Study on the Hydrodesulfurization Catalyst of Residual Fuel (Part 5)

— Deposits on the Used Catalyst* —

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Summary: In the present work, using the catalysts used in the long run activity tests, the deposits of the carbonaceous materials, vanadium and nickel on the catalyst beds or on the surface of the catalyst particles was investigated. From the experimental results, the following conclusions were obtained.

- (1) In the early stage of the formation of the deposits, the amount of deposits was dependent on the temperature distribution inside the reactor. However, with the progress of reaction time, the amount was apt to increase more in the lower part of the catalyst bed rather than in the upper part. The average amount of the deposited carbon became constant after 100 hours on stream and the increase afterward was not recognised. The average amount varied with the kinds of the catalysts and the amount of asphaltene contained in the feed oil.
- (2) Though varied with the catalyst, vanadium deposited more in the upper part of the catalyst bed and less in the lower part. The activation energy of the vanadium was about 10 kcal/mol.
- (3) Though nickel is similar in behavior to vanadium which tends to deposit more in the upper part and less in the lower part, it spreads out more widely on the whole catalyst bed.
- (4) On the catalysts of smaller mean pore diameter, the vanadium deposited in little amount, thinly but densely on the surface. While, on the catalysts of larger mean pore diameter, it deposited in large amount, but sparsely on the surface, and deeply as far as the considerably inner part. Nickel, like vanadium, deposited in much amount and spread to as far as the considerably deep inner part of the catalyst particles. Carbon deposited inside of cracks or holes which had been supposedly produced during preparation of the catalyst.

1 Introduction

Among organic metallic compounds, the following two kinds are generally known.

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Namely, one is what exist by themselves like nickel porphyrin and vanadil porphyrin, and the other is what exist in the form of micelle combined with asphaltene moleculars. These compounds are considered to be very unstable against heat, easily decomposed by contact with catalysts, depositing metals such as vanadium or nickel and forming carbonaceous material. Conceivably, these metals and carbon deposited on the surface of the catalysts will cause a decrease of the catalyst activity. Besides these materials, iron and alkaline earth metals which are contained in feed oil also tend to deposit physically on the surface of catalysts and are supposed to also cause a decrease of the catalyst activity.

In the present work, the factors which would be concerned with a decrease of the catalyst activity were studied. Deposits of carbon, vanadium and nickel which were large in amount, were selected and their state of deposition on the catalyst bed which had been used in the normal activity test and in run length tests¹⁾

(1,000 to 3,000 hours) were investigated. Two catalysts which had different pore properties among the catalysts used in the long run test for 3,000 hours were selected. The state of deposition on catalyst particles of the above materials was observed by the X-ray micro-analyzer.

2 Experiments

2.1 Catalysts

In the present study, the used catalysts in the long run tests for 1,000 to 3,000 hours were mainly used. The reaction conditions were mentioned in the previous paper. Physical properties of new catalysts were also reported in the previous paper¹⁾.

2.2 Analysis of Deposited Materials on Catalysts

To analyse the deposited materials on the catalysts, the oil in the used catalysts was removed by a Soxhlet extractor, refluxing with benzene or trichlene for a given period. After sufficient extraction, the catalysts were picked up, dried at 120°C under a reduced pressure and made for samples.

Analysis of carbon was done by the micro element analysis method. The deposited amount of carbon was shown by wt%, against a new catalyst. Analytical methods of vanadium and nickel were the same as reported in the previous paper²⁾.

2.3 X-Ray Micro-Analyzer Analysis

The X-ray micro-analyzer was ARL EMX-1 type manufactured by Shimadzu Manufacturing Co.. As sample, one particle of catalysts (size was about 1.5 mm×7 mm) was fixed on a thermo plasticizing resin and polished its cross section planely. It was measured by accelerating voltage of 20 kW.

3 Results and Discussion

3.1 Carbon Deposit on Used Catalysts

Up to the present time, in the usual activity test for 100 hours, the formation conditions of carbon were studied from various points; and it became clear that the amount of carbon deposit in the early stage of reaction was mainly

concerned with the temperature distribution inside the reactor. Also, it was studied that the amount of deposits on the surface of catalysts tended to increase much more in the lower part of the bed than in the upper part with progress of reaction time, and an average deposited amount, though different according to kinds of feed oil and catalysts, was in the range from 10 wt% to 20 wt%.

