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NOTE

HYDRODESULPHURIZATION ACTIVITIES AND ELECTRICAL
CONDUCTIVITIES OF $\text{MoO}_3 - \text{Al}_2\text{O}_3$ CATALYSTS

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HYDRODESULPHURIZATION ACTIVITIES AND ELECTRICAL CONDUCTIVITIES
OF $\text{MoO}_3 - \text{Al}_2\text{O}_3$ CATALYSTS

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Although the relationship between the electrical conductivity and the catalytic activity of solids has been considered for a number of years, few hydrodesulphurization catalysts have been examined. In general, studies have been limited to hydrodesulphurization catalysts having very special features. For example, Ng (1) used unsupported MoS_2 powders when making Hall Effect measurements and Aoshima and Wise (2) made electrical conductivity measurements during their MoS_2 single crystal studies. The purpose of the work reported here was to examine supported hydrodesulphurization catalyst systems resembling those used in industrial practice.

In an attempt to keep the experiments as simple as possible, promoters were not used in the catalyst formulations. Each of the catalysts studied contained a different amount of MoO_3 supported on alumina. The alumina support is an insulator and therefore has a low electrical conductivity. It was anticipated that the electrical conductivity of the catalysts would increase with MoO_3 content, since bulk MoO_3 is a semi-conductor. In addition, the possibility of surface conductivity in the molybdenum oxide surface layer was recognized. The presence of a molybdenum oxide surface layer was suggested by Dufaux, Che and Naccache (3) and has recently been reviewed by Abdo, Lo Jacono, Clarkson and Hall (4).

The catalysts used in this study were prepared by spraying aqueous solutions on to batches of alpha alumina monohydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) powder, (Continental Oil Company Catapal SB) as they were being milled in a mix-muller. The first solution added to each batch contained a small amount of nitric acid in water. Then an ammonium paramolybdate solution was added. The impregnated aluminas were dried at 120°C for 10.8 ks (3 hours) and calcined at 500°C for 10.8 ks (3 hours). The calcined powders were mixed with 2 wt % stearic acid and pressed into cylindrical pellets ($L = D = 3.18$ mm) in a continuous pelleting press. The stearic acid acted as a binder and lubricant during pelleting. The pellets were recalcined at 500°C for 14.4 ks (4 hours) to remove the stearic acid. Details of the procedure have been reported elsewhere (5).

Hydrodesulphurization activities of the catalysts were determined using a heavy gas-oil hydrocarbon feedstock having a $345\text{--}525^\circ\text{C}$ boiling range, a specific gravity ($16/16^\circ\text{C}$) of 0.987, a Conradson Carbon Residue of 0.97 wt % and a sulphur content of 3.64 wt %. The feedstock was a portion of the material produced when Athabasca bitumen was thermally hydrocracked in a pilot plant reactor. The catalyst pellets were evaluated in a bench scale fixed bed reactor having a volume of 155 ml and a length-to-

diameter ratio of 12. The reactor was filled sequentially from the bottom with 42 ml of berl saddles, 100 ml of catalyst pellets and 13 ml of berl saddles. Heavy gas-oil, mixed with hydrogen (purity = 99.9 wt %), flowed continuously into the bottom of the reactor and up through the catalyst bed. Product leaving the top of the reactor flowed to receiver vessels where the liquid and vapour separated.

Each experiment was performed at a pressure of 13.9 MPa (2000 psig), a liquid volumetric space velocity of 0.556 ks^{-1} (2.0 hr^{-1}) based on the reactor volume occupied by the catalyst pellets, and a hydrogen flow rate of 0.0718 ls^{-1} at STP (5000 cu ft/bbl). The catalyst was presulphided and stabilized using the mixture of gas-oil and hydrogen at 400°C . Subsequent experiments were performed sequentially at temperatures of 420°C , 400°C and 380°C . Gas-oil and hydrogen contacted the catalyst for 25.2 ks (7 hours) prior to the 420°C experiment. The reaction system was maintained at steady state conditions for 3.6 ks (1 hour) prior to, and for 7.2 ks (2 hours) during, the period in which each sample of liquid product was collected. The liquid product was analyzed for sulphur using an X-ray fluorescence technique (6).

