For such situations, the formation of methyl nitrate via reaction 8 could be an important pathway for formation of an even more stable organic NO_x species. The fate of methyl nitrate is not well understood. It does not appear that it will photolyze under tropospheric conditions and our studies have shown it to be thermally stable in the gas phase to 338 K, indicating that it will not thermally decompose in the atmosphere. Preliminary data indicate that its reaction rate with OH radical is slower than PAN, with lifetimes with respect to OH of greater than a year expected.[24] It has a comparable aqueous solubility to PAN (~5 M atm^{-1}; see ref 9) and has not been observed to undergo hydrolysis. Clearly measurements of the levels of methyl nitrate in the clean troposphere are needed to evaluate its contribution to the NO_x cycles and stratospheric source terms and for its role as a potential trace gas in global greenhouse effects.

It is apparent from this work and previous studies that PAN is much stabler than previously supposed; therefore, its role in the understanding of NO_x long-range transport must not be neglected. It is also clear that the peroxyacetyl radical chemistry may be important in the formation of oxidants other than ozone and PAN. Its ability to react with HO_2 in the clean troposphere is expected to lead to peracetic acid and methyl hydroperoxide.[20,23] Preliminary investigations have shown peracetic acid to be a potentially very active plant and microorganism toxin[25] and, like PAN, should not be ignored when plant and other ecosystem damage effects due to air pollutants are being investigated.

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In Situ Study of the Hydrogenation of Diphenyl Ether in the Presence of Pyrrhotite and H_2S

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In the present study we report the results of measurements of the conversion of diphenyl ether to benzene and phenols in the presence of a pyrrohotite catalyst. In situ Mössbauer measurements were performed during the catalytic conversion of diphenyl ether. The presence of Fe_3O_4 is detected in the residues after reaction; $Fe_{1-x}S$ is also observed. Under high H_2S partial pressures in the reactor, the conversion increases, and for a 10% H_2S partial pressure, the Mössbauer spectrum shows the presence of FeS_2. The amount of Fe_3O_4 is practically reduced to zero in this case with $Fe_{1-x}S$ dominating the spectrum. All the Mössbauer spectra show the presence of a singlet line after reaction. This spectrum results from the interaction of the iron in the pyrrhotites with the compounds present in the reactor at high temperatures. The conversion of diphenyl ether is negligible in the absence of pyrrhotite. The higher activity observed for conversion in the presence of H_2S is related to the effect this compound has in controlling the stoichiometry of the pyrrhotites. The activity observed in the iron sulfides toward hydrogenation of diphenyl ether is suggestive of a catalytic role for such sulfides in the cleavage of oxygen bonds in direct coal liquefaction.

The direct liquefaction of coal is a process that involves the interaction between coal hydrogen, solvent, and catalyst. Many researchers have reported that the addition of mineral matter enhances the conversion of coal to liquid products.[1] A study by Hodek on four German coals showed that the pyrite present in the coal enhances the hydrogenation of the coals.[2] Recycling the mineral matter and liquefaction residues tends to increase the reaction rate and enhance the conversion of pyridine solubles to benzene solubles.[3] The addition or presence of pyrite in coal enhances the production of liquid products of lower viscosity. Because of these facts, many researchers are inclined to consider pyrite (FeS_2) as a catalyst for the hydrogenation of coal.[1] However, one has to remember that, under coal liquefaction conditions, pyrite rapidly transforms to a nonstoichiometric iron sulfide,[4,5] $Fe_{1-x}S$ ($0 \leq x \leq 0.125$). It is noted that the sulfur formed as a result of the decomposition of pyrite is able to extract hydrogen from poor donor solvents. The stoichiometry of the pyrrhotite formed from FeS_2 depends strongly on the partial pressure of H_2S present in the reactor.[4,6] The activation energy of the process of pyrite decomposition is strongly particle size dependent.[5] This is in very good agreement with the suggested mechanism of sulfur diffusion as the rate-controlling process for such decomposition; a smaller particle size facilitates such diffusion.[7] Since pyrite decomposes during coal liquefaction, it cannot be considered a catalyst. The pyrrhotite generated thus appears to play a catalytic role in the conversion of coal into liquid

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products. Montano and Granoff observed that the conversion to liquid products for four different coals correlates with the stoichiometry of the pyrrhotites present in the residues.[8] Stephens et al. carried out a series of experiments with various additives on an IL No. 6 coal and observed an enhancement in conversion to benzene solubles with the addition of pyrrhotite and H_2S.[9] These results strongly indicate that both pyrrhotite and H_2S play a catalytic role in the conversion of coal to liquids. Mössbauer spectroscopy in situ measurements also indicate the existence of an interaction between coal components and the iron sulfides at liquefaction temperatures.[4,6] Recently, an alternate interpretation for the catalytic activity of the iron sulfides suggested that the catalyst was actually H_2S produced from the reduction of pyrite.[10] However, the overwhelming evidence points to a synergistic effect of H_2S and pyrrhotite. Both have been shown to be beneficial to coal liquefaction.[1] This was recently proven in the study of the hydrocracking of diphenylmethane in the presence of Fe_7S_8 and H_2S.[11] These experiments indicated that the partial pressure of H_2S controls the conversion of pyrrhotite to either FeS or FeS_2, which in turn is closely related to the promotional activity of pyrrhotite on the diphenylmethane conversion. An enhanced activity was observed for a partial pressure of H_2S, sufficient for the maintenance of a high iron deficient surface on the pyrrhotite particles.[11] All the research on sulfided catalysts increasingly indicates the importance of nonstoichiometry in the activity of the catalysts.

