

OXYGEN CHEMISORPTION AND ACTIVITY STUDIES ON ALUMINA- AND CARBON-SUPPORTED HYDRO-DESULPHURIZATION CATALYSTS

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ABSTRACT

Co-Mo and a series of Mo catalysts were prepared on alumina and carbon supports and were characterized by low temperature oxygen chemisorption (LTOC) at -78°C . The reactivity of sulphided catalysts for thiophene hydrodesulphurization (HDS) and cyclohexene hydrogenation (HYD) were measured in a flow microreactor at atmospheric pressure. Three commercial HDS catalysts were also subjected to these studies for comparison. A good correlation was found between HDS activity and oxygen uptake. Carbon-supported catalysts had a much higher HDS activity and lower HYD activity than alumina-supported catalysts. The improved HDS activity was related to the better dispersion of the molybdenum sulphide phase on the carbon support.

INTRODUCTION

Hydrodesulphurization (HDS) of sulphur-containing liquids is an important catalytic process in the petroleum and fertilizer industries. Other important reactions [1] that frequently take place under HDS conditions include hydrogenation, hydrocracking and isomerization. Commercial HDS catalysts consist of molybdenum promoted with cobalt or nickel supported on a high surface area γ -alumina. During HDS, extra hydrogen is always consumed owing to the hydrogenation (HYD) of unsaturated hydrocarbons. This is often undesirable, as it leads to loss of hydrogen. In order to minimize the wastage of expensive hydrogen, it has become necessary to develop new catalysts [2] that are active and selective enough (i.e., having high HDS activity and low HYD activity) to be economically viable for the hydro-processing of petroleum feedstocks.

Recently, carbon materials have received increased attention as supports for catalytic systems [3-9]. Potential advantages include low cost and easy metal recovery by burning off the carbon support. As carbons have weak adsorption properties for aromatics and nitrogen-containing compounds, these catalysts are less susceptible to poisoning and fouling than the conventional alumina systems. Further, carbons possessing low acidity compared with alumina reduce deactivation via coke formation [8]. Moreover, carbon-supported HDS catalysts have been shown to have catalytic activities that in some instances are higher than those of alumina-supported catalysts for the hydrodesulphurization of thiophene [9]. However, at present it is not clear whether this improved activity is due to an increase in

the number of active sites, as a result of better dispersion or a more favourable morphology of the molybdenum sulphide phase formed on the carbon carrier, or to an enhancement of the activity per site. In this investigation an attempt has been made to gain more insight into this matter.

The characterization of unsupported and supported molybdenum oxides by low-temperature oxygen chemisorption (LTOC) has been widely used in recent years. The application of LTOC to molybdenum and chromia catalysts in the reduced state has been reviewed by Weller [10]. The application of LTOC to sulphided catalysts was first described by Tauster et al. [11] and has since been studied by Massoth and co-workers [12,13], Bartholomew and co-workers [14-16], Burch and Collins [17] and Reddy and co-workers [18,19]. In spite of these numerous studies, there is much yet to be learned about the adsorption sites of LTOC and its relation to HDS and HYD sites in supported molybdenum oxides and sulphides. There are only a few publications on how different supports affect LTOC and the catalytic properties of the oxides and sulphides [16]. In this paper we report the correlation of LTOC data with catalytic activity for thiophene HDS on alumina- and carbon-supported molybdenum catalysts.

EXPERIMENTAL

Catalyst preparation

The Mo- Al_2O_3 (Harshaw $\gamma\text{-Al}_2\text{O}_3$, S.A. $204 \text{ m}^2 \text{ g}^{-1}$, P.V. 0.65 ml g^{-1}) and Mo-C (Lurgi carbon, S.A. $1160 \text{ m}^2 \text{ g}^{-1}$, P.V. 1.2 ml g^{-1}) catalysts with Mo loadings ranging from 2 to 12 wt% were prepared by pore volume impregnation of the carrier with an aqueous solution of ammonium heptamolybdate (Baker, spectroscopic grade). The impregnated samples thus obtained were dried at 120°C for 16 h and stored in a vacuum desiccator. The Co-promoted catalysts were prepared from oven dried 8% Mo catalyst by impregnation with cobalt nitrate solution of appropriate concentration in an identical manner. All the alumina-supported catalysts were finally calcined at 540°C for 12 h.

