Catalytic Functionalities of Supported Tungsten Sulfide Catalysts

INTRODUCTION

Sulfided Co–Mo and Ni–W catalysts are well established in hydrotreating of petroleum fractions (1). Such catalysts are attracting increased attention in heavy residue processing as well as coal liquefaction and upgrading of coal-derived liquids (2). Various reactions catalyzed by these catalysts are hydrogenolysis, hydrogenation, and hydrocracking. The above three functionalities not only are required for an effective hydrotreating catalyst but also should be appropriately balanced. For example, indiscriminate and excessive hydrogenation consumes costly hydrogen. To be able to prepare effective well-balanced sulfided catalyst it is necessary to gain knowledge on the origin of different functions of the catalyst and their dependence on nature of the support composition, etc., variables. Such studies on molybdenum sulfide catalysts are reported in the literature (3) while corresponding studies on tungsten catalysts are not available. To bridge the gap, we have attempted to evaluate catalytic functionalities of various catalysts derived from a series of SiO_2–Al_2O_3 supports with varying silica/alumina ratios. A series of such catalysts was prepared and their catalytic functionalities were differentiated and assessed by simple model test reaction like thiophene hydrogenolysis and hydrogenation of cyclohexene. Low-temperature oxygen chemisorption is widely used to measure active sites on supported molybdenum catalysts (4). Its use has been extended to Ni–W catalysts recently (4–7). In this investigation, an attempt is made to correlate above-said catalytic functionalities with low-temperature oxygen chemisorption.

EXPERIMENTAL

The catalysts were prepared by incipient wetting of the respective commercial supports with a solution of appropriate concentration of ammonium metatungstate. The impregnated samples were dried in air at 120°C for 16 h and then calcined in air at 540°C for 16 h. The nickel-promoted catalysts were prepared from oven-dried 19% W on various supports by impregnation with the nickel nitrate solution of appropriate concentration in an identical manner.

Oxygen chemisorption was measured using a conventional static high-vacuum system with a provision to sulfide the catalyst in situ by flowing CS_2/H_2 mixture, following the procedure of Parekh and Weller (8). The same system was also used to measure BET surface areas. Details of the experimental setup and chemisorption procedure are given elsewhere (9). X-ray diffractograms were recorded on a Philips P.W. 1051 diffractometer by using nickel-filtered CuK_α radiation.

Thiophene hydrodesulfurization (HDS) and cyclohexene hydrogenation (HYD) activities were evaluated on a catalyst sulfided at 400°C in a flow of CS_2/H_2 mixture, in a fixed bed reactor operating at atmospheric pressure and interfaced with a six-way sampling value for product analysis. Details of the reactor and activity calculation were given elsewhere (9).

RESULTS AND DISCUSSION

The catalysts were characterized by X-ray diffraction, surface area measurement, and low-temperature oxygen chemisorption. The results of these investigations are presented in Table 1. It can be seen that all

277

TABLE 1

Characterization Data on SiO_2–Al_2O_3-Supported Tungsten Catalysts

Catalyst support composition	W^a support			Ni/W^b support	
	Surface area $(m^2 g^{-1})$	XRD	O_2 Chem. $(\mu mol\ g^{-1})$	XRD	O_2 Chem. $(\mu mol\ g^{-1})$
Al_2O_3	182	—	36.58	—	39.71
25% SiO_2–Al_2O_3	402	—	26.14	—	35.46
75% SiO_2–Al_2O_3	406	WS_2	14.81	WS_2	21.05
SiO_2	478	WS_2	12.00	WS_2	16.06

[a] Unpromoted catalysts have 19% W on each support.
[b] Promoted catalysts have 3% Ni + 19% W on each support.

