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Catalytic Functionalities of WS_2/ZrO_2[1]

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The effect of ZrO_2 support on dispersion and catalytic functionalities of WS_2 are investigated using oxygen chemisorption, XRD, and surface area measurements. The surface area studies on oxide catalysts indicated that WO_3 is highly dispersed below 6–8 wt% tungsten. Analysis of X-ray diffraction results also led to similar conclusions. Oxygen chemisorption on sulfided catalysts indicated that tungsten is well dispersed below 6–8 wt% in the sulfided state also. From the trends of activity for HDS and HYD and oxygen chemisorption variation with W loading it is concluded that oxygen chemisorption is not specific to any one of the functionalities. The variation intrinsic activity with loading in case of HDS and HYD indicated that these two functionalities originate from a different set of sites. © 1992 Academic Press, Inc.

INTRODUCTION

Sulfided Co–Mo and Ni–W catalysts are well established in hydrotreating of petroleum fractions (*1*). Such catalysts are attracting increased attention to heavy residue processing as well as in coal liquefaction and upgrading of coal-derived liquids (*2*). Various reactions catalyzed by these catalysts are hydrogenolysis, hydrogenation, and hydrocracking. The above three functionalities are not only required for an effective hydrotreating catalyst but also should be appropriately balanced. To be able to prepare an effective well-balanced sulfided catalyst it is necessary to gain knowledge on the origin of different functions of the catalyst and its dependence on the nature of the support, composition, etc., variables.

Support plays an important role in determining the catalytic activity of the active component by varying the metal-support interactions and thereby influencing the dispersion of supported sulfide. Support effects on catalytic properties of hydrotreating catalysts are studied with great interest (*4–10*). Numerous studies of hydrodesulfurization involved alumina support (*5, 6*). Silica (*4*), titania (*4, 7*), magnesia (*4, 8*), and zirconia (*9, 10*) are also used. De Beer and co-workers (*11, 12*) studied carbon-supported hydrodesulfurization (HDS) extensively and showed how a carbon support enhanced the activity for HDS of thiophene. In a recent review, Abotsi and Scaroni (*13*) discussed in detail the effect of a carbon support on the hydrotreating functionalities. Murali Dhar *et al.* (*3*) and Massoth *et al.* (*14*) studied the effect of support on Mo and Co–Mo supported on various supports for HDS of thiophene and hydrogenation of 1-hexene. Shimada *et al.* (*4*) reported the support effect on HDS of dibenzothiophene and hydrogenation (HYD) of 1-methylnapthalene and hydrocracking of diphenylmethane. In all these cases it was shown that support profoundly influences the catalytic functions. As described above, studies on molybdenum catalysts are available in the literature (*1–12*) while corresponding studies on tungsten catalysts are only a few in number. To bridge the gap, we have attempted to evaluate tungsten sulfide supported on various silica–alumina supports (*15*). In this study, we discuss our results

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on zirconia-supported tungsten sulfide catalysts with respect to thiophene HDS and cyclohexene hydrogenation.

EXPERIMENTAL

The catalysts were prepared by incipient wetting of commercial Harshaw ZrO_2 (Zr-0304) support 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 oxygen chemisorption was measured at −78°C in a conventional high-vacuum system on catalyst sulfided at 400°C for 2 h using a CS_2/H_2 mixture (at a flow rate 40 cm^3/min) following the double isotherm procedure of Parekh and Weller (*16*) for reduced Molybdenum catalysts. The same system was also used for BET surface area measurements. Details of the experimental setup and chemisorption procedure were given by Reddy *et al.* (*17*). X-ray diffractograms were recorded on a Philips P.W. 1051 diffractometer using nickel-filtered Cu$K\alpha$ radiation. Thiophene hydrodesulfurization and cyclohexene hydrogenation activities were evaluated at 400°C, on a catalyst sulfided as above 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 valve for product analysis. The rates were calculated as per the equation $x = r(W/F)$, where r is rate in mol h^{-1} g^{-1} and x is the fractional conversion, W, weight of the catalyst in grams, and F is the flow rate of the reactant in mol h^{-1}. The conversions were kept low (below 10%), where the above rate equation is valid.

RESULTS AND DISCUSSION

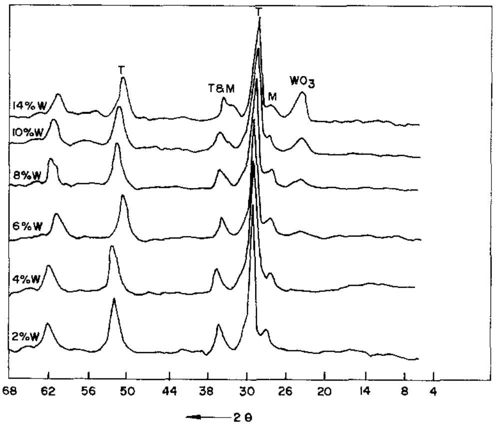

FIG. 1. X-ray diffractograms of fresh catalysts at different loadings.