In the following, the tendency of the formation was further investigated using the used catalysts in the long run activity tests. At first, the catalyst beds which were used for the desulfurization of atmospheric distillation residue of Khafji crude was divided into 5 or 6 parts equally from the top of the reactor and the amount of carbon deposit on each sample was measured. The results were shown in **Table 1**.

As seen in **Table 1**, except catalyst KS-56, the amount of carbon deposit tended to increase slightly from the upper to the lower part of every catalysts. The average deposited amount after 100 hours on-stream and after 1,000 hours on-stream was almost similar as clearly seen by comparing with the value of 13.7 wt% for KS-56. Consequently, it was assumed that carbon was formed rapidly by a decomposition reaction which occurred in a comparatively short period at the start of reaction. Thereafter, the reaction mainly took place for desulfurization and the formation of carbon was restrained. The average deposited amount of carbon on the catalyst KS-52 was high (19.9 wt%) for reason that it was heated at a temperature up to 430°C in an another experiment after the long run activity tests.

Next, using the commercial and test catalysts which were used in the long run activity tests for 2,000 to 3,000 hours where the feed oil was the atmospheric distillation residue of Kuwait crude, the formation of carbon was studied. The catalysts KC-28, KS-83 and KS-97 were divided into two parts; upper and lower parts, and KS-103, KS-111 and KS-124 were divided into four parts on each of the catalyst beds. The results were shown in **Table 2**.

As seen in **Table 2**, on every catalyst, carbon deposited more in the lower parts than in the

Table 1 Carbon Distribution on the Used Catalyst Bed (wt%)

		KS-41 1,134 Hours on Stream	KS-43 1,425 Hours on Stream	KS-22 1,448 Hours on Stream	KS-52 1,256 Hours on Stream	KS-56 100 Hours on Stream
Catalyst Bed	Upper					
	1	13.9	10.9	17.5	19.3	15.2
	2	15.8	10.9	13.9	18.4	14.9
	3	14.3	11.2	13.3	18.9	14.3
	4	15.8	12.9	14.4	20.5	13.8
	5	15.4	14.4	16.4	20.7	10.3
	Lower					
	6		15.6	16.0	21.5	
	Average	15.0	12.7	15.3	19.9	13.7

Table 2 Deposited Carbon on Used Catalyst Bed

Cat. No.	Time on Stream (hr)	Sampling Position	C (wt%)	H (wt%)	C/H	Average C/H
KC-28	100	U	8.75	1.56	5.62	6.11
		L	7.13	1.08	6.60	
KS-124	100	U	11.61	1.59	7.32	7.38
		L	9.76	1.31	7.44	
KS-100	100	U	8.83	1.61	5.48	5.93
		L	6.38	1.00	6.38	
KC-28	3,000	U	8.96	1.05	8.53	8.31
		L	10.1	1.25	8.08	
KS-83	3,000	U	9.86	1.18	8.36	9.54
		L	12.0	1.12	10.71	
KS-97	3,000	U	10.1	1.00	10.10	10.5
		L	13.5	1.24	10.89	
KS-103	2,000	U	11.36	0.84	13.52	13.68
		L	14.12	1.02	13.84	
KS-111	2,000	U	13.20	0.88	15.00	12.7
		L	17.05	1.64	10.40	
KS-124	2,000	U	11.54	1.74	6.08	10.08
		L	18.26	1.35	13.53	

* U: Upper part of catalyst bed.
L: Lower part of catalyst bed.

Fig. 1 Correlation between the Deposited Carbon and Time on Stream

upper parts. The results showed the same tendency as with the experimental results previously obtained about the residual fuel of Khafji crude. Change in amount of carbon deposit with time was measured and plotted in **Fig. 1**, where the ordinate indicates an average amount of carbon deposit and the abscissa indicates time of on-stream.