the supports are of high surface area and the surface area is sufficiently high to accommodate a monolayer of tungsten sulfide on these catalysts. X-ray diffractograms showed no characteristic lines due to tungsten sulfide up to 25% SiO_2 in the support. However, 75% SiO_2-containing catalyst and SiO_2 catalyst showed characteristic tungsten sulfide peaks. These results indicate that tungsten is well dispersed on Al_2O_3 and on catalyst containing a lower percentage of SiO_2. This observation is in agreement with Chan et al. (10). Oxygen chemisorption data on both promoted and unpromoted tungsten sulfide on various SiO_2–Al_2O_3 is also presented in Table 1. It can be seen that in the case of both promoted and unpromoted catalyst oxygen chemisorption decreases linearly with silica contents. Oxygen adsorbs on anion vacan-

cies which are active sites for hydrogenation and hydrogenolysis; the decrease of oxygen chemisorption indicates that active sites are decreasing with increasing silica content in the support.

Catalytic activities for thiophene hydrodesulfurization and cyclohexene hydrogenation on various promoted and unpromoted SiO_2–Al_2O_3-supported catalysts are presented in Table 2. The hydrodesulfurization-to-hydrogenation ratios (HDS/HYD) are also presented in Table 2. Variation of catalytic functionalities of promoted tungsten sulfide catalyst with silica content in the support is plotted in Fig. 1. It can be seen that hydrogenation decreases linearly with silica content and hydrodesulfurization decreases at first sharply at low silica content and more slowly at higher SiO_2 content in the support. It is significant to

TABLE 2

Effect of Support on Catalytic Functionalities of W Catalysts

Catalyst/support composition	Unpromoted[a]			Promoted[b]		
	$r_{HDS} \times 10^3$ (mol h^{-1} g^{-1} cat.)	$r_{HYD} \times 10^3$ (mol h^{-1} g^{-1} cat.)	HDS/HYD	$r_{HDS} \times 10^3$ (mol h^{-1} g^{-1} cat.)	$\gamma_{HDX} \times 10^3$ (mol h^{-1} g^{-1} cat.)	HDS/HYD
Al_2O_3	8.84	47.02	0.18	44.99	86.23	0.52
25% SiO_2–Al_2O_3	4.80	44.89	0.11	15.87	79.46	0.20
75% SiO_2–Al_2O_3	3.05	29.89	0.10	8.56	55.39	0.15
SiO_2	1.05	20.05	0.05	2.5	45.0	0.06

[a] Unpromoted catalysts have 19% W on each support.
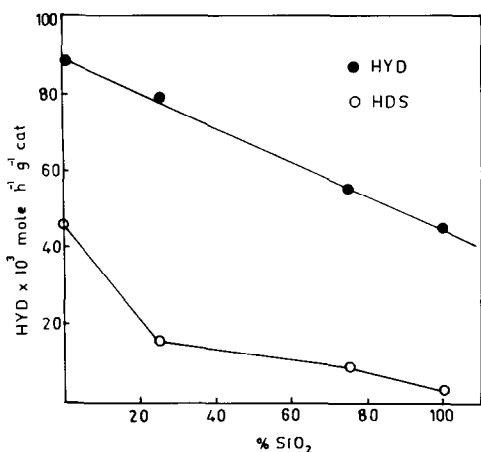[b] Promoted catalysts have 3% Ni + 19% W on each support.

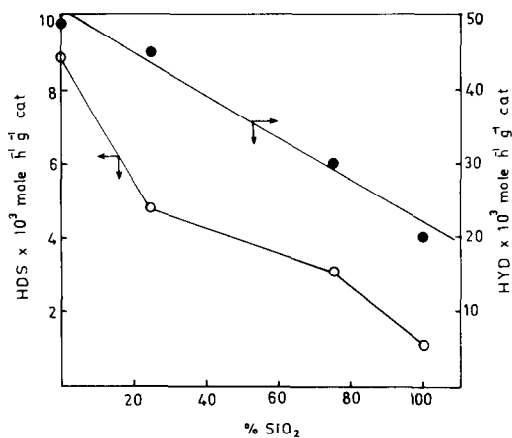FIG. 1. Variation of catalytic functionalities of promoted tungsten sulfide catalysts with silica content.

