Catalysis Letters 10 (1991) 27–34

Hydrodesulfurization on MoS_2/MgO

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Received 2 December 1990; accepted 16 May 1991

A series of Mo/MgO catalysts with loadings ranging from 2–12 wt% Mo were studied by oxygen chemisorption, X-ray diffraction and activity for thiophene hydrodesulfurization (HDS) reaction. The results obtained from the above measurements are compared with those on Mo/γ-Al_2O_3. These results indicated that molybdenum is better dispersed on MgO. Hydrodesulfurization activity per g. Mo is found to be higher in the case of Mo/MgO. The higher activities are attributed to the increase in dispersion of Mo on MgO. A linear correlation is obtained between oxygen chemisorption and HDS activity. The parallelism between HDS and oxygen chemisorption is explained.

Keywords: Hydrodesulfurization; magnesia support; molybdenumsulfide

1. Introduction

Sulfided molybdenum catalysts are well established in hydrotreating petroleum fractions [1–3]. Such catalysts are attracting increased attention in coal liquefaction and upgrading of coal derived liquids [4]. Reactions catalysed by these materials include hydrogenolysis, hydrogenation and hydrocracking. The above functionalities are not only required for effective hydrotreating catalysts but also should be appropriately balanced. To be able to prepare effective well balanced sulfided catalysts it is necessary to gain knowledge on the origin of different functions of the catalyst and their dependence on nature of support, composition etc. variables.

The support plays an important role in determining the activity of the supported catalytic phase. The most efficient utilization of the supported catalyst depends on the dispersion of the active phase. The dispersion is often controlled among other factors by the extent of loading and the nature of metal support interaction. Carbon supported catalysts are also well dispersed and the

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IICT Communication No. 2721.

activity was shown to be several orders of magnitude higher than alumina supported ones [5,6]. Recently Pratt et al. showed that support influences the morphology of MoS_2 phase [7]. Therefore, it is clear that support can influence the catalytic characteristics significantly. Various supports have been used for hydrodesulfurization reaction. These are Al_2O_3 [2], SiO_2 [6], TiO_2 [7], ZrO_2 [7] and carbon [5,6]. In addition to above mentioned supports ternary systems like SiO_2-Al_2O_3 [9,10] TiO_2-ZrO_2 [11] were also employed for HDS reaction. Recently the support effects were also studied with Ni-W system [12]. However, to the best of our knowledge hydrodesulfurization on MoS_2/MgO is not reported so far. In addition, all the supports so far studied have been acidic in nature. It is interesting to see how a basic support like MgO influences the activity of MoS_2 for thiophene HDS reaction. In this communication we report result using MgO as a support for MoS_2.

2. Experimental

A series of Mo/MgO catalysts with loadings ranging from 2–12 wt% Mo were prepared by incipient wetness technique using aqueous solution containing requisite amount of ammonium heptamolybdate. The impregnated catalysts thus obtained were dried at 120 ° C for 16 h and then calcined in air at 500 ° C for 16 h.

The oxygen chemisorption measurements were made at $-78\,^\circ C$ by using conventional static high vacuum system with a facility to reduce the sample in situ, following the procedure of Parekh and Weller [13]. The catalyst was reduced at 40 cm^3/min in flowing H_2 at 500 ° C for 6 hours prior to oxygen chemisorption (~ 400 Torr CS_2 partial pressure). The same system was used for measuring BET surface areas. The X-ray diffractograms were recorded on P-W.1051 diffractometer using Ni filtered CuKα radiation.

The activities for thiophene hydrodesulfurization (HDS) were evaluated at 350 ° C on a catalyst sulfided at 400 ° C for 2 h in a flow of CS_2/H_2 mixture, in a fixed bed differential micro catalytic reactor operating at atmospheric pressure. The products were analysed on a 2 m long stainless steel column packed with 10%OV-17 using as on line gas chromatograph.

