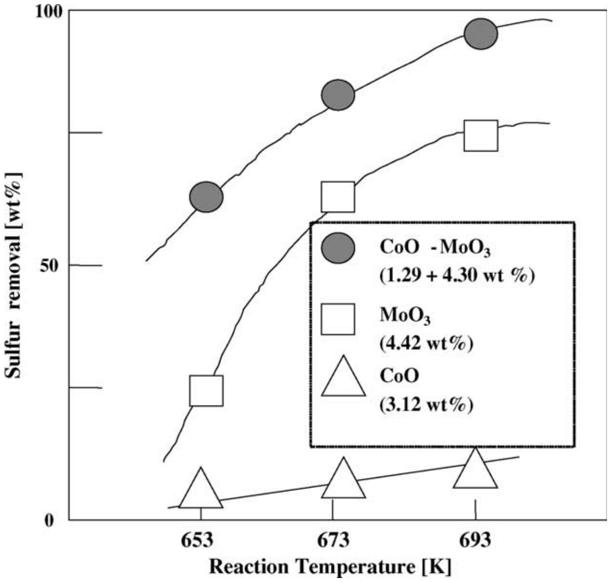

Fig. 2. Relationship between sulfur removal and reaction temperature.

The effects of kind and content of an effective metal on initial HDS activity, asphaltene decomposition activity and HDM activity were examined to prepare a new HDM catalyst. The catalyst support for the preliminary catalysts was an alumina with pore size of 15 nm. The Co (3.12 wt.%) catalyst, Mo (4.42 wt.%) catalyst and Co (1.29 wt.%) + Mo (4.30 wt.%) catalyst were prepared as preliminary catalysts. The hydrotreating of KH-AR was carried out over the preliminary catalysts under the operating conditions as shown in Table 3.

Fig. 2 shows the relationship between extent of desulfurization and reaction temperature over the three kinds of catalysts. The desulfurization activity of the Co catalyst is very low as expected, because Co is not an effective metal for HDS reaction. On the other hand, the HDS activity of the Co + Mo catalyst is highest among the catalysts. These results indicate that the Mo catalyst assisted by Co was suitable for HDS of a heavy residue. The relationship between de-asphaltene activity and removal extent of vanadium is demonstrated in Fig. 3. Although half of the vanadium weight in the KH-AR was removed at the removal rate of asphaltene of 30%, the removal rate was related to the asphaltene removal over the 30% rate. This result suggests that half of the weight of vanadium was contained in high reactive maltene. The vanadium in the maltene was easily removed under moderate reaction conditions, whereas the removal of the rest of vanadium was accomplished with the decomposition of asphaltene. Furthermore, since the relationship between the vanadium removal rate and the extent of asphaltene decomposition is a straight line over the catalysts in the preliminary runs, vanadium can be removed by the decomposition of asphaltene. From these preliminary runs, it is found that the hydrodemetallization of maltene can accelerated by a lower effective metal content than that of a commercially obtained HDM catalyst.

3.2. Hydrodemetallization activity of a new HDM catalyst

The physical properties and chemical composition of a new HDM catalyst (CDS-DM1) are listed in Table 1. The

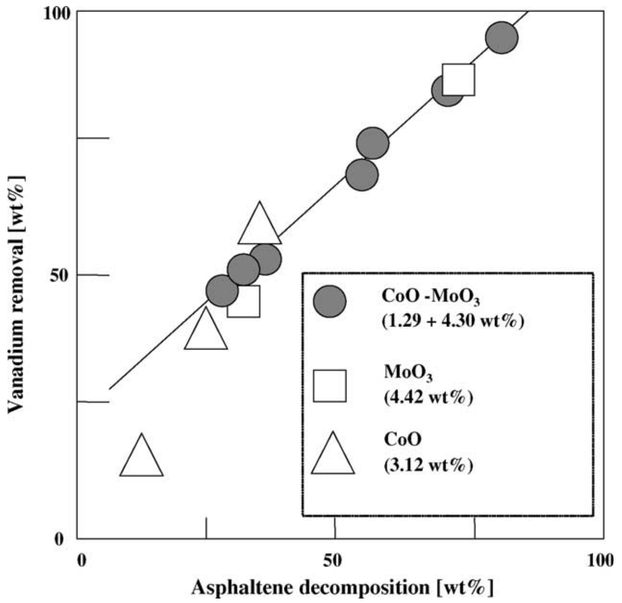

Fig. 3. Relationship between vanadium removal and asphaltene decomposition.

