ELSEVIER

Catalysis Today 29 (1996) 267–271

CATALYSIS TODAY

Characterization of Ni–W/Al_2O_3–SiO_2 aromatics saturation catalysts used in a one-year commercial HDS run

H. Makishima [a,*], Y. Tanaka [b], Y. Kato [c], S. Kure [d], H. Shimada [e], N Matsubayashi [e], A. Nishijima [e], M. Nomura [f]

[a] *Japan Energy ARC Co., Ltd., 3-17-35 Niizo-Minami, Toda-shi, Saitama 335, Japan*
[b] *Showa Shell Sekiyu K.K., 123-1, Shimokawairi, Atugi-shi, Kanagawa, Japan*
[c] *Cosmo Research Institute, 1134-2 Gongendo, Satte, Saitama 340-01, Japan*
[d] *Nippon Oil Co., Ltd., 8 Chidori-cho, Naka-ku, Yokohama, Kanagawa 231, Japan*
[e] *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan*
[f] *Photon Factory, National Laboratory for High Energy Physics, Oho-machi, Ibaraki 305, Japan*

Abstract

A series of Ni–W/Al_2O_3–SiO_2 catalysts with different Al_2O_3/SiO_2 ratios were prepared and loaded in a commercial HDS unit for a year. The catalytic properties of the freshly sulfided and spent catalysts were investigated by performing structural analyses and model test reactions. The aggregation of the WS_2 slabs in the lateral direction, which was observed by EXAFS and TEM, was a major cause of the catalyst deactivation. The addition of SiO_2 into the catalyst support was found to suppress the structural changes of the catalyst.

Keywords: Ni–W catalysts; Al_2O_3–SiO_2 supports; Hydrodesulfurization

1. Introduction

As compared with a large number of studies on the activities and properties of Ni–Mo and Co–Mo [1–4] hydrodesulfurization (HDS) catalysts, smaller number of papers have been published on Ni–W catalysts [5]. In recent years, however, increasing attention has been paid on Ni–W catalysts, which were reported to be superior in aromatics hydrogenation (HY) to Co–Mo or Ni–Mo catalysts [6], because of a concern about the high aromatics contents in diesel fuels [7]. In the present study, we have prepared a series of Ni–W/Al_2O_3–SiO_2 catalysts with different Al_2O_3/SiO_2 ratios by a common preparation method. The main purpose of the present paper is to discuss the deactivation causes through the characterization of the used Ni–W catalysts in a commercial hydrodesulfurization unit for vacuum gas oil.

2. Experimental

2.1. Catalyst preparation

Ni–W/SiO_2–Al_2O_3 catalysts with 6 mol-% loading of Ni and 12 mol-% loading of W were prepared by impregnation using mixed supports with different Al_2O_3/SiO_2 molar ratios of

---

[*] Corresponding author.

SSDI 0920-5861(95)00283-9

100/0 (= Si(0)), 70/30 (= Si(30)) and 50/50 (= Si(50)). A canister packed by the prepared catalysts was located in a HDS unit for vacuum gas oil. The unit was operated for a year under 60 kg/cm^2 of H_2 pressure at a temperature from 633 to 673 K (average 653 K) with maintaining 0.09 wt.-% of sulfur content in the product oil. Freshly sulfided catalysts as references to the spent catalysts were prepared in a flow of 5% H_2S in H_2 at 673 K for 2 h.

2.2. Structural characterization

W L_{III}-edge EXAFS measurements were carried out in the transmission mode at the BL-10B of the Photon Factory in the National Laboratory for High Energy Physics in Japan. TEM photographs and XPS spectra were obtained using a Hitachi H-9000 UHR microscope and a Phi 5000 Ci spectrometer, respectively.

2.3. Catalytic activity

The HY activities of the fresh and spent catalysts were measured in a 50 cm^3 micro autoclave using 1-methylnaphthalene (1-MN) and diphenylmethane (DPM) as probe compounds. A total yield of 1- and 5-methyltetralin from 1-MN and a total yield of dicyclohexylmethane and benzylcylohexane from DPM were indexed as 'HY(1-MN)' and 'HY(DPM)', respectively. The reactions were performed at 583 K (1-MN) and 673 K (DPM) with an initial hydrogen pressure of 6.9 MPa for 1 h.