FIG. 2. Variation of catalytic functionalities of unpromoted tungsten sulfide catalysts with silica content.

note that the two functionalities behave differently with SiO_2 content in the support. Similar behavior indicates that the two reactions originate from two different types of sites on SiO_2–Al_2O_3-supported Ni–W sulfide catalysts. This is in agreement with that reported on supported molybdenum sulfide catalysts (11). While the activities varied with the support it is important that HDS/HYD ratios showed considerable variation. This gives further support to the idea that different catalytic functionalities are associated with different catalytic sites presented in the catalyst, otherwise the activities should show parallel trends and invariant HDS/HYD ratio.

In order to separate the effect of silica content in the catalyst on catalytic activity from nickel promotional effect all the SiO_2–Al_2O_3 supports are tested with only tungsten present. Because of low activity of the catalysts the reactions were run at 400°C. The results of such investigation are presented in Fig. 2. It can be seen that both functionalities behave differently. The trends are generally similar to those observed for Ni–W counterparts. HDS/HYD ratio also showed considerable variation. All these indications point out that hydrodesulfurization and hydrogenation also

originate from different sets of sites on the catalyst containing tungsten. Figure 3 shows a correlation of oxygen chemisorption with catalytic hydrogenation on both promoted and unpromoted tungsten sulfide catalysts. It is evident that in cases of both promoted and unpromoted catalysts the hydrogenation activity varies linearly with oxygen chemisorption. Such a linear relationship of oxygen chemisorption with hydrogenation functionalities was reported
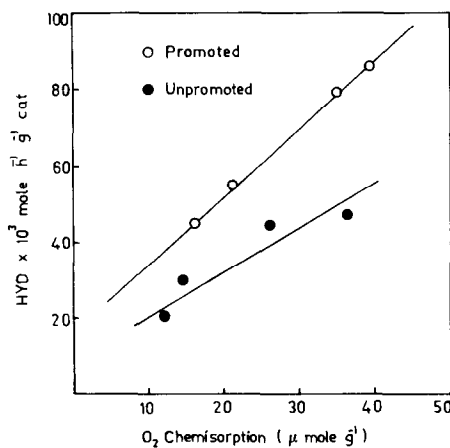

FIG. 3. Oxygen chemisorption as a function of catalytic hydrogenation rate on both promoted and unpromoted tungsten sulfide catalysts.
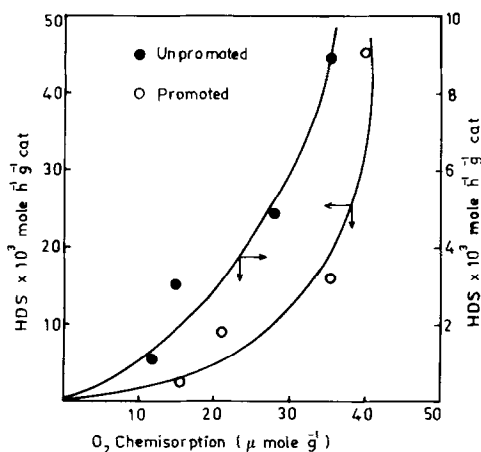
FIG. 4. Oxygen chemisorption as a function of hydrodesulfurization rate on both promoted and unpromoted tungsten sulfide catalysts.

for molybdenum sulfide catalysts (12). Figure 4 displays a correlation between oxygen chemisorption and hydrodesulfurization activity on both promoted and unpromoted catalysts. It can be seen that a nonlinear correlation is obtained for both promoted and unpromoted catalyst. It can be noted that both hydrogenation and hydrodesulfurization correlate with oxygen chemisorption but in two different ways. This observation indicates that two catalytic functionalities originate from two different sets of sites on both of which oxygen chemisorbs. The fact that both functionalities correlate with oxygen uptake indicates that oxygen chemisorption is nonspecific to any one of the sites, probably measuring general state of dispersion.