chemical composition of a conventional HDM catalyst as a reference is also listed in Table 1. The physical properties of a conventional HDM were not published. Since the pore diameter of a HDM catalyst was 20–100 nm, the surface area of the catalyst would be 100 m^2/g, that is smaller than that of CDS-DM1 (175 m^2/g). Furthermore, the pore volume and apparent density of CDS-DM1 are 0.65 and 0.61 g/cm^3, respectively. It was known that vanadium has weak hydrotreating activity for an atmospheric residue. Vanadium is continuously fed by the decomposition of heavy oil after the hydrotreating. However, there was no vanadium at the start of run. Then, vanadium (4.0 wt.% as V_2O_5) was impregnated on the new HDM catalyst. On the other hand, the MoO_3 and NiO contents in CDS-DM1 were smaller than that in a conventional HDM catalyst as shown in Table 1.

The new HDM catalyst (167 cm^3) was loaded in the guard reactor. The HDM catalyst (100 cm^3) and the HDS catalyst (400 cm^3) were loaded in the main reactor. This sequence is named as a ‘‘combined catalyst system’’. The hydrotreating of KW-AR was carried out at *Test 1* conditions. In this operation, the sulfur content in the product oil was designed to be 0.1 wt.% until 4200 h of operation time, whereas the content was adjusted to 0.2 wt.% after 4200 h of the operation time to maintain the HT reaction in the reactors as shown in Fig. 4. The WAT was controlled to attain the sulfur content in the product oil.

Fig. 4 shows the relationship between WAT, sulfur content in the product oil, metals deposited on the catalyst and operation time. The relationship between WAT and operation time for the hydrotreating of the same crude over CDS-R2 and CDS-R7 (500 cm^3) loaded in the main reactor as the HDS catalyst is also shown in the same figure. The chemical composition of CDS-R7 is the same as CDS-R2, but the catalyst was supported on an alumina with pore size of 15 nm (Support C) as listed in Table 1. The initial WAT for the combined catalyst system was higher than those for the HDS catalysts. However, the WAT did not exceed 673 K, that is the maximum operating temperature to protect the hydrotreating apparatus, after 7000 h of operation time. On the other hand, the WAT exceeded 673 K after 1400 h over CDS-R7 and after 2700 h over CDS-R2. Since the extent of metal deposition on CDS-DM1 is proportional to operation time for the combined catalyst system as shown in Fig. 4, metals in KW-AR were steadily removed from the AR. The used CDS-DM1 catalyst was recovered from a prescribed longitudinal distance along the reactor after an operation time of 7000 h. The relationship between longitudinal position and metal deposition was examined. It was found that most of the metals were deposited at the position of 20–30% from the inlet of the guard reactor and quite a few metals were deposited at the CDS-DM1 in the main reactor. The integrated metal weight revealed that half of the metals were deposited on the CDS-DM1 in the guard reactor. Since half of the weight of metals in the AR was involved in the asphaltene [10], it was suggested that the metals in the maltene with high reactivity were quantitatively deposited

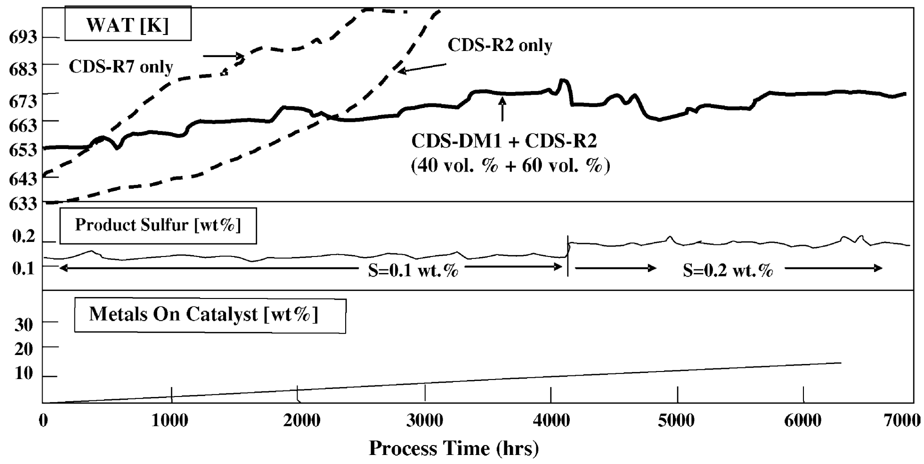

Fig. 4. Relationship between WAT, sulfur content, metals on catalyst and operation time.