In a recent study of the reaction of iron sulfides with model compounds,[12] it was observed that the sulfides react with naphthoquinone forming an intermediate species of Fe_3O_4. Magnetite is transformed to the sulfide phase in an H_2/H_2S environment.[12] We have also observed the presence of magnetite in the coal liquefaction residues of North Dakota and Australian lignites. Conversion electron Mössbauer spectroscopy measurements of the surface phases formed on iron sulfides after reaction with naphthoquinone indicated the presence of a surface layer of Fe_3O_4.[13] By contrast, no evidence was found of the formation of such species on iron metal surfaces.[13] The higher reactivity toward oxygen-containing compounds exhibited by the iron sulfides is suggestive of a possible catalytic role for such compounds in the cleavage of oxygen bonds during coal liquefaction.

To further investigate this point, a systematic study of the hydrogenation of diphenyl ether in the presence of pyrrhotite (Fe_2S_8) and H_2S was undertaken. In order to fully characterize the catalyst, Mössbauer effect measurements were performed in situ under variable partial pressure of H_2S. Using the same experimental conditions (reaction time, H_2 and H_2S pressure, catalyst loading), we analyzed the products of the hydrogenation of diphenyl ether in a specially designed autoclave. Diphenyl ether was selected as a model compound because of its high thermal stability at 440 °C and the fact that ether bonds are believed to represent a great fraction of the oxygen bonds present in coal. The results of these measurements are reported in this paper.

Experimental Section

The in situ Mössbauer measurements were performed using a fully computerized Mössbauer spectrometer. The source used was a 150-mCi ^{57}Co:Rh and all isomer shifts are given in reference to α-Fe. The in situ measurements were performed using a modified version of the reactor described in ref 4. In this reactor we were able to vary the H_2S:H_2 ratio. The samples were measured at room temperature, at 440 °C, and after reaction, always inside the reactor. The ore sample of Fe_7S_8 was provided by the Department of Geology, University of North Dakota. The sample of pyrrhotite was pulverized to ≃200 US mesh prior to its use. The same catalyst was used in the diphenylmethane study.[11]

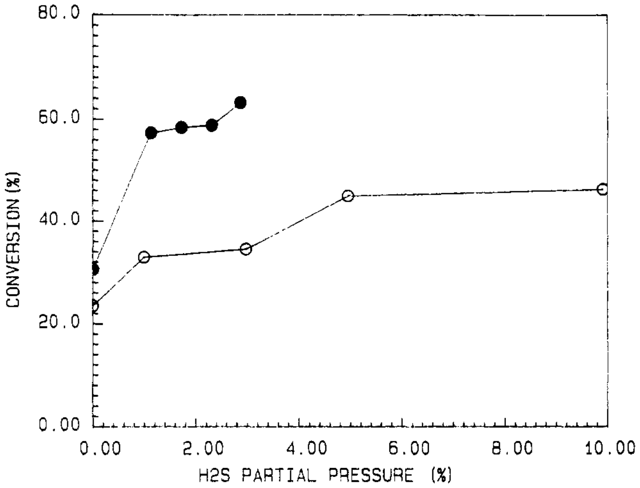

Figure 1. Diphenyl ether conversion vs. H_2S partial pressure: open circles, 10% catalyst; closed circles, 36% catalyst. Reaction conditions: 440 °C, 1470 psig total pressure, Fe_7S_8 catalyst.

All the reactions were carried out in a 12-mL stainless steel autoclave. Details of the experimental setup for the conversion measurements have been described in the literature.[14,15] All the autoclave runs were taken under the following conditions: T = 440 °C, total pressure = 1470 psig, 10% catalyst loading by weight 1-h reaction time. The H_2S pressure was between 0% and 10% of the total pressure; the rest was hydrogen. The products were analyzed by GLPC and also identified by GC–MS.

