Interaction of Sulfur with Carbides and Nitrides: Adsorption Mechanism and Sites

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Introduction
Carbides and nitrides have attracted considerable interest as catalysts for a variety of reactions involving feedstocks containing sulfur. For example, molybdenum nitride and carbide catalysts are known to have higher hydrosulfurization (HDS) activities than conventional sulfide catalysts [1]. In addition, these materials have been reported to be resistant to sulfur poisoning [2], the basis of which is not well understood.

This paper summarizes our most recent work to clearly define the modes of sulfur adsorption and adsorption sites on high surface area, early transition metal carbides and nitrides. The interactions of molybdenum carbides and nitrides with organosulfur compounds including thiophene, benzothiophene (BT), dibenzothiophene (DBT), and tetrahydrothiophene (THT) were investigated using a variety of tools. Previously we reported that these interactions did not produce bulk sulfides based on results from X-ray diffraction (XRD), and that the nature of these interactions was dependent on the types of solvent used and pretreatment conditions employed. Here we detail the mechanism of adsorption and types of sites based on measurements with CO$_2$ and NH$_3$, known acid and base gases, respectively.

Materials and Methods
High surface area molybdenum carbides and nitrides were prepared from their corresponding oxide precursors using temperature program reaction methods [3]. The carburization or nitridation was carried out using a 15% CH$_4$/H$_2$ mixture or NH$_3$, respectively. After synthesis, the materials were passivated using a 1% O$_2$/He mixture. Before exposing the materials to sulfur they were reactivated by heating to 400-600 °C in H$_2$. The materials were then soaked in the sulfur containing liquid for a period of 24 hrs at room temperature with constant agitation. The sulfur content of the liquid before and after exposure to the solid was analyzed using a gas chromatograph with flame photometric detector.

Results and Discussion
Isotherms indicated that adsorption of the model sulfur compounds on Mo$_2$C was Langmuiran, suggesting that the heat of adsorption did not vary significantly with coverage. These materials possessed a greater affinity for non-aromatic sulfur compounds (e.g. THT) as compared to aromatic sulfur compounds (see figure 1). Saturating the surface with NH$_3$ before exposure to sulfur hindered the adsorption of thiophene suggesting the importance of acid sites for Mo$_2$C (open symbols in figure 1). Similar results were obtained for Mo$_2$N.

Figure 1. Adsorption of different sulfur compounds in isooctane on fresh (closed symbols) and poisoned (open symbols) Mo$_2$C surface.

Using benzene as a solvent instead of isooctane resulted in a decrease in the thiophene, BT and DBT uptakes (see figure 2) indicating a competition among these molecules. These organosulfur compounds may have adsorbed via π bonding.

Figure 2. Adsorption of model sulfur compounds on Mo$_2$C surface using isooctane (closed symbols) and benzene (open symbols) as solvents.

On the other hand, THT uptake was not affected by the presence of benzene indicating that THT and benzene adsorb on different sites. A plausible explanation is THT adsorbed through the sulfur atom. Similar behavior was observed for Mo$_2$N.

Significance
Carbides and nitrides show promising sulfur absorption capabilities. An understanding of the sulfur adsorption mechanism and sites on these materials may allow for further optimizations leading to potential commercial applications.

References