

HYDRODESULFURIZATION OF A SPANISH LIGNITE

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The objective of this work is to investigate catalytic hydrodesulfurization (HDS) reactions of lignite under mild conditions. The reactions are conducted in a single stage in the absence of a donor solvent. The lignite being studied is Mequinenza (Spanish) lignite, which has the exceptionally high sulfur content of 12.9% (daf basis). Most of the sulfur in this lignite is present as organic sulfur, the organic sulfur content being 11.6% daf. Since about 90% of the total sulfur is organic, physical coal cleaning methods designed to remove pyritic sulfur are not applicable to this lignite.

On a commercial scale, the role of a hydrodesulfurization operation would be, ideally, to remove the sulfur as H_2S leaving a desulfurized coal or char having a heating value comparable to that of the feedstock. Under the HDS reaction conditions the formation of some hydrogen-rich liquids is inevitable; these liquids could be used either directly or after a second HDS step as raw materials for petrochemical processes. Our research was not primarily concerned with the process development, but rather focused on the chemistry of the HDS reactions of the lignite.

Transition metal catalysts, particularly containing cobalt, molybdenum, nickel, or tungsten, have been widely used in coal and coal liquids processing at high temperature and high pressure conditions, both with and without donor solvents. Sulfides of these metals have activity as hydrodenitrogenation and HDS catalysts. For example, the HDS activities of molybdenum and cobalt/molybdenum sulfide catalysts have been investigated for HDS of thiophenes (1,2). Currently there is extensive interest in HDS catalysts using both alumina and carbon supports (3-8). Zinc chloride has also been shown to catalyze the removal of sulfur from coal-derived compounds (9).

There appear to be no current studies of coal HDS in the absence of donor solvent. In the absence of a solvent, supported heterogeneous HDS catalysts could not be used. Consequently, we have impregnated the lignite with catalyst precursors which subsequently form the active catalysts, dispersed throughout the lignite, at reaction conditions. Collateral research at Penn State has explored the use of dispersed catalysts and absence of solvent for liquefaction (e.g., 10,11) but as far as we are aware the work reported here is the first such study for the principal purpose of HDS.

EXPERIMENTAL

The Mequinenza lignite samples were obtained from the Instituto Nacional del Carbon y Sus Derivados, Oviedo, Spain. On a daf basis the lignite contains 64.81% C, 5.72% H, 12.93% S. The forms of sulfur (dry basis) were 1.17% pyritic, 0.20% sulfate, and 9.20% organic. The ash content was 20.40% (dry basis). The lignite samples were crushed to -60 mesh in a glove box under oxygen-free nitrogen and subsequently vacuum freeze dried to less than 1% moisture. The dried samples were stored under nitrogen.

The general procedure for catalyst impregnation was to dissolve the requisite quantity of the catalyst precursor (a water-soluble salt of the desired metal) in sufficient distilled water to give a water:coal ratio of 1:1. A slurry of the lignite in this solution was stirred for at least two hours. After stirring, the excess water was removed by vacuum freeze drying to less than 1% moisture. Normally, enough lignite for a complete series of experiments would be impregnated in one batch and stored under nitrogen. For experiments with molybdenum, the catalyst precursor was ammonium tetrathiomolybdate, which was prepared by bubbling H_2S through an aqueous solution of ammonium heptamolybdate for 30 minutes.

HDS reactions were conducted in microautoclave reactors (tubing bombs) of 25 - 30 ml capacity. The reactors were pressurized with hydrogen and immersed in a preheated fluidized sand bath. The reactors were oscillated vertically through 2.5 cm at 200 cycles/min for the desired reaction time. For this work initial (cold) hydrogen pressures of 1000 and 1500 psi, reaction temperatures of 250 - 350°C, and reaction times of 0.5 - 4.0 hr were used.

