Effective Active Sites of Hydrodesulfurization Catalyst for Residue Fraction

Ryuichiro Iwamoto* and Narinobu Kagami

Idemitsu Kosan, 28FI JP tower, 7-2 Marunouchi 2-Chome, Chiyoda-ku, Tokyo, 100-7028, Japan

* *ryuichiro.iwamoto@idemitsu.com*

Abstract: Effective HDS reaction pathway for residue hydrodesulfurization (ARDS) catalyst was investigated by characterizing and testing performance of used commercial ARDS catalysts. There are two HDS reaction pathways such as direct HDS route and hydrogenation HDS route. Dibenzothiophene (DBT) HDS testing of used ARDS catalysts clearly revealed that active sites for hydrogenation route easily deactivated under the ARDS reaction condition, while those for direct HDS route stays alive. Therefore, increasing of direct HDS sites might be effective and easier way to improve ARDS catalyst.

Keywords: Residue Hydrodesulfurization, Used catalyst characterization, HDS reaction route.

1.Introduction

Removal of sulfur from petroleum fractions is very important for achieving sustainable society. Especially, desulfurization of residue fuel oil is global urgent issue to meet recent strict regulation proposed by International Marin Organization (IMO). Improvement of HDS catalyst activity could be one of effective ways. HDS reaction has been studied from the aspect of reaction pathway such as direct HDS route and hydrogenation route. Balance of these two reaction pathway is significantly important to get higher HDS performance. In case of deep gas oil HDS, improvement of hydrogenation route is reported to be very effective to get better catalyst performance 1). However, less investigation was reported on effective HDS route for residue HDS catalyst. Only effect of catalyst combinations on deactivation behavior has been studied by some researchers 2-4). In this paper, we focused on the elucidation of effective active sites for residue HDS reaction by comparing used catalysts from commercial unit with fresh catalysts.

2. Experimental

Commercial NiO-MoO_3 based catalysts were used in this study. Catalysts were loaded into a commercial ARDS unit and then operated to produce fuel oil. After commercial operation for one year, catalyst samples with different content of coke and contaminant metals (vanadium and nickel) were taken from different part of the reactor (**Fig. 1**). The used catalysts thus obtained were washed with toluene using soxhlet extractor before characterization such as EPMA and EXAFS. The concentrations of various metals (V, Ni, Mo) on catalyst were determined by inductively coupled plasma analysis (ICP). Coke and sulfur on catalyst were analyzed by LECO meter. DBT-HDS was carried out using a fixed bed high pressure flow micro reactor. The 2.5 ml of catalyst sieved from 16 to 32 mesh without dilution was loaded into the reactor. Then, the catalyst was presulfided at 523 K, LHSV 7.0 h^{-1}, 15 or 30 kg/cm^2 and H2/oil = 250 Nl/l by feedstock containing 1.18 wt% sulfur was prepared by dissolving DBT in tetraline. After presulfiding, the temperature was increased to between 553 and 573 K.

3. Results and discussion

3.1 Characterization of used ARDS catalysts

Table 1 shows properties of used ARDS catalysts obtained from different parts of reactor. The upper part of catalyst contained more contaminant metals (vanadium and nickel) accumulated from the feed. On the other hand, lower part of catalyst contained much higher coke. It is considered coke tends to generate under lower hydrogen pressure and higher temperature condition. Since EPMA result reveals that contaminant metals accumulates preferably on the surface of catalyst particles, it might not be main and direct cause of deactivation. Therefore, coke should be the main cause of deactivation. EXAFS also indicates that the size of active metal (MoS_2) increases during reaction.

