

The Activity of Nanoscale Iron Oxide for Model Compound Reactions

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Abstract

Iron based catalysts have long been known to enhance the conversion in a direct coal liquefaction process. Attempts to increase the moderate activity of these catalysts have focussed on reducing particle size, enhancing and maintaining dispersion, and modifying the structure by addition of promoters. Sulfated hematites have been reported in the literature to exhibit significant activity for low rank coal liquefaction. The use of promoter metals such as molybdenum and tungsten has been shown to further enhance the catalytic effect. The superacidity of these particles has been suggested as a possible explanation for their high activity. The purpose of this study was to ascertain the effect of various promoter metals, both individually and in combinations on different types of reactions commonly associated with coal liquefaction.

Introduction

Iron based dispersed catalysts have been utilized in direct coal liquefaction since the early 1900's, particularly for the liquefaction of low rank coals. Continuing efforts have been directed at improving the activity of these catalysts without significant increases in cost. These efforts have focussed on reducing the particle size, enhancing and maintaining the dispersion, and modifying the structure by addition of promoters.

Several studies have demonstrated the high activity of sulfated hematite for both coal liquefaction, and coprocessing of coal with a petroleum resid.^{1,2,3} The use of molybdenum or tungsten as a promoter metal further improved the activity of these particles.^{4,5} Other research has examined nickel, cobalt, tungsten, and molybdenum as promoter metals, both individually and in combination.⁶ Molybdenum produced the largest increase in activity for singly-promoted sulfated hematite. The influence of tungsten, when used in combination with molybdenum, was essentially additive while the combination of nickel or cobalt with molybdenum exhibited synergistic effects, resulting in enhanced conversions at low promoter loading.

The role of catalysts in coal liquefaction is obscured by the complexity of the coal itself. In order to more clearly understand the role of these promoter metals in enhancing the activity of sulfated hematite catalysts for coal liquefaction, they have been studied in the reactions of selected model compounds. The activity for cleavage of the sulfur bridges may be studied by the hydrodesulfurization (HDS) of benzothiophene. Similarly, the activity for cleavage of the etheric bond may be inferred from the hydrodeoxygenation (HDO) of diphenyl ether and the activity for nitrogen removal by the hydrodenitrogenation (HDN) of quinoline. Hydrogenation (HYD) activity of the catalyst may be studied by the conversion of naphthalene to tetralin.

Experimental

Reactions were carried out using 25 ml stainless steel microautoclave reactors. The reactors were loaded with 5 g of a 5 wt% solution of reactant in hexadecane. The catalysts were loaded at 5 wt% on a reactant basis and 0.017 g dimethyldisulfide (DMDS) was added in most runs. The reactors were purged and pressurized to 800 psig (cold) with hydrogen. The loaded reactors were placed in a heated fluidized sand bath at 385°C and agitated vertically at 400 cycles/minute to minimize any mass transfer constraints. The reactions were carried out for times of 15 to 60 minutes after which the reactor was quenched in a cool sand bath.

The reaction products were removed from the reactor by washing with tetrahydrofuran. A gas chromatograph (Hewlett Packard 5890 Series 2) using both a 30 m DB-5 and a 30m carbowax column was utilized to analyze the products of the reaction. The catalyst activity was determined by the rate of model compound disappearance.

The spent catalyst was collected and stored with the product to reduce oxidation from exposure to air. The major phases present in the catalyst particles were determined by X-ray diffraction (XRD) and the average particle diameter was estimated from the peak broadening using the Debye-Scherrer relationship.

Catalyst Synthesis and Characterization

The iron based catalysts used in this study were prepared using an aqueous precipitation technique. This method involves the coprecipitation of iron and a promoter metal in the presence of sulfate ions. In this study, urea was used to effect the precipitation of ferric ammonium sulfate (iron alum), following the method of Kotanigawa et al.¹ The promoter metal molybdenum was incorporated by addition of ammonium molybdate to the iron alum solution, as described previously.⁶ Ammonium nickel sulfate hydrate and cobalt sulfate hydrate were used to add nickel and cobalt, respectively. The precipitated catalysts were filtered and dried in an air flow oven overnight and then calcined in air at 475 °C for 30 minutes.