on the catalyst. The HDS of the maltene and asphaltene did not proceed over the CDS-DM1, because the effective metal content in the catalyst was too small to accelerate the hydrodesulfurization of the residue. On the other hand, the HDM and HDS of the maltene and asphaltene proceeded simultaneously over CDS-R2 and CDS-R7; the coke produced by the decomposition of the heavy residues deposited on the catalyst. As a result, the catalytic activity of CDS-R2 and CDS-R7 was severely lowered with operation time as shown in Fig. 4.

The deposition of vanadium and nickel on the catalysts was increased with operation time. The vanadium had weak hydrotreating activity as mentioned above. Since the decomposition of maltene including metals was accelerated by the deposited vanadium at the outer surface of the catalyst, the HDS activity was maintained at 7000 h of operation time over the combined catalyst system. When the hydrotreating of AR was carried out over the low active HDM catalyst, the maltene and asphaltene including metals penetrated simultaneously into the pore of the catalyst. The penetrated maltene reacted on the HDM catalyst, whereas the low reactive asphaltene was desorbed from the catalyst without decomposition. The asphaltene with metals flew down the main reactor and gradually decomposed on the HDM and HDS catalysts. Since the metals were smoothly deposited along the flow direction of the guard reactor, stable operation as shown in Fig. 4 was accomplished.

It has been reported that the deep hydrodesulfurization of a treated atmospheric residue, which contained 0.3 wt.% of sulfur but did not contained metal, was carried out over a HDS catalyst to reduce the sulfur content to 0.1 wt.% [11]. As a small amount of sulfur in the AR should be removed by the HDS catalyst, it was considered that this operation was continued for a long period. But the HDS operation over CDS-R2 was terminated at an early reaction period because the coke produced by the decomposition of asphaltene was deposited on the catalyst surface. On the other hand, sulfur reduction from 3.9 to 0.1–0.2 wt.% was accomplished over the combination of a low active HDM catalyst (CDS-DM1: 40 vol.%) and the HDS catalyst (CDS-R2: 60 vol.%). These results indicate that stable hydrotreating was continued by the prevention of local deposition of coke and metals by the use of the combined catalyst system as shown in this section.

3.3. Effect of guard reactor temperature on catalyst life

According to two kinds of temperature profiles as shown in Fig. 1, the hydrotreating of KW-AR was carried out to reduce the sulfur content from 3.9 to 0.6 wt.%. Fig. 5 shows the effect of guard reactor temperature on WAT, the sulfur

