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Reply to the Comments by F. E. Massoth

In his comments, Massoth (*1*) has raised questions concerning the active species in CoO–MoO_3/Al_2O_3 hydrodesulfurization (HDS) catalysts, which was suggested based on X-ray photoelectron spectroscopic (XPS) studies under mild reaction conditions (10 Torr of thiophene/H_2 at 400°C) (*2*). In this letter, our discussions will be restricted mainly to the reasonableness of our experiments and results, since discussions on the validity of the proposed active species for usual flow reaction conditions are beyond the scope of our paper (*2*) because of the large pressure difference between our *in situ* experiments and usual flow systems.

Our results on the unsupported CoO–MoO_3 binary oxide catalysts (*3*) will confirm the validity of our experiments concerning the sulfur content and the sulfidation of Co under the mild reaction conditions. In the cases of the unsupported catalysts, repeated treatments with 10 Torr of thiophene/H_2 at 400°C (the same treatments as those employed for the supported catalysts) caused the sulfidation of Mo to form MoS_2 on the catalyst surface, whereas these treatments did not sulfide Co, which was only reduced to metal. However, repeated exposure of the catalyst to 10 Torr of H_2S/H_2 at the same temperature resulted in the sulfidation of both Mo and Co. A more quantitative analysis (*4*) of the XPS results reveals that MoS_2 is formed by thiophene/H_2 and that MoS_2 and CoS, and/or more likely Co_9S_8, are produced by H_2S/H_2, accompanied by excess sulfur. In addition, the excess sulfur is completely removed by successive H_2 admissions (*4*). Consequently, these results show that the effect of depletion of thiophene or H_2S in gas phase is removed by the repeated introduction of thiophene/H_2 and that the low extent of sulfidation of Mo should be ascribed to a support effect. The absence of sulfided Co with thiophene/H_2 might be due to a low conversion of thiophene to H_2S, since the amounts of the catalysts used in the XPS studies were very small (ca. 10 mg) and the reaction volume was relatively large (ca. 500 cm^3). However, we do not think that the active form of Mo will change completely even if using higher H_2S concentration than that employed in our previous papers (*2*, *3*), although a higher H_2S concentration will produce a slightly higher S/Mo ratio, accompanying more migration of Mo and even of Co (*4*) from the inner surface to the outer surface of a CoO–MoO_3/Al_2O_3 catalyst together with the sulfidation of Co.

In the cases of usual reaction conditions, more stringent conditions will produce corresponding different surface concentrations and sulfided forms of Mo and Co, which result from the migrations and different reactivities for ambient atmosphere of the catalyst components, as can be easily estimated from our results (*2*, *3*). Therefore, it is not easy to deduce the validity of the active species obtained under the mild *in situ* conditions for the usual flow environment. However, the facts that the Mo (5)/Al_2O_3 and Co–Mo/Al_2O_3 catalysts, in which Mo is sulfided less, showed higher activities for thiophene conversion than

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other catalysts under usual flow reaction conditions might correlate to the presence of the active species proposed in our paper (*2*). In addition, DeBeer *et al.* (*5*) have reported that the higher the initial sulfur content, the lower the thiophene conversion for MoO_3/Al_2O_3 catalysts.

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