Table 1 Properties of used ARDS catalysts

		Fresh	U-1	U-2	U-3	U-4	U-5	U-6	U-7	U-8
S.A.	(m^2/g)	195	81	97	107	98	N/A	107	N/A	92
Coke	(wt%)	-	15.2	19	18.6	24.9	23.3	24.3	27.2	29.2
Ni	(wt%)	-	2.8	2.0	1.5	1.0	0.8	0.9	0.7	0.6
V	(wt%)	-	8.1	4.8	3.2	2.1	1.6	1.7	1.3	1.2

**The chemical contents are dased on fresh catalyst*

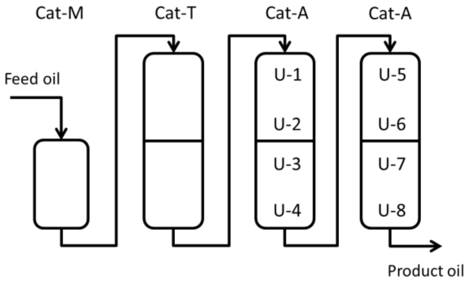

Fig. 1 Sampling points of used ARDS catalyst

3.2 Catalyst performance

Fig. 2 shows yield of product by DBT-HDS reaction using used ARDS catalysts from different loading place in commercial reactor as well as fresh one. Fresh catalyst gave product such as biphenyl (BP) derived from direct HDS route and cyclohexylbenzene (CHB) derived from hydrogenation route as well as unreacted DBT. On the other hand, used catalyst gave the almost same BP yield as fresh catalyst, while extremely lower yield of CHB than fresh catalyst. In addition, the effect of loading position was not obvious in this DBT-HDS reaction. These results mean that the direct HDS route activity rarely deactivates, while hydrogenation route activity deteriorates significantly. **Fig. 3** shows comparison of CHB selectivity for DBT-HDS reaction over different type of ARDS catalysts. The initial CHB selectivity over fresh catalysts was different among some catalysts, while those for used catalyst seemed to be almost same. These results indicate again that active sites for hydrogenation route easily deactivated under the ARDS reaction condition due to mainly coke deposition, while those for direct HDS route stay alive. Therefore, it might be right way to increase direct HDS site for improving ARDS catalyst life.

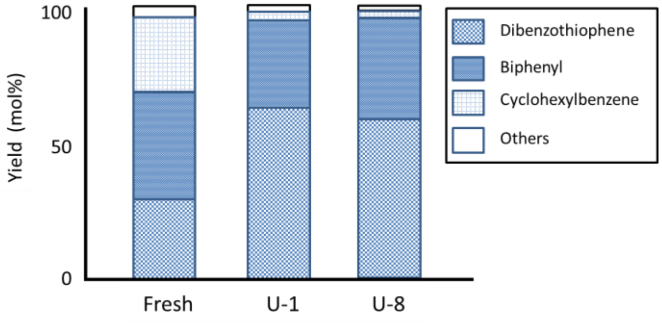

Fig. 2 Product yield of DBT HDS for fresh and used ARDS catalysts

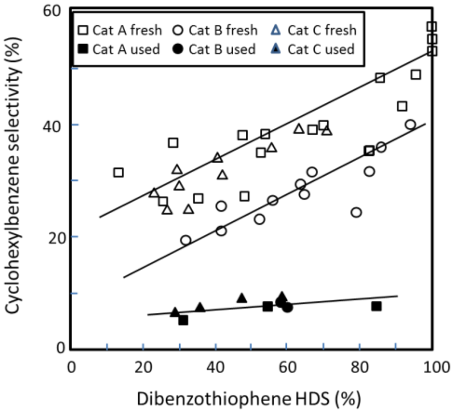

Fig. 3 Selectivity of CHB for DBT HDS reaction

4. Conclusions

Effective active sites for ARDS catalyst were investigated. In case of gas oil deep HDS that improvement of hydrogenation activity is effective to release steric hindrance of refractory sulfur compounds. It seems to be also effective to improve the hydrogenation activity of ARDS catalyst, because more sulfur compounds with steric hindrance exist in heavier feed. However, excess coking circumstance of ARDS reaction makes unable to retain its hydrogenation site. Therefore, in case of ARDS catalyst, it might be effective and better way to improve catalyst life by increasing direct HDS site.

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