The promoted sulfated hematite catalysts were analyzed by a variety of techniques. The results of electron microscopy analysis have shown that the catalysts consist of a loose agglomeration of particles, with acicular shape and average dimensions of ~10x50 nm. Surface areas measured by nitrogen BET adsorption were found to be in the range of 100-200 m²/g. The addition of up to 10 wt% of molybdenum had little effect on the particle size and no apparent effect on the major phase identified by XRD. The XRD spectra of the as-formed catalysts indicate that the major phase is α -FeOOH, although the crystallinity was poorly developed. After calcination the major phase was clearly identified as α -Fe₂O₃.

Elemental analysis of the sulfated hematites indicated sulfur contents of 2-6 wt%. The results of metals analysis are shown in Table 1. Molybdenum is more easily added to the catalyst resulting in a higher concentration than nickel or cobalt. XPS studies have indicated that the molybdenum is present on the surface of the particles while nickel and cobalt are substituted for iron in the particles.⁶

Results

The results of the naphthalene hydrogenation studies are shown in Figure 1. All runs were conducted with an excess of sulfur present to assure complete sulfidation of the catalyst. The unpromoted sulfated hematite resulted in an increase in conversion of ~20% over the thermal baseline. Promotion by nickel and cobalt appeared to slightly inhibit the activity of these catalysts for the hydrogenation reaction. Molybdenum had a very positive effect, producing an increase in naphthalene hydrogenation of ~50% over the unpromoted sulfated hematite after 60 minutes. This result can be related to the high concentration of molybdenum and its well known hydrogenation properties. The data indicate that the catalysts experience an initial period of low activity before the activity begins to increase, as clearly displayed by the molybdenum promoted catalyst. This induction period may correspond to the conversion of the catalyst from the oxide phase to a sulfide phase. XRD spectra of the catalyst recovered from 15 minute runs indicate that pyrrhotite is the major phase present. The activity of the catalyst prior to conversion to the sulfide may be significantly lower than the activity after conversion. Studies at shorter times should help to elucidate the rate of activation the catalysts.

The catalysts followed a similar trend for the HDO of diphenyl ether, as shown in Figure 2. Unpromoted sulfated hematite caused a significant increase over the thermal runs giving a conversion of 40% at 60 minutes. Nickel and cobalt promoters were found to have little additional effect, but molybdenum produced a significant increase to 57% after 60 minutes. The major reactions appears to involve cleavage of one of the carbon oxygen bonds resulting in the formation of equal amounts of benzene and phenol with

some further hydrogenation to cyclohexane and cyclohexanol, respectively. Only the molybdenum promoted catalyst resulted in a slight (<5%) amount of oxygen removal.

Both oxide and sulfide forms of Co/Mo supported on alumina are known to exhibit high activity for HDN reactions ⁷, which may help to explain the rapid reaction rates seen in the studies of quinoline HDN, shown in Figure 3. As observed in the previous reactions, the nickel and cobalt promoters had little effect on the activity of the sulfated hematite, and all three catalysts resulted in a significant increase in conversion over the thermal baseline. Again, the molybdenum promoted catalyst had the most significant effect on rate of quinoline conversion. The main product in all the reactions was 1,2,3,4 tetrahydroquinoline and very little HDN was observed for any of the catalyst.

It has been suggested that the superacidity associated with the sulfate groups chemisorbed on the surface of the hematite particles may explain some of the catalyst function.² This type of acidity should result in significant cracking of the hexadecane solvent used in this study. Since no significant increase in cracking was observed in these experiments, it would appear that the superacid sites are no longer present under reaction conditions.