X-ray diffractograms of various amounts of tungsten oxide supported on ZrO_2 are presented in Fig. 1. Pure ZrO_2 exists in three crystallographic forms, namely monoclinic, tetragonal, and cubic. It can be seen from the diffractograms that ZrO_2 in supported catalysts exist in tetragonal and monoclinic forms. There are no reflections due to tungsten oxide up to 6 wt% of W. Above this loading, however, lines due to tungsten oxide are observed. There is no evidence in the diffractograms for the presence of a compound between WO_3 and ZrO_2. Below 6 wt% level the tungsten oxide is invisible to X rays, which means that tungsten oxide is present as a monolayer or crystallites as small as 50 Å or less. Therefore, it can be said that below the 6 wt% level WO_3 is well dispersed and may be in the form of monolayer. Beyond the 6 wt% level the diffraction lines due to WO_3 begin to appear and these reflections become sharper with increase of tungsten loading. It can also be said that interaction of WO_3 with ZrO_2 becomes weak beyond 6 wt% of tungsten loading.

To understand further whether there is a monolayer formation of WO_3/ZrO_2, the surface area data on the catalyst was analyzed. Measurements of total surface area are useful in ascertaining whether the active component exists as a monolayer. In the case of monolayer, addition of tungsten to fixed weight of alumina will result in a constant surface area per gram of the catalyst. If tungsten crystallites possessing intrinsic porosity and surface area exist, addition of tungsten to fixed weight of alumina results in increased surface area per gram of alumina. By analyzing the surface area data,

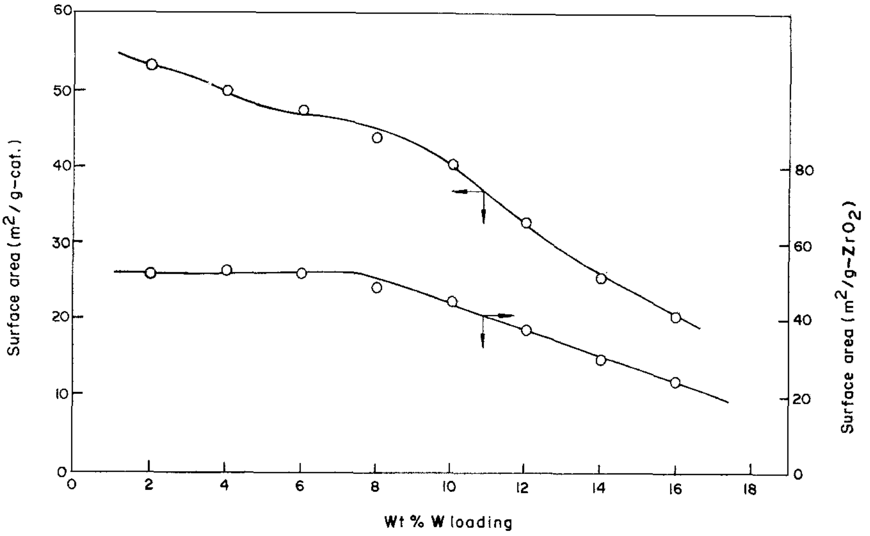

FIG. 2. Variation of surface area with tungsten loading.

Massoth (*18*) has shown that Mo and Co–Mo supported on alumina exist as a monolayer in both oxidized and sulfided catalysts. Liu and Weller (*19*) have shown that in reduced Co–Mo/Al_2O_3 catalysts molybdenum exists as microcrystallites. Figure 2 presents the surface area data per gram of catalyst and per gram of ZrO_2 as function of tungsten loading. It can be seen that area per gram of the catalyst decreases with the increase of tungsten loading. It can also be seen that there exists a plateau-like region around 6–8 wt%. This type of plateau has been attributed in the W/Al_2O_3 to the formation of monolayer (*22*). The surface area per gram of ZrO_2 is invarient with the increase of tungsten loading up to 6 wt% tungsten and decreases beyond that point. The invariance of surface area suggests that tungsten may be existing as a monolayer. This result is in agreement with the XRD results discussed earlier. The decrease in surface area per gram of ZrO_2 beyond the monolayer may be due to plugging of pores by the large tungsten oxide crystallites. Similar analysis on sulfided catalyst appears complicated and did not give any evidence for formation of monolayer or microcrystallites.