3. Results and discussion

Oxygen chemisorption was performed at $-78\,^\circ C$ on Mo/MgO samples reduced at 500 ° C for 6 h and oxygen uptakes as a function of loading are presented in fig. 1. The oxygen uptake increases sharply upto 8 wt% Mo and then levels off. This behaviour of Mo/MgO is similar to that of Mo/Al_2O_3 catalysts [14]. Several authors [14,15] have attributed this levelling off behaviour

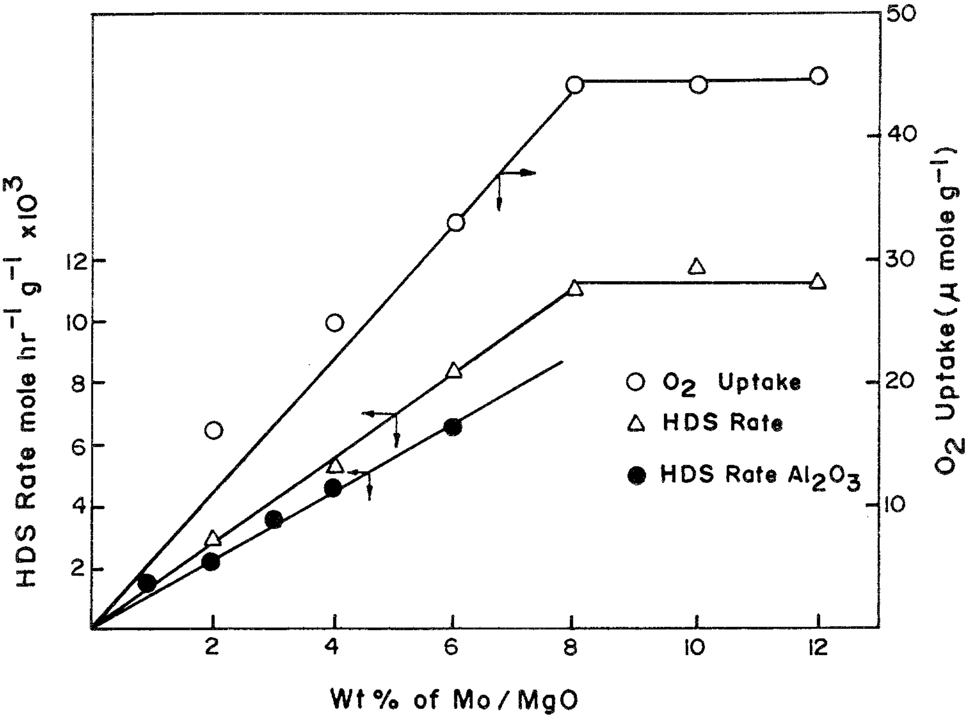

Fig. 1. Effect of Mo loading on oxygen uptake and HDS activity.

to the completion of monolayer of molybdenum oxide on the support. It is interesting to compare the oxygen chemisorption behaviour of Mo/MgO and Mo/γ-Al_2O_3 catalysts. The monolayer composition corresponds to 11.5 μmole $Mo.m^{-2}$. This value is twice as high as that obtained using γ-Al_2O_3 support. The maximum oxygen uptake on Mo/MgO is 0.61 μmole O_2 m^{-2}. The corresponding value on Mo/γ-Al_2O_3 is only 0.25 μmole O_2 m^{-2}. From the above discussion it can be concluded that Mo is better dispersed on MgO compared to Mo/γ-Al_2O_3. This conclusion is based on higher molybdenum coverage and higher oxygen uptake capacities at the monolayer level.

The equivalent molybdenum area (EMA) derived from oxygen uptake, the surface coverage, BET areas and crystallite size in the reduced state are presented in table 1. It can be seen that the EMA values increase upto monolayer coverage and then levels off. It is also evident that surface coverage at maximum oxygen uptake is 18.6%. The surface coverage of Mo/γ-Al_2O_3 is only 7.7%. It is possible to calculate crystallite size from the above said EMA and these values are presented in table 1. It can be noted that the crystallite size is small and increases with Mo loading upto 80 Å. These values are also in agreement with X-ray diffraction (XRD) observation that no peaks are observed at all the loadings studied. Similar XRD results were also reported on Mo/MgO by Crylov's group [16]. The above discussed oxygen chemisorption and XRD

Table 1
Surface area and parameters derived from oxygen uptake

Mo loading (wt%) on MgO	BET area (m^2g^{-1}) after reduction	E.M.A. [a] (m^2g^{-1})	Crystallite [c] size D (Å)	Surface [b] coverage
2	111.0	4.9	37.1	0.044
4	83.0	7.6	48.7	0.094
6	69.4	10.1	55.3	0.145
8	72.3	13.5	55.1	0.186
10	74.6	13.6	68.2	0.182
12	82.7	13.9	80.2	0.167

[a] Calculated using the factor 13.6 m^2 (ml STP)$^{-1}$.