As seen in **Fig. 1**, the amount of carbon deposit is independent on the differences in the preparation methods and the desulfurization activity of catalysts. There was almost no change in the amount of carbon deposit between that after 100 hours on-stream and that after 1,000 hours and 3,000 hours on-stream in both experiments using Khafji residual fuel and Kuwait residual fuel. The amount of carbon deposit in the experiment using Khafji residual fuel was larger by about 5 wt%, than in the experiment using the Kuwait residual fuel. In connection with this, there was a report by Beuther et al.³⁾, that in an experiment comparing the carbon deposit between Kuwait atmospheric distillation residue and its deasphalted residual fuel, the amount of deposit in the deasphalted fuel was less. In consequence, our experimental results were conceivably caused by the difference

of amount of asphaltene in the feed oil, namely, Khafji residual fuel contained more asphaltene than the Kuwait residual fuel.

Also, Beuther et al. reported that the amount of carbon deposit was larger when the reaction pressure was low, than that when the reaction pressure was high and tended to increase even after 100 hours on-stream. The authors of the present work measured tentatively the amount of carbon deposit on a few catalysts selected optionally from the test catalysts used in 100 to 200 hours test on-stream under a reaction pressure 50 kg/cm² and obtained the results of 20 to 25 wt%. As seen in **Fig. 1**, under the experiment of a reaction pressure of 100 kg/cm², deposit of carbon was restrained to about 15 wt% and thus similar tendency to Beuther's experimental results was observed in our experiment. Under the condition of reaction pressure of 100 kg/cm², the amount of carbon deposit became almost constant after 100 hours on-stream. Consequently, it was assumed that the deposit of carbon on the surface of catalysts was formed mostly in the early stage of reaction and the amount became almost constant after 100 hours of on-stream. This fact was considered to explain the phenomenon that in the usual activity test, catalyst activity declined markedly in the early 50 hours from the start. Also considering the relation between the desulfurization activity and the acidity of catalyst, the amount of carbon deposit in the early stage of reaction was supposedly connected with acidic sites of catalyst and when the acidic sites which were concerned with a decomposition were covered with carbon, the catalyst was considered to show a very stable desulfurization activity.

Then, to get some information about the changes of the structure of the deposited carbon

on catalysts, C/H ratios (shown in **Table 2**) were compared each other. As seen in **Table 2**, C/H ratio of deposited carbon on the catalysts after 100 hours on-stream was about 5.5~7, while C/H ratio after 2,000~3,000 hours on-stream was 8~13. Therefore, from these facts, the amount of carbon deposit was supposed to become almost constant after 100 hours on-stream and the increase thereafter was not noticed. Further, the deposited carbon on the catalysts of respectively different time on-stream was investigated by the X-ray diffraction. As a result the carbons were found to be amorphous and such observation as the remarkably progressed crystallinity was not obtained.

3.2 Vanadium

The amount of vanadium deposited on the used catalysts in the long run activity tests was measured and plotted in **Fig. 2**, where the amount of vanadium (wt%) was in ordinate and the position in a catalyst bed was in abscissa. As clearly seen in **Fig. 2**, the vanadium deposited abundantly on the upper part of catalyst bed, and decreased gradually as the position came to the lower part of catalyst bed. Moreover, the following points were especially noticed in the results shown in **Fig. 2**, that on the catalysts KS-22 and KS-124 which had showed superior activity in the long run activity tests, the amount of vanadium deposit decreased almost in a straight line from the upper to the lower part

Fig. 2 Vanadium Distribution on the Used Catalyst Bed

of the catalyst beds, though it was large in average of 5.3 wt% and 7.5 wt% respectively. On the other hand, in case of the catalysts KS-52, KS-103 and KS-111 which showed comparatively inferior activity in the long run tests, though the average amount of carbon deposit was small, it showed the tendency to decrease in a "S" shape curve from the upper to the lower beds. From these differences in the states of deposition, such consideration was made that with the catalysts of superior activity, the vanadium removal ability of per unit volume was large; while with the other catalysts on which the state of deposition of vanadium was in "S" shape curve there was different vanadium removal power per unit volume of catalyst and the catalyst pores were plugged up by vanadium from the upper part of the catalyst bed at first and gradually downward. In consequence, the decline of the catalyst activity after 100 hours on-stream as revealed in the long run tests was assumed to indicate the state of deposited vanadium on the catalysts beds and also the state of pores plugg-up on the catalyst beds.