Amount of low-temperature oxygen chemisorption as a function of tungsten loading is shown in Fig. 3. Oxygen uptake, in sulfided state BET surface area of the fresh and sulfided catalysts and O_2/W are presented in Table 1. It can be seen from Fig. 3 that oxygen uptake increases rapidly up to about 6–8 wt% and then increases very slowly. It is interesting to recall that it is at about the same wt% of tungsten that XRD showed evidence for three-dimensional crystallites and surface area analysis showed that WO_3 deviates from the behavior expected for a monolayer catalyst. Considering the fact that sulfidation of hydrotreating catalyst involves only exchange of surface oxygens with sulfur (*20*), it is reasonable to assume that sulfidation does not cause drastic changes under the mild sulfiding conditions, such as those employed in this work, and the dispersion more or less follows a similar trend after sulfidation. In fact it has been found in the case of supported molybdenum catalysts that dispersion did not change after sulfidation (*21*). Therefore, the point where the oxygen chemisorption levels off indicates the tungsten loading where the sulfided monolayer is completed. Similar conclusions were drawn earlier on Mo/Al_2O_3 (*17*), Mo/ZrO_2 (*10*), and W/Al_2O_3 (*22*).

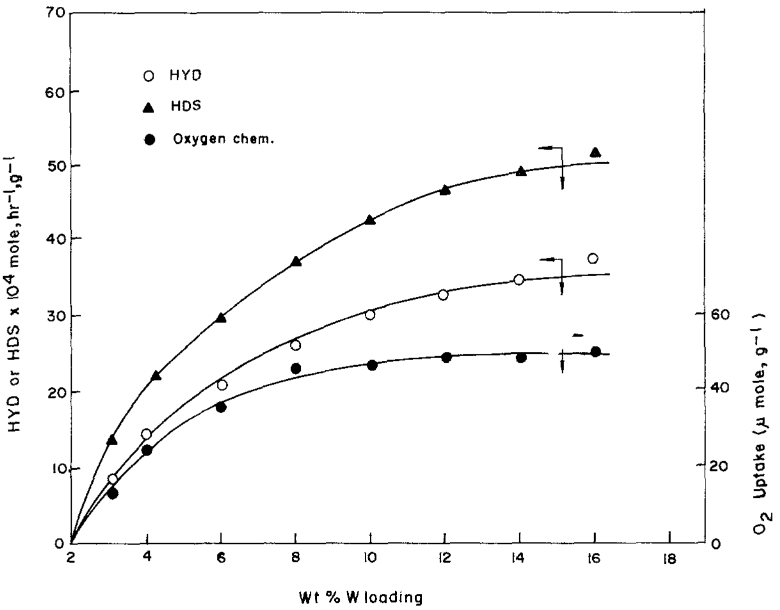

FIG. 3. Variation of oxygen chemisorption, HDS, and HYD with loading.

The hydrodesulfurization and hydrogenation rates on W/ZrO_2 catalyst as a function of loading are also shown in Fig. 3. It can be seen clearly that HDS and hydrogenation activities increase rapidly up to about the 6–8 wt% level and then increase very slowly. This behavior is very similar to that of oxygen uptake discussed earlier. It is also interesting to note that it is at the same wt% level that XRD and surface area measurements indicated completion of WO_3 monolayer on ZrO_2. A close examination of the curves presented in Fig. 3 indicates that there exists a similar trend between the oxygen uptake capacity and hydrodesulfurization and hydrogenation activities. It is believed that HDS and hydrogenation take place on anion vacancies (*23*, *24*). Therefore, a correlation of this tendency indicates that oxygen chemisorption estimates the amount of anion vacancies on WS_2/ZrO_2. Since both these functionalities show similar trend of variations with oxygen uptake it is clear that oxygen chemisorption is not specific to any one of these functionalities.

TABLE 1

Oxygen Chemisorption and Surface Area Results on W/ZrO_2 Catalysts

Wt% W	O_2 uptake (μ mol g^{-1})	BET surface area (m^2 g^{-1})		O_2/W
		Fresh	Sulfided	
2	14.2	52.2	48.4	0.130
4	25.3	50.4	42.8	0.116
6	37.2	48.3	36.4	0.114
8	46.3	44.2	32.6	0.106
10	47.4	40.4	28.7	0.086
12	48.3	32.9	24.0	0.074
14	48.7	25.6	20.9	0.064
16	49.9	20.4	16.2	0.057

It can be noted that the activities presented in Fig. 3 are per gram of catalyst. It is interesting to compare the activities per gram of active component, tungsten. HDS and HYD activities per gram of tungsten are presented in Fig. 4. For comparison purposes, activities per gram of tungsten on WS_2/Al_2O_3 from Nag *et al.* (*22*) are also in-

