Chapter 7

Conclusions and Recommendations

A new class of hydroprocessing catalyst, the transition metal phosphides, was identified and studied in this work. Specifically, molybdenum and tungsten monophosphide, MoP and WP, were investigated. These compounds were prepared in a two step process. In the first step, an oxidic (phosphate) precursor was formed from water soluble salts of Mo, W, and P. In the second step, this precursor was reduced to a phosphide using temperature programmed reduction in flowing hydrogen. Samples were prepared in bulk form, on silica support, and on an alumina support.

Each class of material yielded active catalysts for the hydroprocessing reactions (hdn and hds) of a model oil containing quinoline and dibenzothiophene. The bulk materials were confirmed to be stable toward reaction conditions by XRD analysis, which showed little change from the fresh catalyst. Furthermore, XPS revealed that the WP surface contained only traces of sulfur following catalytic reaction. Silica supported materials had reduction characteristics similar to the bulk materials. In the case of alumina supported materials two new reduction peaks were found, which indicated a strong interaction between the phosphate and the support surface. The presence of highly dispersed MoP particles on the alumina support was confirmed by analysis of the reduction and chemisorptive properties of the materials. Additionally, separate EXAFS experiments confirmed the presence of Mo-P bond distances, and the attenuation of Mo-

Mo bond distances, confirming the presence of small phosphide particles between about 0.5 and 1.2 nm in diameter.

The mechanism of C-N bond cleavage on these materials was investigated by study of a series of amines having different structures, specifically *n*-pentylamine, *tert*-pentylamine, and *neo*-pentylamine. The relative reactivities of these molecules was dependent upon the stability of the carbocation, the steric hindrance around the alpha carbon, and the number of hydrogen atoms located on beta carbons. The primary C-N bond cleavage mechanism was deduced to be bimolecular elimination (E2) from the relative reactivity data. This is in agreement with the results found in the literature.

Piperidine and pyridine were also studied for their hydrodenitrogenation activity. They were, in general, less reactive than the alkylamine species. Piperidine HDN was found to proceed by a second order reaction via N-(*n*-pentyl)piperidine as a reaction intermediate. Pyridine HDN was found to proceed by a zeroth order decomposition of the intermediate piperidine.

Due to the irreplaceable nature of fossil resources, the author recommends that renewable energy resources be developed and implemented. This type of work could include studies of liquids produced from biomass, generation of fuel from microbes, and the increased application of wind and solar energy technology.

Regarding the bulk phosphides, it is of fundamental interest to develop a thermodynamic stability model of the bulk phases under hydroprocessing conditions. This would allow stability comparisons of hydrides, oxides, carbides, nitrides, sulfides, and phosphides, potentially revealing such properties as the equilibrium composition of the catalytic material during reaction testing.

Additional materials which could be developed into hydroprocessing catalysts are the arsenides and antimonides of the transition metals. However, one drawback of these materials is the use of the toxic components arsenic and antimony.

A good model of the nature of the active surface needs to be developed. This means that a coherent match between observed structural features of the material must match observations of kinetic models. Therefore, the determination of the nature and quantity of acid, basic, and coordinatively unsaturated sites on the catalyst surface is desirable. To this effect, diffuse reflectance infrared spectroscopy of adsorbed amine species could confirm the presence of Br□sted acid sites on the catalyst surfaces, and temperature programmed desorption could quantify the strength and amount of adsorbed material on acidic sites. The chemisorption and temperature programmed desorption of an acidic gas, such as BF_3, could be used to quantify the strength and number of basic sites. Similarly, the use of CO chemisorption in this study was based on past experience and seemed to yield valid results. Finally, the strength and quantity of coordinatively unsaturated sites could be investigated by chemisorption and tpd of molecules such as CO, NO, and olefins. This material could be complemented by the characterization of surface species by diffuse reflectance infrared spectroscopy.

The kinetic expressions of the reactivities of the alkylamines need to be developed and consolidated both with the kinetic observations with piperidine and pyridine, but also with the mechanistic theory arrived at in the relative reactivity study. That is, it is desirable to know whether the kinetic expressions agree with the bimolecular elimination mechanism concluded by the relative reactivities. It is conceivable that new theories of mechanistic behavior could arise from this type of work.

Another aspect of developing a coherent kinetic theory would involve the mechanistic study of thiol degradation by a similar technique as used for the amines. It has been proposed in the literature without proof that thiols can undergo direct hydrogenolysis reactions (1). Although it is known that C-N bonds are stronger than C-S bonds by 3 – 6 kcal mol^{-1}, similarity in product distributions found between thiols and amines (noted in the literature review in Chapter 4) suggests that C-S bonds are also broken by bimolecular elimination reactions. It is interesting and relevant that the molecule 4,6-dimethyldibenzothiophene, which has been reported to be one of the most refractory components in fuel liquids, contains no beta hydrogen. The explanations offered so far for this phenomenon have centered on the role of steric hindrance.

The role of hydrogenation was substantially neglected in the alkylamine hdn study. Interaction effects arising from competitive adsorption of active molecules could be uncovered by running simultaneous reactions involving hdn of amines, hds of thiols, and hydrogenation of olefins. It is well known that the presence of each of these species can affect the reactivity of other compounds in the mixture. Careful analysis of the rates of each reaction type as a function of the presence of the other molecules could reveal a general governing kinetic theory, which breaks down into specific kinetic expressions depending on the amounts and materials present. For example, it might be possible to demonstrate that the second order expression found for piperidine hdn changes to the zeroth order expression found in pyridine hdn by incorporation of an additional hydrogenation requirement (e.g. olefins) to the piperidine feed liquid.

References

1. Cattenot, M., Portefaix, J.L., Afonso, J., Breysse, M., Lacroix, M., and Perot, G., Mechanism of carbon-nitrogen bond scission on unsupported transition metal sulfides *J. Catal.* **173,** 366 (1998).