3.3 Nickel

The state of deposition of nickel on the catalyst beds with used catalysts KS-41, KS-22 and KS-52 from the long run activity tests were shown in **Fig. 3**. As seen in **Fig. 3**, in the order

Fig. 3 Nickel Distribution on the Used Catalyst Bed

of the amount of nickel deposit, KS-22 was placed firstly, then KS-52 and in last KS-41, and the deposited nickel was distributed almost in a straight line from the upper to the lower part of the catalyst beds of every catalyst. This was very similar in tendency to that of vanadium. However, the gradient of each straight line shown in the figure was found to be simple compared with that of vanadium. Hence, nickel compounds were supposed to have a very difficult inclination in their decomposition compared with the vanadium compounds.

3.4 Effects of Reaction Temperature on Metal Removal Reaction

From vanadium removal and nickel removal obtained in the long run activity tests of the catalysts KC-28, KS-83 and KS-97, the ratio of vanadium removal against nickel removal was calculated and plotted in **Fig. 4**, where the ordinate indicates the ratio and the abscissa indicates the reaction temperature. From **Fig. 4**, the relations as expressed by the following formulas were obtained;

regarding KC-28

$$y = 0.00030000x^2 - 0.2454x + 51.15$$

regarding KS-83

$$y = 0.00088571x^2 - 0.7006x + 39.56$$

regarding KS-97

$$y = 0.00033571x^2 - 0.2709x + 55.70$$

In the experimental results up to the present, both vanadium removal and nickel removal were observed to increase in a straight line in proportion to the increase of the reaction temperature when their relations against the reaction temperature were plotted separately. However, their ratio was expressed by a quadratic function against the reaction temperature as shown above, and it seemed to suggest that selectivity for vanadium removal and nickel removal of the catalysts varied with reaction temperature. From the results of observation shown in **Fig. 4**, such considerations would be made that under the reaction temperature of 400°C, the selectivity of the catalysts was more for nickel removal, and in reverse, above the temperature of 400°C, the catalysts showed a preferential selectivity for vanadium removal. And in KS-83, this tendency was seen remarkably as the temperature was raised higher compared with KC-28 and KS-97. Further, the above facts were confirmed by measurements of physical

Fig. 4 Correlation between Reaction Temperature and Vanadium Removal/Nickel Removal

properties of KC-28 and KS-83. As a result, pore size distribution and mean pore diameter were found to be very different and conceivably the mechanism of changes in pore properties of catalysts seemed to vary differently and remarkably according to differences of reaction conditions.

3.5 Metal Removal Reaction Rate

Tentatively, to study the reaction rate of metal removal, the reaction order concerning vanadium removal was investigated as an instance. From the vanadium content in the desulfurized oil obtained in our test, it was assumed that the vanadium removal reaction against the vanadium concentration could be expressed by the following equation;

$k_1 = -\text{LHSV} \ln(1-C)$ in a first order reaction rate equation

$k_2 = \text{LHSV} C/C_0(1-C)$ in a second order reaction rate equation

where

C: Fractional conversion, calculated by the equation

$$C = 1 - \frac{\text{Vanadium in Product, ppm. by wt.}}{\text{Vanadium in Charge, ppm. by wt.}}$$

C_0 : Vanadium concentration in charge, ppm. by wt.

k_1, k_2 : Reaction rate constant

values of $-\ln(1-C)$ or $C/C_0(1-C)$ in the ordinate and reciprocals of LHSV in the abscissa were plotted in **Fig. 5**.

Regression line formulas:

— First order $y_1 = 0.2831x + 0.4997$
(confidence limit of 99.9%)
---- Second order $y_2 = 0.0135x + 0.0104$
(confidence limit of 99.9%)

Fig. 5 Reaction Order of Vanadium Removal Reaction

As seen in **Fig. 5**, between the function shown in $-\ln(1-C)$ or the function shown in $C/C_0(1-C)$ and the reciprocals of LHSV, Liquid Hour Space Velocity, the linear relations were obtained as expressed by the following equation;

$y_1 = 0.2831x + 0.4997$ in a first order reaction
where

$$y_1 = -\ln(1-C)$$

$$x = (\text{LHSV})^{-1}$$

and

$y_2 = 0.0135x + 0.0104$ in a second order reaction
where

$$y_2 = C/C_0(1-C)$$

$$x = (\text{LHSV})^{-1}$$

and these equations were valid with the confidence limit of 99%.

