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LETTERS TO THE EDITORS

The Nature of Hydrodesulphurization on MoS_2

Tauster *et al.* (*1*) have recently reported a linear relationship between the ability of MoS_2 to chemisorb oxygen and its catalytic activity for hydrodesulphurization (HDS) of dibenzothiphene. No correlation of HDS activity with surface area was observed. It was suggested that since the edge plane of single-crystal MoS_2 has been observed to oxidise much more readily than the basal plane (*2*), the amount of O_2 chemisorbed by the MoS_2 catalysts was a measure of the edge-to-basal plane ratio. Therefore, they have concluded that the HDS activity of MoS_2 is related to the proportion of edge sites.

The above conclusion conflicts with the earlier work of Stevens and Edmonds (*3*) who investigated MoS_2 samples with widely different edge-to-basal plane ratios. It was found that thiophene HDS conversion was lower for the MoS_2 sample with the higher proportion of edge sites, while the activity for butene hydrogenation was increased. In a comparison of the MoS_2 samples with sulphided Co, Mo, and Co–Mo/alumina catalysts, it was found (*3*) that the selectivity for butene hydrogenation of the supported catalysts resembled the MoS_2 sample with the lower edge-to-basal plane ratio. These results led Stevens and Edmonds (*3*) to conclude that the edge plane of MoS_2 was more active for hydrogenation reactions while the basal plane was more active for thiophene HDS.

Despite the conflict over which plane of MoS_2 is more active for HDS, there is agreement between the two studies on two points. Although Stevens and Edmonds (*3*) determined the proportion of edge sites by butanol adsorption, they did observe by ESCA a higher oxygen 1*s* peak intensity from chemisorbed oxygen on the MoS_2 sample with the greater proportion of edge sites, which supports the assumption of Tauster *et al.* (*1*) that the amount of chemisorbed oxygen measured the density of edge sites. Furthermore, both studies found that HDS activity was not well correlated with BET surface area.

The notion that the HDS activity of MoS_2 is related to the edge sites is supported by a recent study of unsupported Ni–Mo catalysts by transmission electron microscopy. Pratt and Sanders (*4*) found that the optimum Ni/Mo ratio for high HDS activity occurred when the MoS_2 crystallites exposed a high proportion of edge sites. At other Ni/Mo ratios "skin" structures were formed which exposed few edge sites. However, in this preliminary work the proportion of edge sites in the active catalysts was not quantified. Thus, while this work clearly demonstrates the importance of edge sites, it is difficult to make a direct comparison with the results of Tauster *et al.* (*1*) and Stevens and Edmonds (*3*).

There are a number of important experimental differences between the work of Tauster *et al.* (*1*) and that of Stevens and Edmonds (*3*). The former measured HDS activity using dibenzothiophene at 450 psi in Decalin, while the latter used thiophene in the gas phase at atmospheric pressure. However, if it is assumed that the comparison between the results of these two studies is valid despite these differences, it is possible to devise a mechanism for HDS reactions on MoS_2 which resolves the apparent conflict over the importance of edge sites. In order to do this, we make the assumption that HDS proceeds by dissociative chemisorption of hydrogen on the edge sites followed by spillover of hydrogen atoms onto the basal plane where the active sites

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for hydrogenolysis exist or are generated. The exact nature of the spillover process is not important to the model. This proposal is supported by studies of hydrogen adsorption on MoS_2 (*3*, *5*) which indicate that adsorption is an activated process which occurs much more readily on the edge plane. In addition, Delmon (*6*) has suggested that there are different hydrogenation and HDS sites on MoS_2. There is also considerable evidence from studies of metal crystals that step sites are very active for hydrogen dissociation (e.g. (*7*)). In the proposed model, HDS activity would increase as the proportion of edge sites increases, since more spillover hydrogen would be available, as long as sufficient basal plane area is still present. However, since increasing the proportion of edge plane decreases the basal plane area, the HDS activity would be expected to fall off at high edge-to-basal plane ratios. On the other hand, the selectivity for butene hydrogenation would continue to rise, because hydrogenation takes place preferentially on the edge plane (*3*). Stevens and Edmonds (*3*) found that increasing the proportion of edge sites from 28 to 95% resulted in a lowering of HDS activity and an increase in O_2 chemisorption. This is understandable if 28% edge sites lies closer to the maximum in the HDS/edge-to-basal plane ratio curve. We calculate that the regime explored by Tauster *et al.* (*1*) corresponds to 2 to 27% edge sites (assuming two adsorption sites per unit cell edge plane) and, therefore, a rise in HDS activity with O_2 uptake would be expected, as indeed they observed. The fact that the results of Stevens and Edmonds (*3*) and Tauster *et al.* (*1*) are consistent with our basic assumption does not preclude the possibility that the origin of the conflict lies in the experimental differences referred to above. Clearly, further work on well-characterized MoS_2 is required before the issue can be completely resolved.

It is worth noting that the model for HDS on MoS_2 suggested above is consistent with recent proposals by Delmon (*6*) and Fraser *et al.* (*8*) concerning the role of Co and Ni promoters. That is, the promoter may be an additional source of spillover hydrogen. It is also consistent with the work of Pratt and Sanders (*4*) if one assumes that the promoter influences the morphology of MoS_2 such that the proportion of edge sites is close to the optimum. An intriguing aspect of the spillover mechanism of promotion is that many different Co or Ni compounds may be able to provide spillover hydrogen to variable extents. Perhaps this goes some way to explaining why identification of a unique promoter species has proved so elusive.

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