3. Results and discussion

3.1. EXAFS

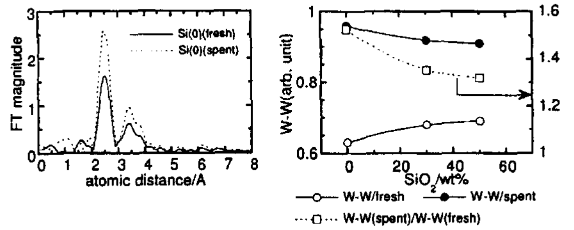

Fig. 1. EXAFS results. (a) Fourier transforms of the fresh and spent catalysts Si(0). (b) Change in the W–W peak magnitude of the Fourier transformations of the EXAFS spectra during the run.

Fig. 1a shows the Fourier transformations of the W L_{III}-edge EXAFS spectra for the fresh and spent catalysts. Two peaks at about 2.43 and 3.35 Å are assigned to W–S and W–W, respectively. Although the features of all the catalyst spectra are same as those of crystalline WS_2, the magnitudes of W–S and W–W peaks are quite different, as shown in Fig. 1b.

For the fresh catalysts, the magnitude of the W–W peak increases as the SiO_2 content in the support increases. The W–W peak magnitude in each spent catalyst is significantly higher than that of the corresponding fresh catalyst, indicating that the WS_2 slabs grow in the lateral direction during the run. Among the spent catalysts, the W–W magnitude decreases with increasing SiO_2 content, in contrast to the fresh catalysts. The crystal growth of the WS_2 slabs during the run, which is calculated by dividing the W–W (spent) by the W–W (fresh), is less evident on the support with higher SiO_2 content, as shown in Fig. 1b.

As reported in many papers [8,9], the Al_2O_3 supports anchor the catalyst species more tightly as compared to the SiO_2 supports. The interaction between W and Al_2O_3, thus, leads to less aggregated sulfide structure on the Al_2O_3-rich support during the sulfiding procedure. However, Fig. 1b suggests that the WS_2 slabs on Al_2O_3 are more mobile during the run as compared to those on the Al_2O_3–SiO_2 supports.

3.2. TEM

Fig. 2 shows the TEM photographs of the fresh and spent catalysts. The fresh catalyst Si(0) contains mostly single- or two-layer slabs, while the other fresh catalysts with SiO_2 in the supports contain three-layer or thicker slabs.

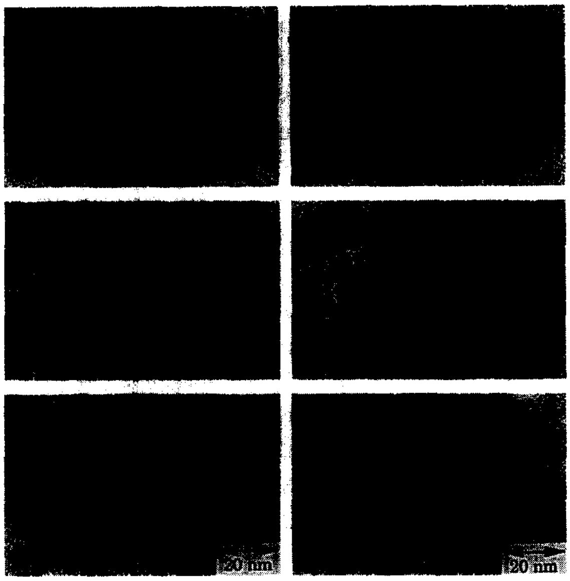

Fig. 2. TEM photographs of the catalysts studied. In the left side, fresh catalysts. Si(0), Si(30), Si(50) from the top. In the right side, spent catalysts. Si(0), Si(30), Si(50) from the top.

The addition of SiO_2 into the catalyst support promotes the formation of the multilayer slabs.

