

289ao Interactions of Sulfur with Carbides and Nitrides

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Carbides and nitrides are active for a variety of reactions including hydrodesulfurization and hydrodenitrogenation. In addition, some materials in this class have been reported to be tolerant to sulfur. The basis for their sulfur tolerance, however, is not well understood. In this work, we studied the interaction of various organosulfur compounds with several early transition metal carbides and nitrides as part of a more comprehensive investigation of the sulfur tolerance of these materials.

A series of monometallic carbides and nitrides was prepared from their corresponding oxide precursors using temperature program reaction methods. The carburization or nitridation was carried out using either a mixture containing 15% CH₄ in H₂ or NH₃, respectively. After synthesis, the material was passivated using a mixture of 1% O₂ in He. Before exposing the materials to sulfur they were activated in 400-600°C using pretreatment gases including He, H₂, CH₄ in H₂, and NH₃. The materials were then exposed to a solution containing the organosulfur compound for a period of 24 hrs at room temperature. The sulfur content of the liquid before and after exposure to the solid was analyzed using gas chromatograph equipped with a flame photometric detector.

The interactions of carbides and nitrides with organosulfur compounds including thiophene, benzothiophene (BT), dibenzothiophene (DBT), and tetrahydrothiophene (THT) were investigated. X-ray diffraction (XRD) indicated that bulk sulfides were not formed on exposing these materials to the sulfur compounds at room temperature. The results indicated that the interaction was limited to the surface. The character of the interactions was dependent on the type of solvent used and pretreatment conditions employed. Thiophene adsorption onto the degassed Mo₂C (in He) was best-fit using a Langmuir isotherm while adsorption onto degassed Mo₂N was best characterized using a Freundlich isotherm. On the other hand, trends for the reduced materials were the opposite of those for the degassed materials. Moreover, both materials showed reversible thiophene adsorption under different pretreatment of the spent catalyst.

Solvent effects were examined for benzene, toluene, and isooctane. While each solvent competed for sites with the organosulfur compounds, isooctane was the least interactive. Additional results regarding competitive adsorption and the surface character of the carbides and nitrides will be described.