Activity measurements

Thiophene (Fluka, 99%) HDS and cyclohexene (Merck-Schuchardt, 99.9%) HYD were chosen as model reactions for testing the hydrogenolytic and hydrogenation functionalities of the catalysts. A fixed-bed differential flow microreactor, operating under normal atmospheric pressure and interfaced to a gas chromatograph by a six-way gas-sampling valve, was used to measure the activities of the catalysts. Before introducing the feeds by means of bubblers, all the catalysts were pre-sulphided at 400°C for 2 h with a stream of hydrogen saturated with CS_2 . Pre-sulphiding is generally carried out with $\text{H}_2\text{S-H}_2$ or $\text{CS}_2\text{-H}_2$ or $\text{C}_4\text{H}_4\text{S-H}_2$ mixtures [20]. The reaction temperatures were 400°C for thiophene HDS and 350°C for cyclohexene HYD. The conversions were kept within the 15% level and all the rates were measured under steady-state conditions in the absence of any diffusional effects. Further details of the experimental procedure and the activity calculations can be found elsewhere [19].

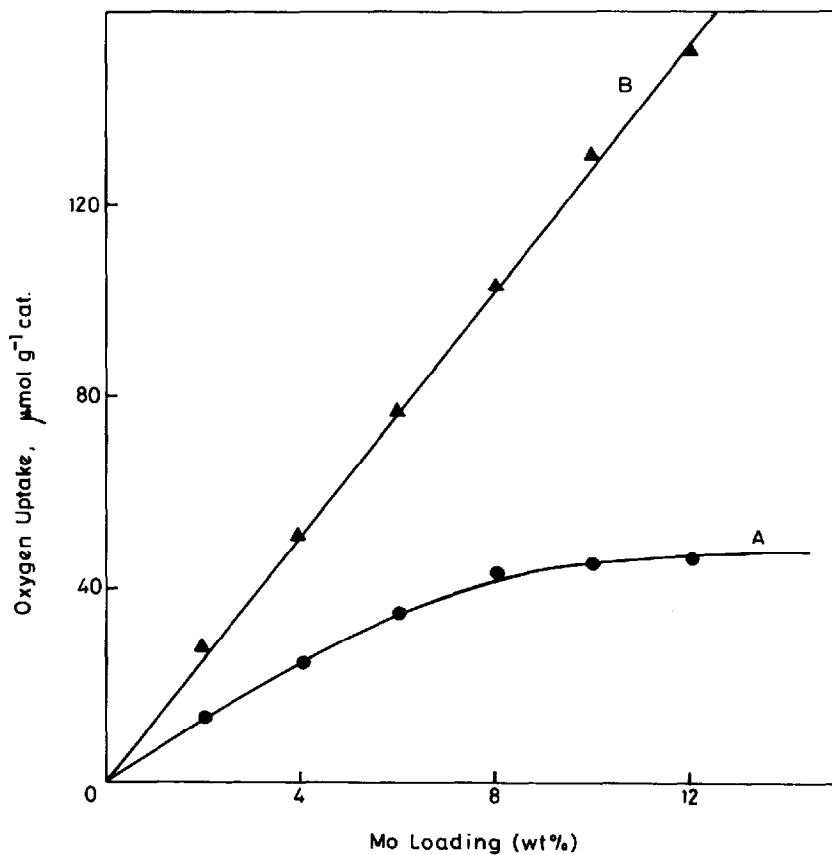


FIGURE 1 Variation of oxygen uptake with Mo loading: (A) alumina support; (B) carbon support.

Chemisorption measurements

A conventional static volumetric high-vacuum (10^{-6} Torr) system, with the facility for reducing the samples *in situ* by flowing hydrogen ($30 \text{ cm}^2 \text{ min}^{-1}$), was used for LTOC measurements. The standard procedure employed was the reduction of a catalyst sample for 6 h at 500°C , followed by evacuation for 2 h (10^{-6} Torr) at the same temperature prior to oxygen chemisorption. Before introduction of oxygen the system was further evacuated for 1 h at the temperature of chemisorption (-78°C). Allowing purified oxygen from a storage bulb into the catalyst chamber, the first adsorption isotherm representing the sum of physisorbed and chemisorbed oxygen was determined. The physisorbed oxygen was then removed by evacuating (10^{-6} Torr) for 2 h at the same temperature. Immediately afterwards a second isotherm representing only the physisorbed oxygen was generated in an identical manner. From these two isotherms, which were parallel in the pressure range studied (100-300 Torr), the volume of chemisorbed oxygen was determined [21].