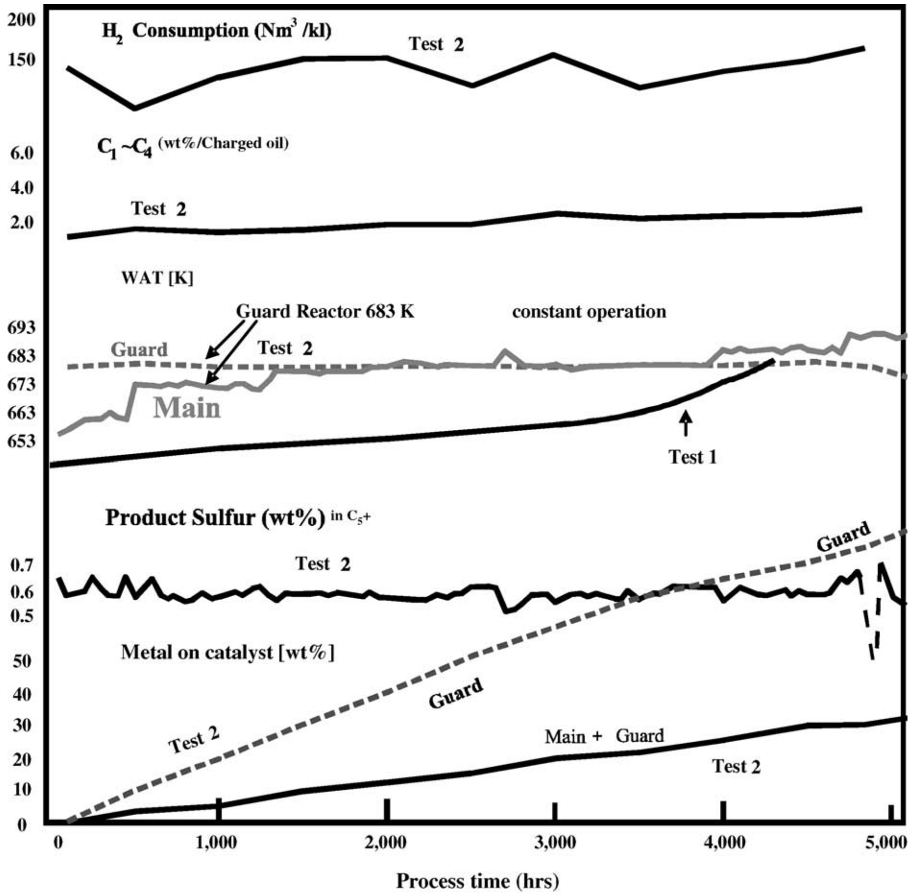

Fig. 5. Comparison of reaction results between *Test 1* and *Test 2*.

Table 6
Properties of product oil at different operation time

	Feed oil	SOR		MOR		EOR	
	AH-AR	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1
Operation time (h)		500	2500		4000		
Fraction							
C1–C4 (wt.%)	–	1.4	0.82	1.88	1.36	2.42	1.53
C5-464 K (vol.%)	0.2	1.0	1.0	0.9	0.8	1.4	1.2
464–616 K (vol.%)	4.3	14.0	13.9	16.5	16.8	20.9	17.5
616K$^+$ (vol.%)	95.5	84.8	85.1	83.0	81.5	76.5	80.9
Product oil							
Specific gravity (15/4 °C)	0.990	0.924	0.925	0.920	0.920	0.914	0.917
S content (wt.%)	4.08	0.59	0.57	0.64	0.61	0.61	0.62
Viscosity (cSt at 323 K)	2930	91	110	67	90	20	60
CCR (wt.%)	15.1	5.8	5.9	5.7	5.8	5.8	5.3
Asphaltene (wt.%)	8.2	4.3	4.7	3.7	5.3	4.8	4.6
Ni content	26	22/11	21/10	19/9	22/13	22/9	23/12
Guard/main (ppm)							
V content	91	44/22	54/24	39/15	58/27	51/20	59/24
Guard/main (ppm)							
Dry sludge (wt.%)	1	2	1	4	1	5	2

content in the produced oil and the extent of metal deposition on the catalyst (metal on catalyst; MOC). When the metal was rapidly removed by the HDM catalyst loaded in the guard reactor under high temperature operation (*Test 2*), it was considered that the WAT in the main reactor under *Test 2* should be lower than that under *Test 1*. It means that the catalyst life under *Test 2* should be longer than that under *Test 1*. The temperature of the guard reactor was adjusted to high in most of the hydrotreating process in Japan.

However, the WAT curve for *Test 2*, shown by the dotted line in Fig. 5, rapidly increased with operation time and reached the guard reactor temperature at 1300 h of operation time. On the other hand, the WAT for *Test 1* gradually increased with time and was 683 K after 4200 h of the operation time. Although the sulfur content in the production oil shows some scatter, the content is about 0.6 wt.% under the both operation conditions. Furthermore, the metal content on the HDM catalyst at the guard reactor was 76 wt.% at 5000 h of operation time under *Test 2* conditions, whereas the metal content on the HDM catalyst averaged at the guard reactor and main reactor was 28 wt.% at 5000 h of operation time under *Test 1* conditions. From these results, it was found that when the temperature in the guard reactor was increased up to the limit of the catalyst tolerance temperature, the catalyst life, not only in the guard reactor but also in the main reactor, decreased.

