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The Nature of Hydrodesulfurization on MoS_2. Reply to Chianelli and Tauster

In making any comparison between the results of Tauster *et al.* (*1*) and our earlier results (*2*), the key feature to remember is that one is not comparing equivalent systems. Tauster *et al.* prepared their MoS_2 by a variety of chemical methods, tested the material at 350°C and 450 psig using a liquid-phase feedstock containing 5% dibenzothiophene (DBT) in decalin. They subsequently removed the catalyst from their reactor, treated it with 14% H_2S in hydrogen at 350°C, and measured the oxygen adsorption at ambient temperature. In our work (*2*), we took MoS_2 powder of 99% purity and subjected it to grinding in a ball mill either in heptane or in air. This increased the BET surface area, and the relative proportions of edge sites and basal plane were determined by the heat of adsorption ratio of *n*-butanol to dotriacontane. These measurements were made prior to studying the chemical properties of these materials for adsorption and in hydrodesulfurization reactions. Both thiophene and hydrogen chemisorptions were measured, as well as the reactivity of thiophene at 325°C and CS_2 at 225°C, each in an atmospheric microreactor.

In oxygen chemisorption, we reported a higher O 1*s* signal in ESCA on the air-ground material. We would not agree with Chianelli and Tauster (*3*) that this is due to "lattice oxygen incorporation" in the bulk of the catalyst due to air-grinding itself since there is no evidence in the Mo 3*d* signal for the formation of either MoO_3, which would predominate over MoO_2, or in the S 2*p* signal for the formation of sulfate anions. We did not measure oxygen chemisorption directly, and we used *n*-butanol to measure the *proportion* of edge sites and not their absolute number. Hence we only quoted the percentage edge sites for each sample.

The repeatability and the morphologies of our samples are questioned (*3*), particularly the high proportion of edge sites obtained by air-grinding. The samples we used were fresh samples giving the same proportion of edge to basal planes as that reported earlier by Groszek and Witheridge (*4*). The relative properties can, of course, be varied by the length of grinding. The high edge-to-basal ratio in air-ground samples arises because the materials are not solid needles but contain defects with the appearance of pinholes. There may also be highly faulted basal planes.

Our conclusions are very carefully stated at the end of our paper (*2*) and we feel no reason to change them on the basis of all the data we presented. The conclusions were that the edge plane appears to be a strong hydrogenating centre, while the basal plane, though active for thiophene conversion, gave low levels of thiophene and hydrogen adsorption and low levels of product hydrogenation. Indeed, Tanaka (*5*), using MoS_2 single crystals sliced to increase the proportion of edge sites, has also concluded that these are the hydrogenating sites.

The reasons for the differences between our results and those of Tauster *et al.* are probably due to the fact that our data were obtained in the gas phase whilst their data were obtained in the liquid phase in the presence of a competitive adsorbate, namely, decalin, which is moreover a hydrogen donor. Frye and Mosby (*6*) showed

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that a competitive adsorbate such as an aromatic light-cycle oil can inhibit the kinetics of DBT desulfurization and hence possibly the mechanism and even the reaction site. The presence of the hydrogen donor decalin, a second source of hydrogen, adds a further variable to the system. These differences need further consideration. For instance, in the results of Tauster *et al.*, it would be interesting to know how the ratio of biphenyl to cyclohexyl benzene varied with the proportion of edge sites.

Thus, when all the data which we reported are taken into account, and when the real differences in the conditions of measurement between our results and those of Tauster *et al.* are considered, it is evident that the roles of the basal and edge sites in MoS_2 have not been unambiguously identified under all reaction conditions.

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