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LETTERS TO THE EDITORS

Comments on "Stabilization Effect of Co for Mo Phase in Co–Mo/Al_2O_3 Hydrodesulfurization Catalysts Studied with X-Ray Photoelectron Spectroscopy"

Okamoto *et al.* (*1*) have recently suggested that the active species in hydrodesulfurization (HDS) of thiophene (TP) over molybdena catalyst has the composition S/Mo(IV) = 1. This was based on X-ray photoelectron spectroscopy (XPS) on catalysts exposed to a thiophene/H_2 mixture in a sample pretreatment chamber attached to the XPS instrument. This writer wishes to question the validity of their supposed active species for HDS reaction carried out under normal flow conditions and to offer an explanation for their unusual results, *vis-à-vis* low S/Mo ratio and presence of Co metal in their treated catalysts.

There can be significant differences in catalyst gas-phase reactions when conducted in a static or a flow system. Exposure of the catalyst to a TP/H_2 mixture results in the catalyst undergoing reduction–sulfidation reactions, liberating water as a product. In a static system, poor gas circulation can result in buildup of a gaseous layer of water around the catalyst particles, partly restricting free flow of reactant TP and H_2 to the catalyst. Also, H_2 could diffuse faster through this layer than TP, resulting in a higher H_2/TP ratio at the catalyst surface. In addition, depending on the amount of catalyst used, the limited XPS chamber volume and low total pressure employed (10 Torr) make it possible that TP (and H_2S from the reaction) may have been substantially depleted from the gas phase, leaving an essentially reducing atmosphere of H_2. Under flow conditions, these effects would be essentially eliminated due to removal of water and continual resupply of TP.

The following points may be made relative to the results obtained by Okamoto *et al.* and those obtained by others in flow systems

1. Under flow conditions, reaction of TP/H_2 with an 8% Mo/γ-Al_2O_3 for 2 hr at 343°C, Massoth and Kibby (*2*) obtained S/Mo values around 1.4 (a somewhat higher value would be expected for reaction at 400°C). This is significantly higher than the S/Mo = 1 reported by Okamoto *et al.* in their XPS measurements at 400°C over a comparable catalyst. De Beer *et al.* (3) also report S/Mo ratios appreciably greater than 1 for similar catalysts and pretreatments.

2. Patterson *et al.* (*4*) reported the presence of cobalt sulfide on their TP-reacted catalyst at 400°C. They used a separate, flow pretreatment reactor, transferring the reacted sample into the XPS instrument without contact with air. Likewise, Friedman *et al.* (*5*) found CoS on their sulfided catalyst. Thermodynamic data (*6*) show that, for Co metal to be a stable phase at 400°C, H_2S/H_2 must be less than about 10^{-4}. Therefore, the fact that Okamoto

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et al. found Co metal is most likely an indication that severe depletion of H_2S occurred in their sample treatment chamber due to insufficient gas sample and/or preferential sulfiding of the Mo.

3. Higher values of S were found by De Beer *et al.* (*3*) for Co–Mo as compared with Mo catalysts, as is generally reported in the literature for presulfided catalysts. Yet Okamoto *et al.* (*1*) found no increased S content for their Co–Mo catalyst.

From the above comments, it seems to this writer that *in situ* treatment of catalyst samples in a static chamber can result in significantly different results than obtained in a flow environment. If this is true, the interpretation of Okamoto *et al.* relative to the active species present under dynamic HDS reaction conditions must be considered questionable.

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F. E. Massoth

Department of Mining and Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

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