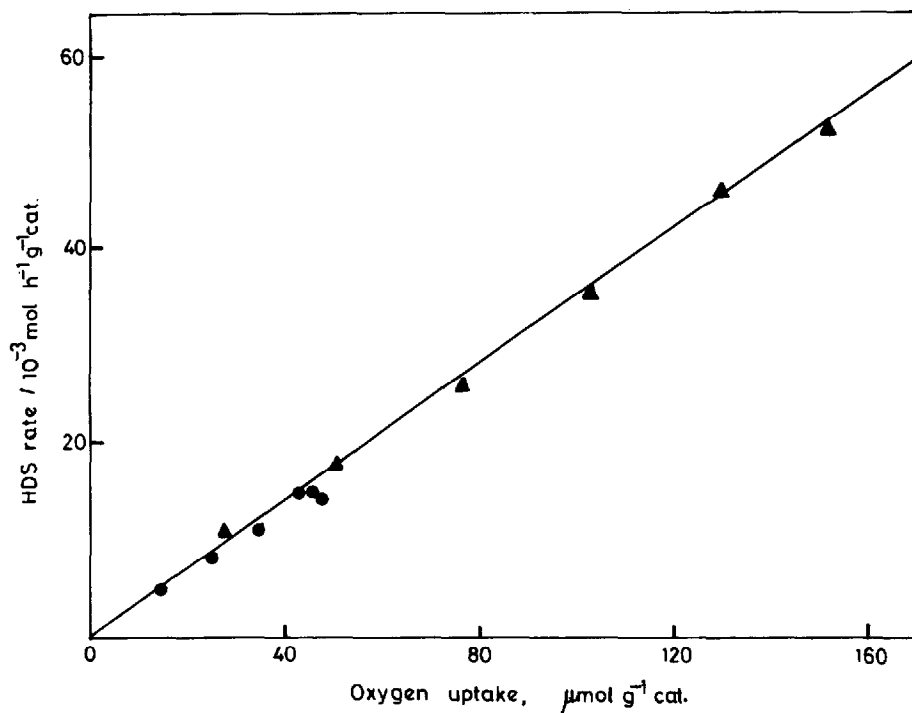


FIGURE 2 HDS activity as a function of oxygen uptake: ● , alumina support; ▲ , carbon support.

RESULTS AND DISCUSSION

Oxygen uptake values as a function of catalyst composition are presented in Figure 1. The oxygen uptake per gram of catalyst increases linearly as a function of Mo loading even up to 12 wt% on carbon-supported catalysts, whereas on alumina-supported catalysts the uptake increases up to 8% Mo loading and then levels off. This saturation level indicates the completion of a monolayer coverage of the active alumina support surface by Mo oxide. The maximum oxygen uptakes at 12 wt% by Mo-C and Mo-Al catalysts are found to be 0.243 and 0.075 oxygen atom per atom of Mo. These results indicate that Mo oxide is dispersed better on carbon than on alumina. Pure supports were found by an independent experiment to chemisorb some oxygen under the experimental conditions used. Therefore, the amount of chemisorbed oxygen corresponding to the amount of support present in each catalyst was subtracted from the oxygen uptake values for the catalysts before reporting the results.

The HDS activity of the catalysts, reported as the steady-state rate, is plotted as a function of oxygen uptake in Figure 2. There is a good correlation between oxygen uptake and HDS activity for the carbon-supported catalysts. However, for alumina-supported catalysts this correlation again applies up to the 8 wt% Mo level. This level corresponds to an Mo loading that is generally reported to give

monolayer coverage [22] of the support surface. All the chemisorption studies are based on two very important assumptions: first, that oxygen chemisorbs selectively on the edge planes and corners of MoS_2 (or MoO_2) crystallites, and second, that active sites for HDS reactions are also located on these planes as coordinately unsaturated Mo sites (CUS) [11,12,19,23-26]. The present results also conform to the above ideas that the HDS active sites, i.e., the CUS, are titratable by oxygen chemisorption irrespective of their location.

Variations of oxygen uptakes, thiophene HDS and cyclohexene HYD activities with the addition of cobalt promoter to the 8% Mo catalysts are presented in Table 1, together with results for three commercial catalysts. It can be seen that the cobalt promotes both HDS and HYD activities. However, the extents of promotion for both the reactions and for both the supports are different. The Co-Mo/C catalyst shows a better activity for HDS and a lower activity to HYD compared with the alumina-supported catalyst. This better HDS activity of the carbon-supported Mo catalysts appears to be mainly due to the better dispersion of the molybdenum sulphide phase on the support, or in other words, an increase in the number of active sites. We failed to detect any XRD lines due to MoS_2 or MoO_2 crystallites even with 12% Mo/C catalyst. This observation and the O/Mo ratios mentioned earlier support the above argument. It is not clearly known at present why these catalysts show low HYD activity. Further work is needed on this aspect. However, an important point to note is that the sites involved for HDS and HYD seem to be different, which is in agreement with earlier observations [27]. Regarding the promotional role of cobalt in HDS catalysts, some workers claim that cobalt increases the number of active sites [28,29], whereas others [13,30] favour the idea that cobalt does not affect the number of active sites but promotes the intrinsic activity of the sites. From the results in Table 1, it can be seen that HDS and HYD activity showed dramatic improvements with the addition of cobalt promoter to the 8% Mo catalysts. However, oxygen chemisorption did not show a corresponding increase, which is expected if cobalt increases the number of active sites. Therefore, it can be concluded that cobalt as a promoter increases the intrinsic activity of the sites rather than their number. This observation is in agreement with the earlier reports [13,30].

