

In Situ Study of the Surface Interactions
In Coal Liquefaction Catalysts

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There is an increasing interest in the development of better catalysts for the hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) of coal derived fuels and oil heavy residues. These synthetic feedstocks and heavier petroleum fractions contain a higher concentration of heteroatoms than light petroleum stocks and are much more difficult to process. Metal sulfides catalysts play a very important role in HDN and HDS processes as well as in direct coal liquefaction. There is concrete evidence of the direct role played by iron sulfides in direct coal liquefaction. We have investigated the surface reactions on iron sulfides, especially pyrrhotites using standard surface techniques, EXAFS and in situ Mossbauer spectroscopy. We find clear evidence of the involvement of the iron sulfides surfaces in the cleavage of oxygen bonds in coal and coal derived products. In HDN and HDS reactions, the role of the iron sulfides is less important than that of Mo-Co or Mo-Ni supported catalysts. We have performed a systematic in situ study of Ni-Mo supported on gamma alumina using x-ray absorption techniques as well as in situ Mossbauer spectroscopy. The HDN of quinoline was studied by both techniques between room temperature and 440°C at high hydrogen pressures. We find clear evidence of Ni association to Mo, there is also Ni in separated islands and a third phase of Ni interacting strongly with alumina and forming nickel-aluminate. When sulfidation takes place immediately after calcination two sulfide phases are identified, one associated with the MoS₂ islands on the support and the other, probably, with a non-stoichiometric nickel sulfide compound. Very small amounts of nickel aluminate are observable.

The HDS of dibenzothiophene was studied using a pure MoS₂ catalyst and a commercial Ni-Mo catalyst. The structure of the catalysts was investigated using x-ray absorption techniques. All the measurements were performed in situ between -195°C and 440°C. It was observed that the presence of nickel tends to stabilize the MoS₂ islands on the support; in the absence of nickel there is very clear evidence of irreversible sulfur loss.

The difference in catalytic activity between iron sulfides and Mo sulfides is related to the difference in crystallographic structures, which favors in the case of Mo a high dispersion of the catalyst on the support.

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