JOURNAL OF CATALYSIS 78, 262–263 (1982)

LETTERS TO THE EDITORS

Comment on the Nature of Iron Sulfides during Catalytic Reactions

In their paper entitled "Hydrodesulfurization Catalysis by Transition Metal Sulfides" Pecoraro and Chianelli used iron sulfides in some of their experiments (*1*). However, the paper does not clearly specify which iron sulfides they used. Sulfides of iron exist in several forms, for example, pyrite, FeS_2; pyrrhotites, $Fe_{1-x}S$; troilite, FeS; and others. In Table 3, page 437, the authors mention troilite as the stable phase in a mixture of 85% hydrogen and 15% hydrogen sulfide (this disagrees with Table 1, page 432) and they mention FeS_x as the stable phase in 100% hydrogen. This strikes us as the reverse of expectations.

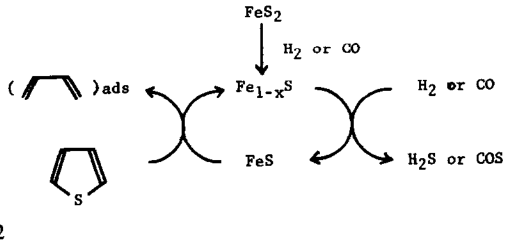
We have been examining iron sulfides as catalysts for hydrodesulfurization and other reactions and believe we can comment on the nature of the iron sulfides present under certain conditions. We find, under conditions of flowing hydrogen or flowing carbon monoxide gas at 400°C and 25 psig, that pyrite and pyrrhotites are converted to troilite. These results are in substantial agreement with earlier work (*2*) which demonstrated this conversion above 500°C. Our results are similar, but are derived from experiments done at a lower temperature. At first we thought this was due to the presence of graphite, an additive we use to facilitate the preparation of the pyrrhotites (*3*); however, later we found that pyrite converts to troilite at 400°C in hydrogen in the *absence* of graphite. Additionally, we find the reaction is reversible. Treatment of the troilite with thiophene in flowing helium produces pyrrhotite.

Our experiments were carried out in a plug flow tube reactor into which pyrite or synthetic pyrrhotite was packed. Appropriate gases, hydrogen, helium, carbon monoxide, or mixtures of these, were passed continuously over the iron sulfides under study. Various organic compounds, such as thiophene, alcohols, and aldehydes, were injected into the carrier gas stream to determine their reactivities. Reaction products were monitored by gas chromatography and the solid iron sulfide materials were analyzed by Mössbauer spectroscopy and X-ray diffraction methods reported previously (*4*).

When we examined the Fischer–Tropsch reaction over synthetic pyrrhotites we discovered the presence of only troilite after reaction. Similarly, when studying the hydrodesulfurization of thiophene with hydrogen over both pyrite and synthetic pyrrhotites, we recovered only troilite.

The similarity of results obtained under a variety of conditions suggests that the same surface is catalyzing the reactions. We suggest that under our conditions the surfaces of pyrite and pyrrhotites are rapidly converted to troilite which is the active catalyst for hydrodesulfurization and the other reactions mentioned above, as well as for isopropanol conversions (*5*).

This latter mechanism of cycling iron sulfides between troilite and pyrrhotites offers a chemical explanation for the *in situ* desulfurization of organic sulfur compounds in coal by iron sulfides.



0021-9517/82/110262-02$02.00/0

REFERENCES

1. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67,** 430 (1981).
2. Attar, A., *Fuel* **57,** 201 (1978).
3. Shiley, R. H., Russell, S. J., Dickerson, D. R., Hinckley, C. C., Smith, G. V., Twardowska, H., and Saporoschenko, M., *Fuel* **58,** 687 (1979).
4. (*a*) Hinckley, C. C., Smith, G. V., Twardowska, H., Saporoschenko, M., Shiley, R. H., and Griffin, R. A., *Fuel* **59,** 161 (1980). (*b*) Saporoschenko, M., Hinckley, C. C., Smith, G. V., Twardowska, H., Shiley, R. H., Griffin, R. A., and Russell, S. J., *Fuel* **59,** 567 (1980). (*c*) Shiley, R. H., Cluff, R. M., Dickerson, D. R., Hinckley, C. C., Smith, G. V., Twardowska, H., and Saporoschenko, M., *Fuel* **60,** 732 (1981).
5. Joly, J. P., and Ollis, D., *J. Catal.* **60,** 216 (1979).

G. V. SMITH
C. C. HINCKLEY
O. ZAHRAA
T. NISHIZAWA

Laboratory of Catalysis
Department of Chemistry

M. SAPOROSCHENKO

Department of Physics
Southern Illinois University
Carbondale, Illinois 62901

R. H. SHILEY

Illinois State Geological Survey
Champaign, Illinois 61820

Received March 9, 1982