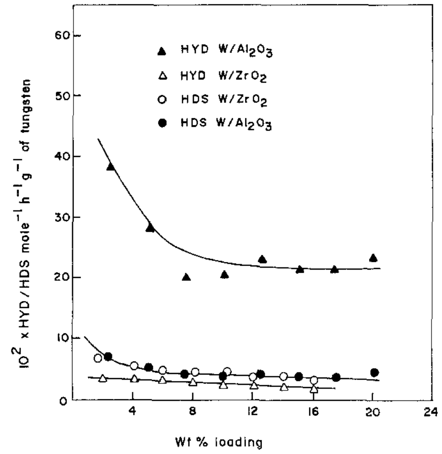

FIG. 4. Variation of HDS, HYD rate per gram of W as a function of loading.

cluded. It is clear that HDS and HYD activities per gram of tungsten decrease with increase of tungsten loading in both WS_2/ZrO_2 and WS_2/Al_2O_3. It can also be seen that the HDS activities for WS_2/ZrO_2 and WS_2/Al_2O_3 fall on the same curve indicating that WS_2/ZrO_2 is as active as WS_2/Al_2O_3, even though the Al_2O_3 support has surface area 4–5 times higher than that of ZrO_2. It can also be noted that hydrogenation activity of WS_2/Al_2O_3 is much greater than that of WS_2/ZrO_2. It is clear, therefore, that the support shows a profound effect on catalytic functionalities of tungsten catalyst. The hydrogenation activity is higher than HDS and WS_2/Al_2O_3 while that on ZrO_2 is lower than HDS. This independent variation of specific activity suggests that HDS and HYD originates from different sites on the catalyst surface. Further evidence can be deduced from the variation of intrinsic activity (rate/O_2) of the two functionalities with tungsten loading. Data presented in Fig. 5 indicate that there are differences in behavior between hydrodesulfurization and hydrogenation. In the monolayer region, while the intrinsic activity of HDS decreases with W loading, the hydrogenation activity remains invariant. In the post monolayer region both the functionalities show a rise in activity. Such a difference in behavior suggests that the two functionalities may originate from two different sites.

It is clear from the above discussion that WO_3/ZrO_2 in the oxide precursor is dispersed as a monolayer up to 6–8 wt% of tungsten. The oxygen uptake data and their variation with loading indicated that dispersion in the oxidized state runs parallel to the one in the sulfided state. It was also observed that oxygen uptake increases with tungsten loading and then levels off at higher loadings. The hydrogenation and hydrodesulfurization follow a similar trend. It is interesting to consider how and why the oxygen uptake and activities show initial increase and then leveling off tendencies. The following discussion deals with this point.

Yermakov and co-workers (*23–26*) have extensively studied silica-supported tungsten sulfide catalysts. They have proposed from their high-resolution electron microscopic studies (*23*) that supported sulfide is present on the catalyst as a monolayer thread-like structure of 25-Å length. They have further indicated that a single WS_2 sheet, like the one mentioned above, is the minimal structural element sufficient for formation active sites. Nag *et al.* (*22*) reported that tungsten sulfide is present as isolated small patches or sheets anchored to selected

FIG. 5. Variation of intrinsic activity with W loading.

regions of the support. Therefore, from these data it is reasonable to believe that WS_2 is present as monolayer sheets or patches on zirconia support. In the monolayer region, the above-described tungsten sulfide sheets grow in number. However, this is not strictly true in the present case since O_2/W values given in Table 1 show a decreasing trend, which indicates that slab size is increasing. This analysis is based on the results reported by Miciukiewicz *et al.* (*27*) on the MoS_2/Al_2O_3 system using NO as a probe molecule. As a result of this, the anion vacancies at the edges and corners of the monolayer sheets increase and hence oxygen chemisorption, which is an estimate of anion vacancies, also increases. Beyond the monolayer level the growth of three-dimensional crystallites reduces the anion vacancies formed and thereby showing a leveling off tendency. Since HDS and HYD take place on anion vacancies at the edges and corners, these two functionalities also follow a similar trend.

The following conclusions can be drawn from these studies (*1*). Tungsten is dispersed as monolayer sheets in the oxidized state and this dispersion is probably retained in the sulfided state (*2*). There exists a trend between oxygen chemisorption and HDS and HYD reactions. Since oxygen chemisorption exhibits a similar trend of variation with both the functionalities, oxygen chemisorption is not specific to any one of these functionalities (*3*). It appears from oxygen chemisorption results that tungsten is better dispersed on zirconia than alumina (*4*). Specific activities, i.e., activities per gram of tungsten, indicated that WS_2/ZrO_2 is as active as $WS_2/\gamma\text{-}Al_2O_3$ (*5*). The trend of variation intrinsic activities on WS_2/ZrO_2 and WS_2/Al_2O_3 suggested that the two functionalities originate from different sites on the catalyst surface.

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