Interaction between tungsten and support plays a major role in determining the dispersion of the tungsten sulfide phase which is directly reflected on the activity of the sulfided catalyst (10). The fact that X-ray results showed three-dimensional crystallites beyond 75% silica content indicates that tungsten sulfide dispersion is poor in these catalysts. However, Al_2O_3-supported catalyst and catalyst containing low silica indicated good dispersion. Therefore, X-ray results indicate that tungsten is well

dispersed on Al_2O_3 and the dispersion gradually decreases as the silica content increases. It was shown in Figs. 1 and 2 that hydrodesulfurization and hydrogenation activities also decrease with the increase in silica content. Therefore, the decrease in activity can be attributed to a decrease in the dispersion of the sulfided phase. Then the question arises, How does the dispersion decrease? It is known that molybdenum and tungsten have similar chemistries. Molybdenum reacts with surface hydroxyl groups to form oxomolybdenum species. Similar types of species are also formed with supported tungsten catalysts (13, 10). Yamagata et al. (14) suggested that strongly adsorbed molybdenum depends on the OH content replaceable by F ions on the support. Massoth et al. (15) proposed that the Mo cluster size depends on the OH groups which in turn are related to SiO_2 content in the support. Considering the similarity in the chemistries of molydbenum and tungsten it is reasonable to assume that a similar situation also exists for supported tungsten. As SiO_2 is added to Al_2O_3 the OH group concentration decreases (14, 15) resulting in less bonding to the surface. As the silica content continues to increase, sufficient bonding sites remain and three-dimensional growth of WS_2 occurs. Therefore, the decrease in activity with silica content is due to growth of three-dimensional crystallites of WS_2 which in turn is due to lack of sufficient binding sites to bind tungsten sulfide to the support surface.

REFERENCES

1. Speight, J. G., "Desulfurization of Heavy Oils and Residue." Dekker, New York, 1981.
2. Wilson, M. F., Fischer, I. R., and Kriz, J. F., J. Catal. 95, 155 (1985).
3. Muralidhar, G., Massoth, F. E., and Shabtai, J., J. Catal. 85, 44 (1984).
4. Rao, K. S. P., Khajamastan, S., Muralidhar, G., Chary, K. V. R., and Subrahmanyam, V. S., J. Chem. Soc. Chem. Commn. 5, 375 (1988).
5. Ramanathan, R., and Weller, S. W., J. Catal. 95, 249 (1985).
6. Chung, S. K., and Weller, S. W., Ind. Eng. Chem. Prod. Res. Dev. 22, 662 (1983).

7. Nag, N. K., Rao, K. S. P., Chary, K. V. R., Rama Rao, B., and Subrahmanyam, V. S., *Appl. Catal.,* in press.

8. Parekh, B. S., and Weller, S. W., *J. Catal.* **47,** 100 (1977).

9. Reddy, B. M., Chary, K. V. R., Subrahmanyam, V. S., and Nag, N. K., *J. Chem. Soc. Faraday Trans. 1* **81,** 1655 (1985).

10. Chan, S. S., Wachs, I. E., Murrell, L. L., and Dispenzire, N. C., *Stud. Surf. Sci. Catal.* **19,** 259 (1984).

11. Massoth, F. E., and Muralidhar, G., "Proceedings, Climax Fourth International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry, Eds.), p. 343. Climax Molybdenum Co., Ann Arbor, MI, 1982.

12. Zmierzak, W., Muralidhar, G., and Massoth, F. E., *J. Catal.* **77,** 432 (1982).

13. Iawasawa, Y., "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 35, p. 187. Academic Press, New York, 1987.

14. Yamagata, N., Owada, Y., Okazaki, S., and Tanabe, K., *J. Catal.* **47,** 358 (1977).

15. Massoth, F. E., Muralidhar, G., and Shabtai, J., *J. Catal.* **85,** 53 (1984).

K. SAIPRASAD RAO
G. MURALI DHAR[1]

Catalysis Section
Regional Research Laboratory
Hyderabad 500 007, India

---

[1] To whom correspondence should be addressed.