Task 4.7 - Diesel Fuel Desulfurization

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TASK 4.7 - DIESEL FUEL DESULFURIZATION

1.0 INTRODUCTION

Reductions in the maximum permissible sulfur content of diesel fuel to less than 0.05 wt% will require deep desulfurization technologies to meet these standards. In some refineries, a new hydrogenation catalyst may be required for diesel fuel production.

2.0 OBJECTIVES

Some of the major components of diesel fuel are dibenzothiophenes and its alkyl derivatives. These components are desulfurized by the *Rhodococcus rhodochrous* IGTS8 enzymes. But when the compounds are highly diluted with other hydrocarbons in the diesel fuel, will there be enough specificity for their absorption and degradation by the enzyme systems? The extent to which a diesel fuel or middle distillate feed can be desulfurized by desulfurization enzymes will be determined. In addition, the effectiveness of molybdenum sulfide catalysts in removing sulfur from the middle distillate cut will be determined. The catalyst preparation involves creation of the molybdenum sulfide in a highly dispersed form essentially between the layers of a hydrotalcite material, which is then dissolved away to expose the active sites.

Catalytic reactions performed earlier in this project effectively removed sulfur from dibenzothiophene, but was not as selective in sulfur removal as desired for the production of diesel fuels. An alternative approach has been to utilize the catalysts with inexpensive agricultural feedstocks to produce sulfur-free diesel additives containing oxygen to lower the pollutant emission potential of the fuel.

3.0 WORK PERFORMED

In the previous period, molybdenum sulfide dispersed on a layered hydrotalcite support was prepared and then utilized for hydrotreatment reactions of dibenzothiophene. In this period, further investigation of the hydrotalcite-supported molybdenum sulfide was carried out in the catalysis of the reaction of ethanol to higher alcohols.

4.0 RESULTS/CONCLUSIONS

The molybdenum sulfide catalyst was prepared by ion exchange of thiomolybdate anions into the interlayer of the terephthalate form of aluminum-magnesium hydrotalcite, exchanging for some of the terephthalate ions. Heating this material decomposed the thiomolybdate to a molybdenum sulfide and also decomposed the remaining terephthalate to form a carbonaceous deposit in the interlayer.

The reaction of the hydrotalcite-supported molybdenum catalyst was carried out with ethanol at 250°C in a batch reactor. The reaction was highly selective for 1-butanol, the only other product

being a very small amount of 1-hexanol. Thus a very clean reaction to alcohol products can be obtained with this solid base catalyst. Since the catalyst contains the hydrogen-activating MoS_2 needed for the dehydrogenation and hydrogenation steps, the reaction with this catalyst can be performed at lower temperatures and higher selectivity for alcohol products. The catalyst was also very stable and not destroyed by the water produced in the reaction.

5.0 FUTURE WORK

Similar reactions with this type of catalyst and a variety of alcohols should be further explored and demonstrated. Reactions of syngas with ethanol should also be explored using this catalyst.