In order to examine which of the rate equations would be an applicable one, the variances of the plotted dots from the regression were expressed in the standard deviations, and then the values obtained by dividing the standard deviations by the gradient were compared. As a result, no remarkable differences among them were recognized. On the other hand, concerning the desulfurization reaction, the reaction rate of individual sulfur compounds was expressed by the first order, in the residual oil where the desulfurization reactions regarding various sulfur compounds progressed successively, the over-all desulfurization was consolidated apparently in the second order equation. In the same manner, though the reaction rate of simple organometallic compounds such as vanadilporphyrin etc. was shown by the first order⁴⁾, as it was supposed that various kinds of metallic compounds of different composition might be contained in the vanadium organic compounds in the residual oil similarly to the sulfur compounds in the residual oil, the vanadium removal reaction of various vanadium compounds was considered to progress one after another, and it was satisfactory to consider that the vanadium removal reaction was expressed apparently by the second order equation.

Then, for trial the activation energy of the vanadium removal reaction was calculated from the vanadium removal obtained when the reaction temperature was raised high, using the catalysts KS-103, KS-111 and KS-124 which were used in the long run tests. The rate constant k calculated from the second order reaction rate equation was shown in the common logarithms and was indicated in the ordinate and the reciprocal of the absolute temperature was indicated in the abscissa. The results were shown in Fig. 6, with the Arrhenius plots.

As seen in Fig. 6, though the Arrhenius-plotted dots were scattered considerably widely, the following regressive line formulas were obtained for KS-103

$$y = 8.28 - 2.365x$$

a straight line which was valid with confidence

Fig. 6 Correlation between Reaction Rate Constant and Reaction Temperature

limit of 99%. As for KS-124,

$$y = 7.59 - 1.967x$$

a straight line which was valid with confidence limit of 90%, where

$$y = \log k$$

$$x = 1/T$$

From the gradient of each straight line, the activation energy of the catalysts were calculated as follows; 8.2 kcal/mol in KS-103, 10.8 kcal/mol in KS-111 and 9.0 kcal/mol in KS-124. In consequence, the activation energy at the vanadium removal reaction was estimated to be about 8~10 kcal/mol.

3.6 Observation of Catalyst Surface by the X-ray Micro-Analyzer

The authors carried out the observation of the catalyst surface by the X-ray micro analyzer to investigate the state of the deposited materials on the catalysts after 3,000 hours on-stream.

Namely, using the used catalysts KC-28 and KS-83, the section of a particle of each catalyst (the particle was an extrudate of 1.5 mm in diameter and from 5 to 10 mm in length), which was collected from the upper and the lower part of the catalyst beds, was irradiated with electron and analysed for elements with the generated X-ray. Among the elements, there were aluminum contained in the support alumina, Mo and Ni which were contained in the loaded metals on the support, vanadium, sulfur and carbon which were deposited on the catalysts. The results were shown on the pictures A-F, where white part indicates elements and the arc indicates the outer surface of the catalysts.

First of all, aluminum was shown. As seen in the picture, aluminum was found to exist uniformly on every section of the catalysts. It was a matter of course because alumina was used as the support of all the catalysts. Among a series of the pictures, black dots or black ditches which were seen in the picture of KS-83 (lower) Al,

were thought to be of holes which were brought about at the time of preparation of the support.

Next, observing Mo and Ni which were the loaded metals on the catalyst supports, Mo was loaded comparatively uniformly dispersed, while Ni was considered to be somewhat unevenly dispersed. Next, observing Ni on KC-28, though it was distributed widely as far as the center of the catalysts, comparatively large

amount was found on the surface. However, as for the loaded metals, only Mo-Co were used and Ni was not used. Subsequently, Ni seemed to be the deposited nickel formed by the decomposition of nickel porphyrin etc. contained in the residual oil. Our observation that large amount of nickel existing on the surface of the catalyst was somewhat different from Beuther et al.'s consideration that nickel deposited evenly as

A₁ KC-28 (upper)
Support Alumina
Al

B₁ KC-28 (upper)
Supported Metal
Mo

C₁ KC-28
Deposited Metal
Ni

A₂ KS-83 (upper)
Support Alumina
Al

B₂ KS-83 (upper)
Supported Metal
Mo

C₂ KS-83
Supported Metal
+
Deposited Metal
Ni

A₃ KS-83 (lower)
Support Alumina
Al

F KS-83 (lower)
Deposited Carbon
C

Observation of the Surface of Used Catalyst Particle by the X-ray Micro Analyzer

far as the center of the catalyst. These differences in the state of deposition of nickel were considered to come from the difference in pore structure between the catalysts.