The linear correlations shown in Figures 1 and 2 can be explained in the light of the structural models proposed by Topsøe [26] for sulphided Mo catalysts and Hall [31] for Mo oxide catalysts. Nag [32] observed a parallelism between the oxygen chemisorption characteristics of reduced and sulphided $\text{Mo-Al}_2\text{O}_3$ catalysts. Based on Hall's "patch" model, the results for Mo- ZrO_2 catalysts [33] and Mo- TiO_2 catalysts [34] were interpreted by Reddy and co-workers. Hall [31] proposed that at low Mo loadings small patches of Mo oxide, two layer thick with Mo in octahedral coordination, are formed on the alumina support surface. The same structure, however, remains on the support surface as small patches of MoS_2 on

TABLE 1

Composition, oxygen uptakes and activities of various catalysts

Catalyst	Composition ^a /wt%			O ₂ uptake /μmol g ⁻¹ cat.	BET SA ^b /m ² g ⁻¹ cat.	10 ³ x	10 ³ x
	Mo	Co	SiO ₂			r _{HDS} /mol h ⁻¹ g ⁻¹ cat.	r _{HYD} /mol h ⁻¹ g ⁻¹ cat.
Mo/Al	8.0	-	-	44.1	175.0	14.5	39.1
CoMo/Al	8.0	3.0	-	52.2	171.0	25.9	53.0
Mo/C	8.0	-	-	103.0	878.0	35.6	5.4
CoMo/C	8.0	3.0	-	110.0	857.0	52.4	6.1
Ketjen- fine-124	7.7	2.44	1.16	50.4	267.0	14.0	51.9
Ketjen- fine-742	10.0	3.34	0.91	53.5	253.0	29.6	55.2
Harshaw HT-400	10.0	2.36	-	46.9	200.0	34.1	48.0

^aThe balance was Al₂O₃.

^bThe BET surface areas were calculated on fresh samples by N₂ adsorption at -196°C by taking 0.162 nm² as the area of cross-section of N₂.

sulphidation [32]. On reduction, CUS are generated by the removal of oxygen (or sulphur) from the surface molybdenum patches. These are the sites on which oxygen chemisorption and HDS and related reactions take place. As the Mo loading increases, the number of these patches increases with an attendant increase in the number of CUS. However, on an alumina support this increase is up to a monolayer level. Beyond the monolayer level these patches grow three-dimensionally, thus decreasing the dispersion of Mo oxide. This growth in size, rather in number, of small patches is expected not to add new CUS per unit of Mo as a function of Mo loading. As the HDS activity is correlated with the CUS, their initial increase and subsequent levelling off tendencies can also be explained by the same mechanism.

It can be recalled from Figure 2 that a linear correlation of oxygen uptake with thiophene HDS activity on various catalysts based on Mo-Al₂O₃ and Mo-C is observed, which indicates that oxygen chemisorption is related to HDS active sites. However, there is no clear consensus about the sites on which oxygen chemisorbs and also sites on which the HDS reaction takes place. For example, Tauster et al. [11] proposed that edge sites are most active for oxygen chemisorption whereas others [35] disputed this observation. Similarly, there is still controversy about basal plane sites or edge sites that are exactly related to HDS activity [35]. However, it is generally accepted [23-25] that HDS takes place on CUS sites and also it is reasonable to assume that oxygen chemisorption also takes place on CUS sites, so a linear relationship is not surprising.

CONCLUSIONS

The major findings may be summarized as follows:

(1) LTOC data can precisely determine the Mo level where the formation of monolayer attains completion; (2) Mo oxide is dispersed well on the carbon support; (3) cobalt as a promoter increases the intrinsic activity of the sites rather than their number and the effect is different for different reactions and for different supports; (4) Co-Mo/C catalysts show exceptionally better activity for HDS of thiophene and a low activity for HYD of cyclohexene. Further work is needed to understand fully the behaviour of carbon-supported hydrodesulphurization catalysts.

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