After reaction, the yields of CO , CO_2 , C_{1-4} hydrocarbons and H_2S were determined by GC. The reactor contents were washed with solvent (chloroform, tetrahydrofuran (THF), and ethanol were tested) into an alundum thimble and extracted under nitrogen in a Soxhlet apparatus for 20 - 24 hr. Solvent was removed from the extracts in a rotary vacuum evaporator. The extracts and insoluble residue were dried in a vacuum oven for 18 - 20 hr at 100°C before weighing. Yields of extract and insoluble residue were directly determined; total gas make was calculated by difference.

RESULTS AND DISCUSSION

Total Sulfur Removal

To establish a set of baseline conditions, a set of standard conditions was established using ammonium tetrathiomolybdate catalyst precursor, 1000 psi H_2 pressure, 0.5 hr reaction time, and THF as the extraction solvent. The catalyst loading was equivalent to 1% by weight of molybdenum. The results obtained with these conditions at five temperatures are summarized in

Table 1 below.

TABLE 1. Results of HDS with Standard Test Conditions, dry basis

Temp., °C	Conversion	Extract	H ₂ S Yield	Total S Removed
250	12.8%	12.6%	-	9.57%
275	13.8%	13.6%	-	13.1%
300	20.8%	19.1%	0.18%	23.9%
325	38.0%	33.0%	1.4%	47.7%
350	68.1%	53.6%	7.1%	77.2%

A marked shift in the reaction chemistry occurs in the temperature range of 300 - 325°C. First, below 300° the catalyst has essentially no effect on the reaction. For example, in reaction at 275° without catalyst impregnation but at otherwise identical reaction conditions, a conversion of 10.3% and total sulfur removal of 16.2% were observed; these results are very close to those shown in Table 1 for the catalytic experiment. By contrast, at 350° in the absence of catalyst, the conversion is only 33.7% and total sulfur removal, 48.1%. Two alternative explanations may be proposed to explain these observations: The active form of the catalyst, which is presumed to be molybdenum disulfide, may not yet have formed from the precursor at the relatively low temperature reaction conditions. Alternatively, the MoS₂ catalyst may not be active for HDS in this system below 300°.

A second aspect of the change in reaction chemistry at the higher conditions is the form in which sulfur is ultimately being removed from the system. At or below 300° essentially all of the sulfur is removed in the form of organosulfur compounds which are taken out with the extract. At the higher temperatures, most of the sulfur is removed as H₂S. Specifically, at 350° 84% of the sulfur lost from the lignite appears as H₂S, whereas at 300° only 7% (of a smaller total amount of sulfur removed) appears as H₂S. In a reaction at 350° in the absence of catalyst, the proportion of the sulfur removed as H₂S is 33%.

In this system at temperatures above 300°, the catalyst is performing two roles. First, it facilitates the breakdown of the coal structure, as shown by the higher extract yields in the catalytic vs. non-catalytic experiments. Second, it facilitates HDS, as shown by the much higher proportion of the total sulfur removed being lost as H₂S in the catalytic experiments (e.g., 84% vs 33% at 350°). There are two mechanisms by which the total HDS may be proceeding under these conditions. One possible mechanism is the direct reaction of hydrogen with sulfur functional groups in the lignite to form H₂S. The second is the liquefaction of the lignite to form sulfur-rich liquids which then undergo a subsequent HDS in situ to produce the H₂S. (A third option is that both mechanisms are proceeding simultaneously.) At present we do not have enough data to suggest which, if either, is the predominant mechanism.

Catalyst Screening

Although a 77% reduction in total sulfur is encouraging, the reaction conditions, particularly the temperature, needed to achieve this reduction are severe. Thus it is of interest to evaluate other potential catalysts to determine whether greater sulfur reduction, lower reaction temperatures, or both, are possible. This section is a brief review of results obtained with dispersed catalysts other than the standard MoS₂.