Fig. 2 indicates that the WS_2 slabs in the spent catalysts are much larger in the lateral direction than the slabs in the fresh catalysts. Among the spent catalysts, the slab sizes evidently decrease with increasing the SiO_2 content in the support. These observations are well consistent with the results from the EXAFS spectra which give more averaged information including very small clusters invisible by TEM [3]. The above results indicate that the addition of SiO_2 into the catalyst support suppresses the growth of slabs in the lateral direction.

3.3. XPS

Table 1 summarizes the semiquantitative analytical results of the catalysts. For all the catalysts, irrespective of fresh or spent, the atomic ratios of W/S are about 2.3, indicating that the major tungsten species in the catalysts are WS_2. Some amounts of silicon species are deposited on the catalyst during the run, as observed in the spent Si(0) catalyst. On the assumption that the same amount of silicon is deposited on the other catalysts, the catalyst/support ratios are calculated by dividing the concentration of tungsten by that of the sum of aluminum and silicon after the subtracting the concentration of the deposited silicon. Higher W/(Al + Si) ratio is observed for each spent catalyst than the corresponding fresh catalyst, suggesting that more coke is deposited on the support than the catalytically active Ni–W sulfide.

The Ni/W ratio of each spent catalyst is lower than that of the corresponding fresh catalyst, as shown in Table 1. This implies that the tungsten species reside on the catalysts surface, while nickel species are covered by coke or migrate inside during the run. The change in the Ni/W ratio during the run, which decreases with increasing SiO_2 content in the support is presumably related to the structural change of the active sites.

3.4. Catalytic activity and property

HY activities of the catalysts as a function of the SiO_2 content are shown in Fig. 3a. Among

Table 1
Semiquantitative analysis of the fresh and spent catalysts by XPS

		atom.-%						W/(Al + Si)	S/W	Ni/W
		O 1s	Ni 2p3	S 2p3	Al 2p	Si 2p	W 4f7			
Si(0)	fresh	50.9	1.4	7.8	36.5	–	3.4	0.09	2.3	0.41
	spent	46.8	1.4	11.1	29.8	5.8	5.0	0.17	2.2	0.28
Si(30)	fresh	49.0	1.7	9.7	26.3	9.3	4.1	0.12	2.4	0.41
	spent	49.1	1.7	10.3	21.7	12.7	4.7	0.17	2.2	0.36
Si(50)	fresh	50.1	1.2	8.7	19.7	16.3	3.9	0.11	2.2	0.32
	spent	49.9	1.4	9.7	17.1	17.7	4.4	0.15	2.2	0.31

Each atomic concentration is calculated using sensitivity factors in Ref. [10] and normalized excluding carbon.

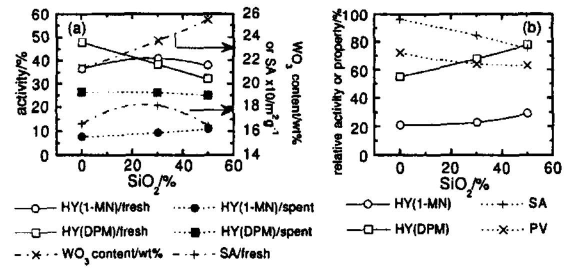

Fig. 3. HY activities and physical properties of the catalysts. (a) HY activities of the fresh and spent catalysts, and surface area and WO_3 content of the fresh catalysts. (b) Relative HY activity, surface area and pore volume of the spent catalysts relative to the fresh catalysts.

the fresh catalysts, the HY(DPM) activity decreases as the SiO_2 content increases. The increase in the HY(DPM) corresponds to the decrease in the magnitude of W–W peak in EXAFS spectra, indicating that the small WS_2 slabs with relatively large numbers of edge sites are needed for the enhancement of the HY(DPM) activity. As shown in the TEM photographs, the increase of the SiO_2 content in the support causes the development of multilayered WS_2 structure. Thus, the multilayered structure is not advantageous for the HY(DPM) activity, consistent with a previous discussion that the HY active sites are located at the edge sites of MoS_2 slabs having direct interaction with the support [4].