Then, looking at the state of disposition of vanadium, remarkably large amount of deposit was observed only on the surface of every catalyst. Here, a very interesting point was that in the upper part, the vanadium deposited into a rather deeper point from the surface than in the lower part on the catalyst KC-28. Its deposited amount was about 5.5 wt% in the upper part, while in the lower part was about 4.5 wt%. Further, it was found that on the test catalyst KS-83, the vanadium deposited up to the depth of about 300~400 μ from the surface, compared with about 150~200 μ in depth on KC-28. This seemed to mean that on the catalysts whose mean pore diameter were smaller (the mean pore diameter of KC-28 was 76.5 Å and that of KS-83 was 114.6 Å), the vanadium deposited on the catalysts in a thin-layered and densely state and, on the catalysts whose mean pore diameter were larger, the vanadium deposited up to the inner part of the catalysts sparsely. The catalyst life of KC-28 was calculated to be

179.4 days and of KS-83 to be 285 days. From these results, it might be considered that such catalysts where the vanadium deposited uniformly and deeply up to the inner part of the catalysts would be preferable since deposited vanadium would give the least effects on the catalyst life.

Then, as for sulfur on the surface of the catalysts, as seen in the analytical results of the vanadium and the loaded metals on the catalyst KC-28, the loaded metals on the catalyst and the vanadium deposited on the catalyst were noticed to exist in the form of sulfides.

The deposited carbon on the surface of the catalysts concentrated in the cracks which were supposedly produced at the time of the formation or calcination of the support, and it was not observed so remarkably on the surface judging from the comparison of the analytical results of the support of KS-83 (Al) with the analytical results of the carbon. These experimental results seemed to explain the observation in the long run tests that independent on the time of on-stream, the amount of carbon deposit on the catalyst surface was kept a constant. Therefore, the facts that the amount of carbon deposit was

different with the catalysts which had been prepared by the same method were supposed to suggest the difference of volume of the cracks which grew inside the catalysts at the time of the formation and calcination of the support.

4 Conclusion

From the above considerations, the following conclusions were obtained;

(1) In the early stage of the formation of the carbon deposit, its amount varied according to the temperature distribution inside the reactor. However, with the progress of reaction time, the amount was apt to increase more in the lower part of the catalyst bed rather than in the upper part. And its average amount became definite after 100 hours on-stream and the increase afterward was not noticed. The average amount of deposit differed with the kinds of catalysts and was remarkably effected by amount of asphaltene in the feed oil.

(2) Judging from the increase of the C/H ratio of the carbon deposit on the catalyst, the crystallinity of the carbon was considered to be progressing with time on-stream.

(3) The decline of the catalyst activity in the early stage of the reaction (1~50 hours on stream) was assumed to be due to the formation of the carbon deposit and the decline of activity afterward was assumed to be due to the deposition of metals, such as vanadium etc. on the catalysts.

(4) Vanadium, though different with the catalyst, deposited more in the upper part of the catalyst bed and as the position came downward, the amount decreased. The activation

energy was about 10 kcal/mol.

(5) Nickel, similar to the behavior of vanadium, had a trend to deposit more in the upper part and less as the position came downwards. Comparing with the state of deposition of vanadium, nickel deposited widely on the whole catalyst bed.

(6) On the catalysts having small mean pore diameter, vanadium deposited in small amount, thin-layered and densely on the surface, while on the catalysts with large mean pore diameter, it deposited in large amount but sparsely on the surface and deeply as far as the considerably inner part of the catalysts. Nickel, like vanadium, deposited in large amount and considerably deeply as far as the inner part of the catalyst particles. The carbon deposited inside the cracks or holes which were supposedly produced at the time of preparation of the catalyst.

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