Prior to making measurements of catalyst pellet resistance, all samples were held under vacuum at a pressure of 665 mPa at room temperature for 86.4 ks (24 hours). Extensive evacuation was required since the measured resistance of a sample was found to decrease rapidly, by factors of up to five, when it was transferred to normal moist atmospheric conditions. After evacuation the catalyst pellets were stored in a desiccator. Subsequently each sample was transferred to the large evacuated bell jar where its electrical resistance was measured. The pellet was held between two electrodes, one of which was spring loaded. In order to prevent contact resistance, the surfaces of the electrodes were covered with indium foil. A cubic Faraday cage, having linear dimensions of 0.2 m, surrounded the electrodes. Each sample was evacuated for an additional 7.2-14.4 ks (2-4 hours) before measuring the resistance, R , at room temperature. The electrical resistances were measured with a solid-state Keithley electrometer, model 602. The conductivity, σ , was calculated from the formula $\sigma = L/RA$, where L and A are the pellet length and cross-sectional area respectively.

The hydrodesulphurization activities of the catalysts at 420°C are shown in Figure 1. The activity increased sharply up to 3 wt % MoO₃, increased more gradually from 3 to 12 wt % and was reasonably constant at concentrations above 12 wt %. Reaction temperature did not have a great effect on the pattern of catalyst activity. For example, at 400°C the greatest increase was from 0 to 3 wt % MoO₃ with much smaller increases above 3 wt % (7).

The densities of the catalyst pellets used for the resistance measurements and the resulting electrical conductivities are shown in Figure 2. It is apparent that density increased reasonably uniformly with MoO₃ concentration. In contrast, the electrical conductivity increased rather uniformly up to 9 wt % MoO₃, reached a maximum between 9 and 12 wt % MoO₃ and finally declined as the MoO₃ concentration increased above 12 wt %. Since the surface areas of the catalyst are known to vary with MoO₃ content (7), the electrical conductivities were also calculated on the basis of unit surface area. When this was done the peak at 9-12 wt % MoO₃ did not change although different numerical results were obtained. This suggests that the maximum in the electrical conductivity can not be explained by surface conduction.

It is tempting to suggest that there is a correlation between the increases in electrical conductivity and in catalytic activity from 0 to 12 wt %. It is also tempting to suggest that the maximum at 9-12 wt % MoO₃ may be caused by the formation of a molybdenum oxide surface layer and by the maximum in Mo(V) ion concentration discussed by Petrakis and Seshadri (8). Although the above phenomena may be related, there are at least three additional points which must be examined before such a conclusion can be reached. First, due to the method of catalyst preparation it is likely that all of the molybdenum was not located on the catalyst surface. Therefore, 12 wt % MoO₃ is probably not sufficient to form a complete surface layer on our catalyst. Second, when the electrical conductivities were measured the molybdenum was in the oxide form. In contrast, under reaction conditions the molybdenum oxides are at least partially converted to sulphides (9) which are also semi-conductors. Third, while catalytic activity is a surface property, the electrical conductivity is a bulk property. Although the electrical properties of the bulk are sometimes influenced by surface properties, this is not always the case (10). In spite of these uncertainties

the results presented here do show that the addition of even small amounts of MoO_3 to alumina, an insulator, causes significant changes in electrical conductivity. Furthermore, they suggest that there may be a relationship between electrical conductivity and catalytic activity of supported hydrodesulphurization catalysts.

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LEGENDS FOR FIGURES

- Figure 1 Hydrodesulphurization Activity of $\text{MoO}_3\text{-Al}_2\text{O}_3$ Catalysts. Percent sulphur removed from feedstock versus catalyst content of MoO_3 .
- Figure 2 Density (g/cm^3) and Electrical Conductivity (Siemens/meter) of Catalyst Pellets versus Catalyst Content of MoO_3 .