Table 6 lists the properties of the product oil under both temperature conditions for the guard reactor. The properties of the feed oil are also listed in the first row of Table 6. The properties of the product oil at operation time were specified as: the time up to 500 h after the reaction was ‘‘Start of Run’’ (SOR), the time after 2500 h was ‘‘Middle of Run (MOR)’’ and the time after 4000 h was ‘‘End of Run’’ (EOR). The metal content obtained from the guard reactor outlet and from the main reactor outlet is shown in Table 6. The asphaltene content for *Test 2* at SOR and MOR is smaller than that for *Test 1*, but no difference between *Test 2* and *Test 1* is observed at EOR. The properties of the product oil did not change between *Test 1* and *Test 1*. In the experiment, the WAT was controlled to attain 0.6 wt.% of sulfur content in the product oil. The WAT of the main reactor for *Test 1* is 675 K after 4200 h of operation time, whereas the WAT for *Test 2* exceeded 683 K after 2500 h as shown in Fig. 5. The temperature of the guard reactor was maintained at 683 K for *Test 2*; the asphaltene in the AR easily decomposed at that temperature and changed to coke or its precursor in the guard reactor. The deposition of coke should be responsible for the catalyst deactivation. These results indicate that the guard temperature affected catalyst deactivation, even when the same catalysts were loaded in the guard reactor and main reactor.

The used catalysts were collected from the guard reaction and main reactor after 4000 h of operation time under two kinds of operation procedures to clarify the effect of guard reactor temperature on catalyst deactivation. The longitudinal distribution of metal and coke on the catalyst fixed in the guard reactor and main reactor was measured. The metal and coke content was calculated on the base of the weight of fresh catalysts. The metal and coke distribution is shown in Figs. 6 and 7, respectively. When the guard reactor was maintained at 683 K (*Test 2* conditions), the metal content deposited in the guard reactor is almost 100% at the inlet of the reactor as shown in Fig. 6. This means that the same weight of metal with the catalyst is deposited. On the other hand, the content of the metal deposition for *Test 1* conditions is maximum at 15% at a down flow position from the inlet of the guard reactor. The maximum deposition of metal is about 60 wt.% of the fresh catalyst. The content of the metal deposition decreases with the distance from the inlet of the reactor. The clear difference of metal deposition between *Test 1* and *Test 2* is not observed over the HDS catalyst as shown in Fig. 6. The average metal deposition

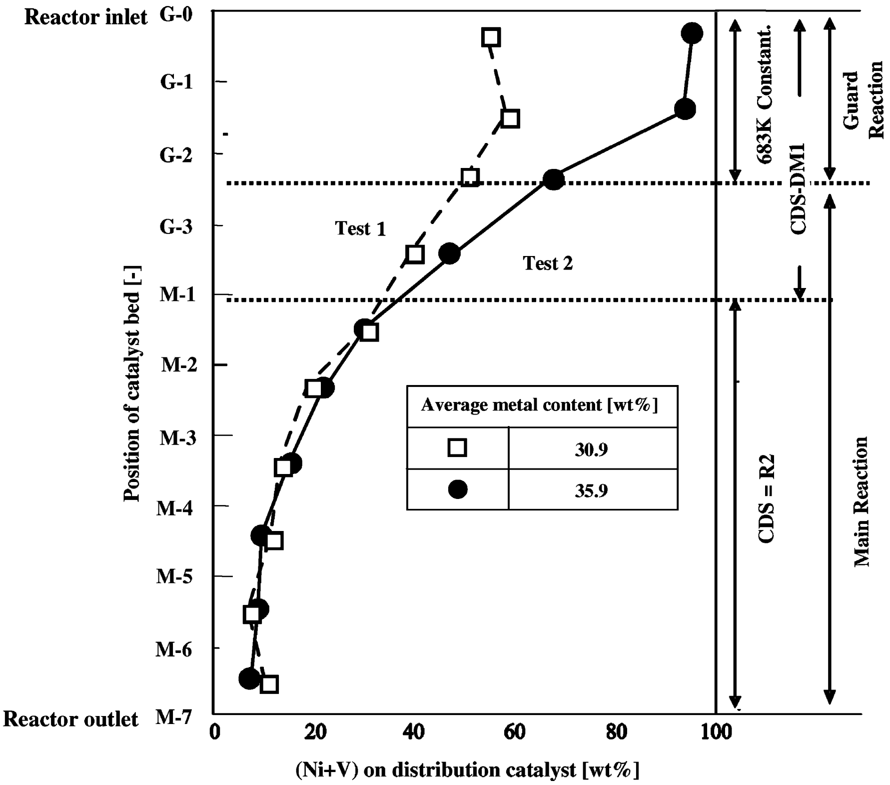

Fig. 6. Metal distributions on catalyst bed.

