

INTERACTIONS BETWEEN HYDRODESULFURIZATION
AND HYDRODENITROGENATION REACTIONS

by

Charles N. Satterfield, Michael Modell

and

Jerome F. Mayer

Massachusetts Institute of Technology, Cambridge Massachusetts

ABSTRACT

Interactions between the hydrodesulfurization (HDS) of thiophene and the hydrodenitrogenation (HDN) of pyridine on commercial CoMo, NiMo and NiW sulfided catalysts were studied using a flow microreactor at pressures up to 11.1 atm and temperatures up to 425°C.

Pyridine HDN is more difficult than thiophene HDS, and above 350°C there is a thermodynamic limitation on the first step of the HDN reaction mechanism, in which the pyridine ring is saturated to piperidine. Sulfur compounds have a dual effect on HDN. At low temperatures, thiophene inhibits the reaction, which is postulated to occur by competition with pyridine for hydrogenation sites on the catalyst, retarding the hydrogenation of pyridine to piperidine, and thus reducing the overall reaction rate. At high temperatures sulfur compounds enhance HDN. It is suggested that the dominant effect here is interaction of hydrogen sulfide, an HDS reaction product, with the catalyst to improve its activity for rupture of the C-N bond. This increases the rate of reaction of piperidine, which is rate-determining at the latter conditions, and enhances the overall rate of HDN.