Conclusions

Sulfated hematite catalysts appear to exhibit moderate activity for hydrogenation reactions. The use of nickel and cobalt as promoter metals had only slight effect on the activity of the sulfated hematite. Molybdenum promoted sulfated hematite showed significantly higher activity than the unpromoted catalyst. This agrees well with the results from coal liquefaction experiments. From these investigations it would appear that hydrogenation and ether cleavage are relevant catalyst functions in the liquefaction of a low rank coal.

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Table 1. Elemental Analysis of Promoted Catalysts.

Promoter Metal	Promoter Concentration (wt%)
Nickel	1.8%
Cobalt	2.0%
Molybdenum	8.0%

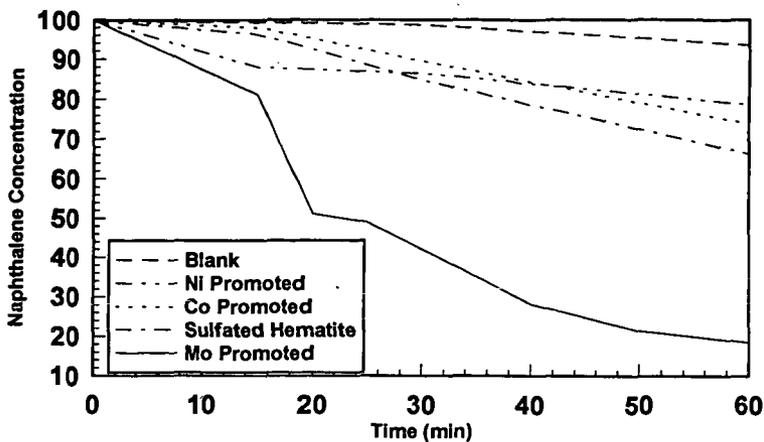


Figure 1. Hydrogenation of Naphthalene

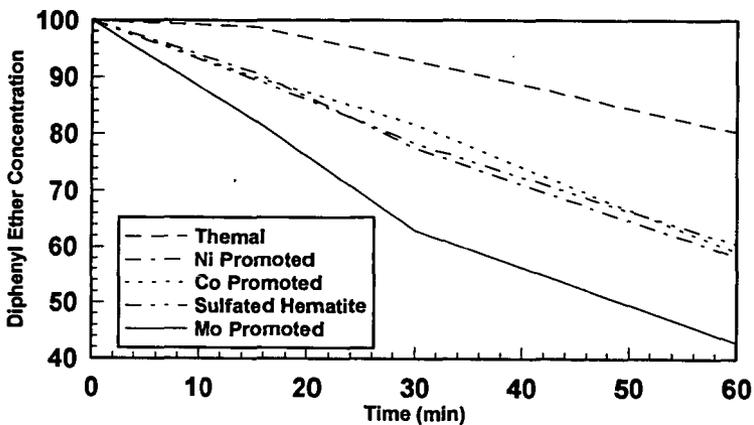


Figure 2. HDO of Diphenyl Ether

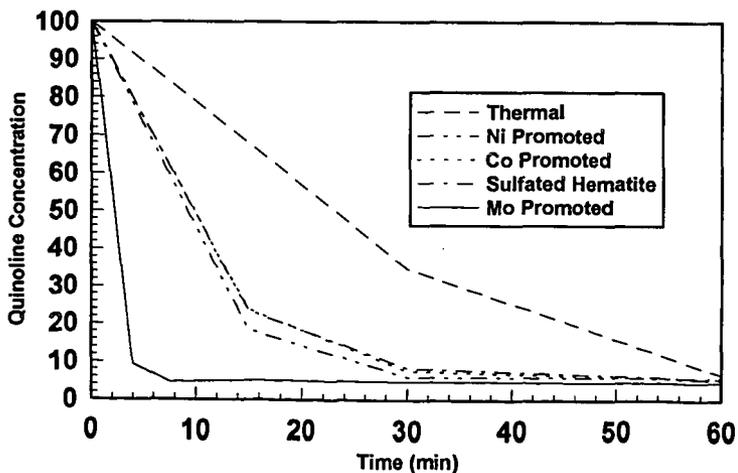


Figure 3. HDN of Quinoline