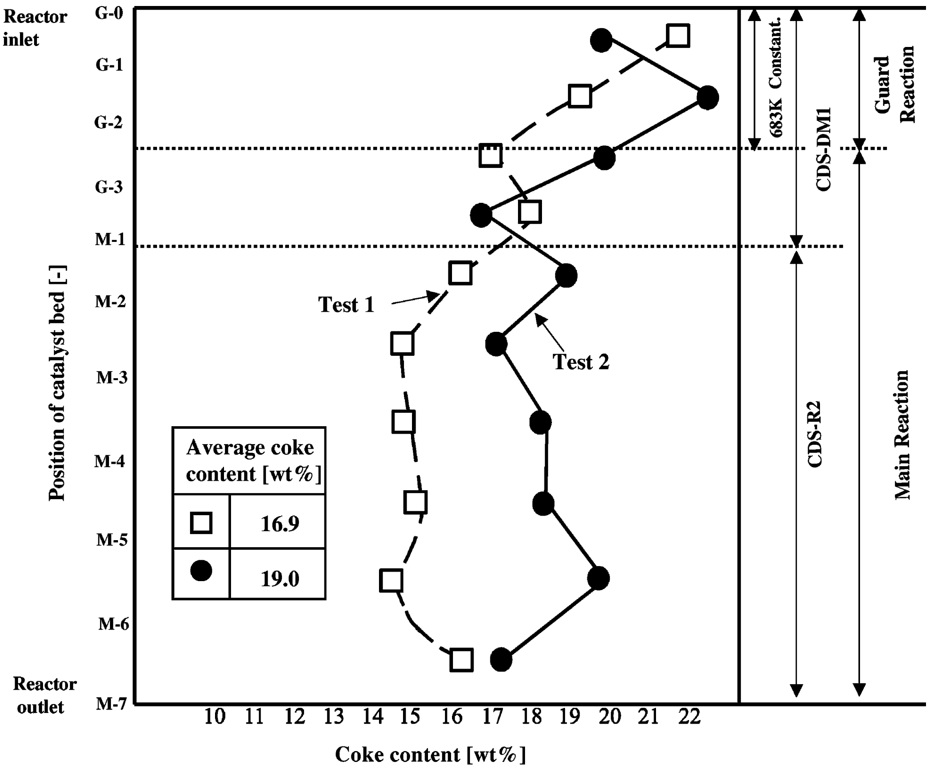

Fig. 7. Coke distributions on catalyst bed.

rates for *Test 1* and *Test 2* were 30.9 and 35.9 wt.%, respectively.

The metal removal ratio for *Test 2* calculated from product oil at SOR and MOR was larger than that for *Test 1* as shown in Table 6; it was considered that the deposited metal content for *Test 2* was larger than that for *Test 1*. It was found that the content of metals on the HDS catalyst decreased with the distance from the reactor and reached 5 wt.% at the outlet of the main reactor. The metal content in the product oil at EOR is 25–31 wt.% of the feed oil. Furthermore, since the metal content in the product oil at the outlet of the guard reactor is 62–70 wt.%, the HDM reaction occurred on the HDS catalyst. Although the content of nickel in the product oil was 50 wt.% of the feed oil, the content of vanadium was about 25 wt.%. Nickel in the feed oil was not removed in the guard reactor at the SOR to EOR as shown in Table 6. These results indicate that the residue with vanadium is more reactive than that with nickel.

The content of coke deposition for *Test 2* is larger than that for *Test 1* as shown in Fig. 7. The content is especially large in the guard reactor maintained at 683 K and it decreases in the main reactor operated at lower temperature than the guard reactor. The content in the main reactor is 18–20 wt.% for *Test 2* conditions. On the other hand, the content is largest at the inlet of the guard reactor and decreased with the distance from the inlet. The average coke content deposited on the HDS catalyst is 14–16 wt.%. The average coke contents from the guard reactor to main reactor were 16.8 wt.% for the *Test 1* operation and 19.0 wt.% for the *Test 2* operation. It was considered that a part of the coke or its precursor was removed as a dry sludge shown in the last row in Table 6 from the outlet of the main reactor. The content of dry sludge for *Test 1* is almost same as that in feed oil, but the content for *Test 2* increased from the SOR to EOR. At the same time, since the fraction of gas, gasoline and light oil increased, the heavy residue predominantly decomposed with the increase in reaction temperature for *Test 2* operation.