Cobalt and cobalt/molybdenum. The catalyst precursor for cobalt was Co(NO₃)₂; for the cobalt/molybdenum system, a solution of cobalt acetate and molybdenum oxalate. At 300°, 1000 psi H₂, and 0.5 hr reaction time the results show slight improvement compared to the MoS₂ and non-catalytic systems. The results are summarized in Table 2. The catalyst loadings were 1% Mo and 0.6% Co by weight daf, which gives equal atomic amounts of the two metals.

TABLE 2. HDS by Cobalt and Cobalt/Molybdenum Catalysts, 300°C, 1000 psi H₂, 0.5 hr; dry basis.

<u>Catalyst Precursor</u>	<u>Conversion</u>	<u>Extract</u>	<u>Total S Removed</u>
None	17.7%	15.7%	26.7%
(NH ₄) ₂ MoS ₄	20.8%	19.1%	23.9%
Mo(C ₂ O ₄) ₂	27.1%	23.3%	28.9%
Co(NO ₃) ₂	25.8%	23.5%	28.7%
Mo(C ₂ O ₄) ₂ /Co(OAc) ₂	24.3%	23.9%	25.9%

Tungsten sulfide. The precursor was ammonium tetrathio-tungstate. The catalyst loadings were 1.9 and 5.7% by weight daf, giving the same tungsten loading in the lignite as would be equivalent on an atomic basis to 1 and 3% by weight Mo. At 300°, 1000 psi H₂ and reaction time of 1 hr, the conversion and extract yield were both below the values obtained under the same conditions without catalyst: conversions of 16.0 vs 19.1% and extract yields of 13.0 and 16.7%, respectively. However, reaction in the presence of the tungsten sulfide catalyst generally gave the highest concentrations of hydrogen sulfide in the gaseous products. At the reaction conditions of 300°, 1000 psi H₂ and 1 hr, the gas yields were 3.1% for molybdenum sulfide catalyst and 3.0% for the tungsten sulfide, but the hydrogen sulfide in these gases was 1.05 and 3.0%, respectively, essentially a three-fold increase. These results suggest that the mechanism of tungsten sulfide catalysis may be different from that of molybdenum sulfide. We plan further work with tungsten sulfide in both hydrodesulfurization and liquefaction studies.

Zinc chloride. The results obtained at 275°, 1000 psi H₂ and 2 and 4 hr residence times are very similar to those obtained under the same conditions using molybdenum sulfide catalyst (with comparable metal loadings on an atomic basis). Under these

conditions the only advantage of the zinc chloride catalyst in comparison to molybdenum sulfide is that the zinc chloride does not introduce additional sulfur into the system, though of course the introduction of chloride may be undesirable in its own right. Mobley and Bell found that zinc chloride promotes desulfurization of aliphatic sulfides and disulfides via H_2S evolution (9). In our work, the H_2S formation in the presence of zinc chloride catalyst was of the same magnitude as from experiments without catalyst addition. There are several explanations for this observation. The organosulfur groups in the Mequinenza lignite may be of the aromatic sulfide, thiophene, or benzothiophene type, which are not susceptible to hydrocracking at our reaction conditions in the presence of zinc chloride. The liberated sulfur may react with the zinc to produce zinc sulfide, which would remain with the THF-insoluble residue. Also, our experiments were at temperatures about 50° below other work done with this catalyst (9).

CONCLUSIONS

It is possible to achieve significant reduction in the sulfur content of this remarkable lignite by HDS in the presence of a molybdenum sulfide catalyst at temperatures of 350° . A distinct change in HDS chemistry occurs around 325° . Below that temperature, most of the sulfur removed from the lignite is removed as organosulfur compounds in liquid products, whereas at 325° and above most of the sulfur is removed as H_2S . The use of zinc chloride and cobalt or cobalt/molybdenum catalysts did not appear to offer any significant advantages over the use of molybdenum sulfide. In terms of total sulfur reduction, the same is true of tungsten sulfide. However, the fact that tungsten sulfide catalysis significantly increases H_2S formation relative to comparable experiments with molybdenum sulfide suggests that the chemistry of HDS over tungsten sulfide is worthy of further investigation.

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