[b] Defined as EMA/surface area of reduced catalyst.

[c] Obtained using the equation $D = 6 \times 10^4/\rho \times M$, where ρ is density of MoO_2 (gr/CC) and M is the EMA per gram MoO_2).

data suggest that Mo is well dispersed on MgO support.

Thoiphene HDS rate as a function of Mo loading on Mo/MgO is presented in fig. 1. Data on Mo/γ-Al_2O_3 are also included for comparison. It can be observed that HDS rate increases sharply at low loadings and then levels off beyond 8% Mo loading. Seshadri et al. [17] observed a similar maximum in activity at 9 wt% of Mo, for the condensation of butryl aldehyde on Mo/MgO. It can be also noted from the surface area values given in table 1, that the variation in activity is not due to changes in surface area of the support. It is interesting to recall that oxygen uptakes also showed similar behaviour viz. increasing sharply and levelling off with Mo loading.

Oxygen uptake is plotted against HDS activity in fig. 2. For comparison purpose, rates on Mo/γ-Al_2O_3 from ref. [18] are also shown in the same figure. It can be noted that a nice linear correlation passing through the origin is obtained throughout the composition range studied. This correlation demonstrates that oxygen chemisorption gives a measure of the sites responsible for HDS activity. Since it is generally believed that HDS takes place on coordinatively unsaturated sites (CUS) and since it is known from the work of Millman and Hall [19] that the oxygen chemisorption correlates linearly with CUS sites, it appears that oxygen chemisorption evaluates a property intimately related to HDS activity. Since the linear relationship holds good over the entire composition range studied, it can be concluded that same kind of active sites are present throughout the composition.

Quasi turnover frequencies (QTOF) in activity per g. Mo per hour as a function of loading are presented in fig. 3. In the same figure the dispersion (O/Mo) × 100 calculated from oxygen chemisorption data are also shown. QTOF and dispersion corresponding to Mo/α-Al_2O_3 are also presented in the

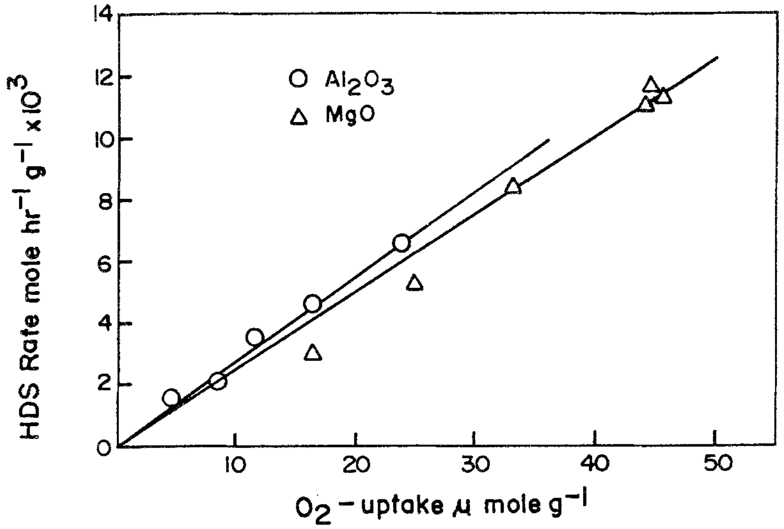

Fig. 2. Correlation between O_2 uptake and HDS activity.

figure for comparison purpose. It can be noticed that as expected the dispersion and activity show similar kind of variation with Mo loading. It is interesting to compare QTOF values of Mo/MgO with Mo/γ-Al_2O_3. From such a comparison (fig. 3) it is evident that Mo/MgO has higher activity compared to Mo/γ-Al_2O_3 and the dispersion of Mo/MgO is better than that of Mo/γ-Al_2O_3. The