Idei et al. examined the relationship between coke content on an HDS catalyst and operation time in a pilot plant size fixed bed reactor [12]. They found that the coke was deposited on the HDS catalyst in early operation time and decreased with the deposition of metals. The deposited coke was gradually hydrogenated on the catalyst. The non-volatile metals were deposited on the catalyst for the coke. The coke content at early operation time was 20 wt.%, but decreased as shown in Fig. 7 with the deposition of metals in this study. Since part of coke was removed as dry sludge, the coke content was 19 wt.% for *Test 2* operation.

When the reaction temperature in the guard reactor loaded the HDM catalyst was raised to 683 K, it was found that the catalyst deactivation rate in the main reactor loaded the HDM and HDS catalysts was significantly accelerated. Since the temperature in the guard reactor was maintained at 683 K, the maltene and asphaltene in the heavy residue easily decomposed to coke or its precursor and light fractions, such as gases, gasoline and light oil. The produced coke was deposited on the HDM and HDS catalysts and the catalytic activity was lost in a short operation time. From these results, it was considered that the reaction temperature in the guard reactor loaded with the low active HDM catalyst should be maintained at a low level to preferentially decompose the maltene with metals. Then the metals from maltene were deposited on the HDM catalyst. These operations should be effective to prevent the deactivation of the HDM and HDS catalysts.

4. Conclusion

A new HDM catalyst with a smaller amount of effective metals than a conventional catalyst was prepared to prolong the life of the catalyst for deep desulfurization conditions. The HDM catalyst combined with the HDS catalyst supported on alumina with medium pore size was used for hydrotreating of the residue (sulfur content was 3.9 wt.%) obtained from Kuwait crude oil. The new developed HDM catalyst (100 cm^3) and the HDS catalyst (400 cm^3) were loaded in the main reactor. The hydrotreating was carried out on the combined catalyst system to elucidate the effect of the HDM catalyst on catalyst deactivation at the deep desulfurization conditions [sulfur content in product oil was 0.1 (up to 4200 h) to 0.2 wt.% (after 4200 h)]. Catalyst deactivation was examined from the relationship between weight average temperature to attain the specified sulfur content (WAT) and operation time. The HDS catalyst used in the study (HDS-R2, 500 cm^3) and an HDS catalyst with larger pore (HDS-R7, 500 cm^3) than the HDS-R2 was also loaded in the main reactor. The relationship between WAT and operation time over the catalysts was also obtained as a reference. The WAT for the combined catalyst system did not exceed 683 K after 7000 h of operation time, whereas the WAT for CDS-R7 and CDS-R2 exceeded 683 K after 1400 and 2700 h, respectively. These results indicate that the combination of a low active HDM catalyst to HDS-R2 was effective for prolonging catalyst life.

The 167 cm^3 of the HDM catalyst (HDS-DM1) was loaded in the guard reactor and 100 cm^3 of the HDM catalyst and 400 cm^3 of the HDS catalyst (HDS-R2) were loaded in the main reactor. The hydrotreating of the atmospheric residue was carried out in the reactors under two conditions for different temperature gradients; that is, the temperature was continuously controlled from the inlet of the guard reactor to the outlet of the main reactor (*Test 1*) and the temperature in the guard reactor was constant at 683 K (*Test 2*). The effect of temperature gradient on catalyst deactivation was examined by experiments. When the temperature in the guard reactor, loaded with HDM catalyst, was maintained at 683 K (*Test 2*) to decompose rapidly a maltene and asphaltene with metals, the removal rate of metals in the guard reactor increased, but the deactivation rate was significantly increased due to coke deposition on the HDM and HDS catalysts in the main reactor, even low active HDM catalyst was loading. The increasing of guard reactor temperature resulted into the acceleration of the decomposition rate of maltene and asphaltene, and the deposition of metal and coke on the inlet of the guard reactor. This deposition was responsible for the rapid catalyst deactivation.

It is considered that the separate decomposition of maltene and asphaltene over low active HDM catalyst and at low reaction temperature is important for deep hydrodesulfurization of atmospheric residue.

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