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The Nature of Hydrodesulfurization on MoS_2. Reply to Chadwick and Breysse

We should like to reply to the comments by Chadwick and Breysse (*1*) regarding our recent report relating O_2 chemisorption to the hydrodesulfurization (HDS) activity of MoS_2 (*2*). They state correctly that our conclusion from this correlation that the HDS activity of MoS_2 is related to the proportion of edge sites is in conflict with the work of Stevens and Edmonds who concluded that the basal plane of MoS_2 was more active for HDS (*3*). Chadwick and Breysse go on to suggest a mechanism which would resolve this apparent conflict. We do not wish to take issue with this proposed mechanism at this time but rather to question the conclusions of the earlier work of Stevens and Edmonds (*3*).

All parties seem to be in agreement concerning the ability of O_2 chemisorption to measure the edge area of MoS_2 crystallites and the noncorrelation of BET surface area with HDS activity. We take issue however with the statements of Stevens and Edmonds (*3*) regarding the relative amounts of edge area in the *two* MoS_2 catalysts on which they made their activity measurements. We reproduce in Table 1 the results they reported for these two catalysts. Their conclusion that the HDS activity occurs on the basal plane more effectively than on the edge plane results from the observation that the heptane-ground MoS_2 with 28% edge has a thiopene conversion of 82% and that the air-ground MoS_2 with 95% edge has a conversion of 77%. It would seem to us that the data obtained with two catalysts with activities differing by so little are insufficient to reach their stated conclusion. Further, if we assume the measured BET surface areas are made up of the stated proportion of basal and edge areas, we then find that the heptane-ground MoS_2 has *higher* edge area ($0.28 \times 52\ m^2/g = 14.6\ m^2/g$) than the air-ground MoS_2 ($0.95 \times 10\ m^2/g = 9.5\ m^2/g$). Thus, it would seem that the results of Stevens and Edmonds *are not in conflict* with those that we reported. Stevens and Edmonds do not explicitly state the source of their MoS_2 but described it as prepared by the methods of Groszek and Witheridge (*4*), and the basal-to-edge area of the MoS_2 was measured by the method of Groszek (*5*). It is interesting to note that two samples of MoS_2 with exactly the measured edge area of Stevens and Edmonds (28 and 95%) appear in Ref. (*4*). It is difficult to envision MoS_2 with 95% edge area unless we consider an unusual morphology (i.e., *c*-axis needles). We find it difficult to believe that these unusual morphologies could be obtained by any method of grinding. Thus, we believe that there is perhaps some problem in the method of determination and can see no way in which the conclusion of Stevens and Edmonds is supported by their data. As for the higher ESCA peak for O(1*s*) observed for the air-ground sample (*3*) we believe that this is due to lattice oxygen incorporation in the bulk of the catalyst due to the air-grinding itself, the ESCA analysis not being fully surface sensitive due to photoelectron escape from the interior of the sample.

Our correlation (*2*) was based on *15* samples; all characterizations were carried out after activity testing. We found that characterization prior to activity testing was unreliable due to the fact that the active catalyst had not been stabilized under reaction conditions. Most of the charac-

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TABLE 1

	BET surface area ($m^2\ g^{-1}$)	Basal (%)	Edge (%)	Thiophene conversion (%)
Heptane-ground MoS_2	52	72	28	82
Air-ground MoS_2	10	5	95	77

terization performed by Stevens and Edmonds was done *prior* to reaction. Further, in a preliminary note, one of us has indicated that the HDS correlation to O_2 chemisorption is also valid for Al_2O_3-supported and Co-promoted catalysts (*6*).

Finally, we agree with Chadwick and Breysse (*1*) that more work must be done on MoS_2 catalysts to determine precisely the mechanism and active site location for HDS catalysis, which is a difficult task. However, while basal plane adsorption may be important we still believe that based upon the available evidence and the previous work of Voorhoeve and Striver (*7*) and others the simplest interpretation is to locate the active sites on the MoS_2 edge plane.

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