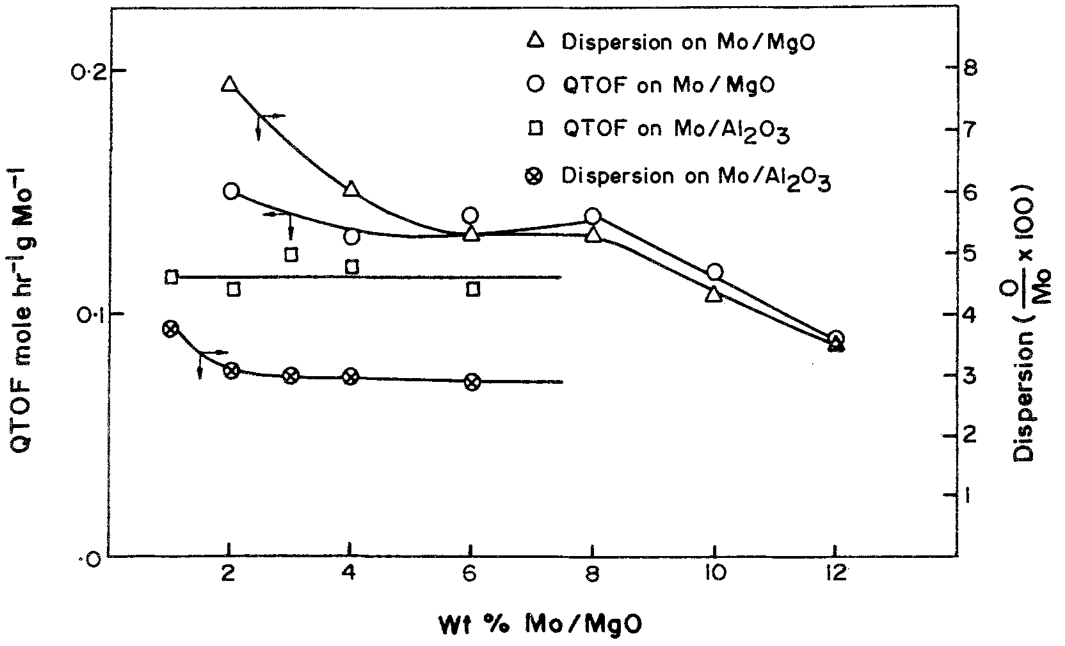

Fig. 3. Effect of Mo loading on QTOF and dispersion.

turn over frequencies calculated based on oxygen chemisorption for 8 wt% Mo were found to be 3.5×10^{-2} sec^{-1} and 3.7×10^{-2} sec^{-1} for Mo/MgO and Mo/Al_2O_3 respectively. These values indicate that activity per site are comparable. Therefore these results indicate that the observed higher activity in the case of Mo/MgO is due to an increase in dispersion of molybdenum on MgO support.

Earlier it was observed (fig. 3) that oxygen chemisorption increases sharply at low loadings and then levels off. It is also noted that thiophene HDS activity also behaves in a similar way. It is interesting to dwell upon this aspect and understand why this is so. In this connection the patchy model of Hall [20] and the discussion about the same on $Mo/\gamma\text{-}Al_2O_3$ by Nag [21] are very useful. It has been envisaged by them that at low loadings the molybdena exists as small patches of few layers thick, on the support surface. Similar observation was also reported by Pratt et al., from the electron microscopic study on sulfided catalysts [7]. These patches as a result of reduction generate coordinatively unsaturated sites at the edges and corners of the molybdenum patches. It has also been visualized that with the increase of molybdenum loading the number of patches increase and these patches upon reduction give more sites for oxygen chemisorption. At this juncture it should be mentioned that Millman and Hall [19] have shown that oxygen adsorbs on coordinatively unsaturated sites. This two dimensional increase of number of patches continues upto monolayer coverage of the support by molybdenum. After the attainment of monolayer, these patches grow three dimensionally thus decreasing the dispersion of Mo. A similar behaviour is also possible for Mo/MgO. Therefore the initial increase in HDS activity and oxygen chemisorption and subsequent levelling off of the above two parameters as a function of loading may be due to generation of CUS sites upto monolayer coverage. Beyond the monolayer loading the CUS sites decrease as a result of crystal growth and oxygen chemisorption levels off and so does the HDS activity. Since it is known that oxygen chemisorbs on CUS sites and HDS reaction takes place on anion vacancies at edges and corners, the oxygen chemisorption and activity behaves in a similar manner.

Acknowledgements

We thank the referees for their valuable suggestions and Dr. A.V. Rama Rao, Director, IICT, for his encouragement. H.R.K. thanks the C.S.I.R., India, for a Senior Research Fellowship.

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