The relative HY activities of the spent catalysts relative to the fresh catalysts are shown in Fig. 3b, together with the relative surface area (SA) and pore volume (PV). As the SiO_2 content increases, the relative HY activities increase in spite of the decrease in the SA and PV. The reduction in the pore diffusion, mainly due to coke deposition, is not the cause of the difference in the catalyst deactivation among the catalysts.

For the spent catalysts, the HY(DPM) activity decreases as the SiO_2 content increases in spite of the small WS_2 slabs in the SiO_2-rich catalysts. The dependence on the SiO_2 content is, however, much smaller than that among the fresh catalysts (Fig. 3a). The interaction between W and Al_2O_3 is presumably more advantageous for HY(DPM) activity than that between W and SiO_2. However, the active sites on Al_2O_3 is more easily deactivated than those on Al_2O_3–SiO_2. As a result, the relative HY(DPM) activity of the spent catalyst (Fig. 3b) increases with increasing SiO_2 content, corresponding to the smaller structural changes of the catalyst observed by EXAFS, TEM and XPS.

As shown in Fig. 3b, the relative HY(1-MN) activity of the spent catalyst increases with increasing SiO_2 content. The tendency is in agreement with that observed for the HY(DPM) activity, indicating that the HY(1-MN) active sites on Al_2O_3 are deactivated to a greater extend than those on Al_2O_3–SiO_2. For the fresh catalysts, however, the HY(1-MN) activity is less dependent on the SiO_2 content than the HY(DPM) activity, as shown in Fig. 3a. This may imply that the catalytically active sites for HY(1-MN) are not completely identical to those for HY(DPM) and less sensitive to the catalyst structures.

4. Conclusion

The EXAFS and TEM analyses have evidently indicated the growth of WS_2 slabs in the lateral direction during the commercial HDS run. The WS_2 aggregation which decreases the number of the catalytically active sites is found to be a major catalyst deactivation cause. It is also found that the addition of SiO_2 to the catalyst support decreases or suppresses the growth of WS_2 slabs.

Acknowledgements

The authors greatly appreciate the cooperation of Koa Oil Co., Ltd. for charging our prepared catalysts into the commercial plant. The authors also thank Mr. T. Kameoka of Catalysts and Chemicals Industries Co., Ltd. for the activity measurements. The EXAFS measurements have been performed under the collaboration agreement between the National Laboratory for High Energy Physics and the Petroleum Energy Center in Japan.

References

[1] H. Topsøe and B.S. Clausen, Catal. Rev. Sci. Eng., 26 (1984) 295.

[2] R. Prins, V.H.J. de Beer and G.A. Somorjai, Catal. Rev., Sci. Eng., 31 (1989) 1.

[3] Eijsbouts, J.J.L. Heinerman and H.J.W. Elzerman, Appl. Catal. A, 105 (1993) 53.

[4] T. Kameoka, T. Sato, Y. Yoshimura, H. Shimada, N. Matsubayashi and A. Nishijima, Sekiyu Gakkaishi, 37 (1994) 497.

[5] D. Gachet, M. Breysse, M. Cattenot, T. Decamp, R. Frety, M. Lacroix, L. de Mourgues, J.L. Portefaix, M. Vrinat, J. Bachelier, D. Cornet, P. Engelhard, C. Gueguen and H. Toulhoat, Catal. Today, 4 (1988) 7.

[6] J.P. Frank and J.F. Le Page, Proc. 7th Int. Congr. Catal., (1981) 792.

[7] A. Stanislaus and B.H. Cooper, Catal. Rev. Sci. Eng., 36 (1994) 75.

[8] H. Shimada, N. Matsubayashi, T. Sato, Y. Yoshimura, A. Nishijima, N. Kosugi and H. Kuroda, J. Catal., 138 (1992) 746.

[9] G. Muralidhar, B.E. Concha, R.L. Barthlomew and C.H. Barthlomew, J. Catal., 89 (1984) 274.

[10] J. Chastain (Editor), Handbook of X-ray Photoelectron Spectroscopy, Perkin–Elmer, 1992.