Experimental Results and Discussion

Diphenyl ether (DPE) thermal hydrocracking at 440 °C is less than 1% for 1-h reaction time. In the presence of Fe_7S_8 the conversion increases to 24%; the major conversion products are benzene and phenol. When one compares the results between pure H_2 and pyrrhotite, it is noted that the presence of pyrrhotite increases significantly the conversion and bond cleavages in DPE. During this reaction monoclinic Fe_7S_8 is converted to a hexagonal pyrrhotite following the reaction.[4,11]

$$Fe_7S_8 + nH_2 \rightarrow Fe_7S_{8-n} + nH_2S \quad (n \leq 1) \qquad (1)$$

If the partial pressure of H_2S is reduced by removal of the gases (for example, in a continuous unit), the final iron sulfide obtained is troilite (FeS), which is characterized by the absence of metal vacancies. In an early study of the hydrocracking of diphenylmethane, we observed that FeS did not show as great an activity as the nonstoichiometric phase.[11]

When the partial pressure of H_2S is increased, the conversion of DPE to benzene and phenol also increases. This result is summarized in Figure 1. These results are in good agreement with early observation of a synergistic effect of the pyrrhotite and H_2S in conversion of diphenylmethane. The same phenomenon occurs in the catalytic conversion of DPE: if the catalyst loading is increased to 36% of DPE weight, an increase in conversion is observed (see Figure 1). Such an increase is related to the availability of more active sites on the pyrrhotite surface. We must point out that the surface area of the Fe_7S_8 used in these experiments ranges between 5 and 8 m^2/g. It is reasonable to assume that, by reducing the particle size, we could increase the surface area. However, in recent surface studies it was demonstrated that iron sulfides show great affinity toward atmospheric oxygen;[15] very small particles are rapidly oxidized at room temperature in the presence of oxygen. Consequently, great care must be taken in preparing and loading the catalyst. For the pure

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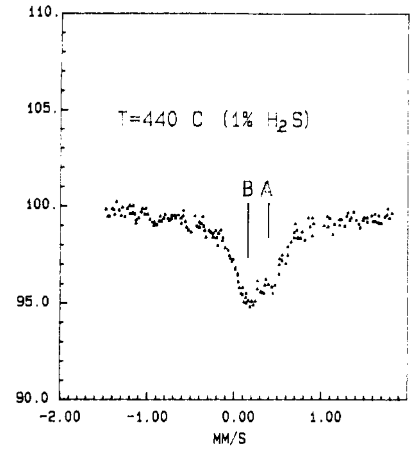

Figure 2. Mössbauer spectrum at 440 °C (1% H_2S). The lines are indicated in the figure.

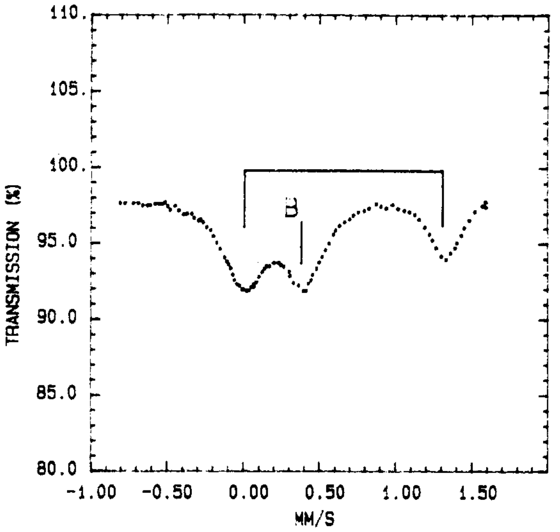

Figure 3. Mössbauer spectrum at room temperature after reactions (low-velocity scan).

compounds, 200 US mesh seems to be an optimum size.

Mössbauer in situ measurements were performed under conditions similar to those described for the DPE conversion measurements. In the absence of H_2S the Mössbauer spectrum shows the presence of three different phases at the end of the reaction: troilite (FeS), $Fe_{1-x}S$ with 47.4 at. % iron, and Fe_3O_4. The ratio of FeS to $Fe_{1-x}S$ is about 4; the amount of Fe_3O_4 is between 5% and 10%. In earlier experiments using lignites and naphthoquinone as a model compound, we have found that magnetite tends to form on the pyrrhotite surfaces.[13] If the reactions are performed with hydrogen flow instead of a static atmosphere, more FeS is formed and no Fe_3O_4 is observed. It is noted that during the measurements the samples were never exposed to the atmosphere. In order to observe the effect of H_2S, measurements were performed by varying its partial pressure in the reactor. The ranges covered in these experiments were 1%, 5%, and 10% of the total pressure in the reactor. The Mössbauer spectrum for the 1% H_2S in situ measurement is shown in Figure 2. A two-line spectrum is observed, one with an isomer shift (IS) of 0.21 ± 0.04 mm/s and the second around 0.38 ± 0.04 mm/s. The second peak, attributed to pyrrhotite ($Fe_{1-x}S$), is a broad singlet above its magnetic transition temperature (around 320 °C, depending on stoichiometric). The first peak is tentatively identified as surface iron on the pyrrhotite which has interacted with the compounds present in the reactor to form a phase similar to austenitic iron. This phase is not well characterized and was also detected in earlier measurements.[11] Figure 3 shows the spectrum at room temperature; a low-velocity scan is shown. The doublet indicated belongs to the pyrrhotite inner lines; the singlet is still present with an IS = 0.41 mm/s. It is noted that some of the iron on the surface of the pyrrhotite could have reacted with benzene (one of the products) to produce graphite with some metal intercalation.[17] The full Mössbauer spectrum of the residue at room temperature is shown in Figure 4. One can easily observe the presence of magnetite (Fe_3O_4), identifiable by the external lines. The pyrrhotite present in this spectrum has 48 at % iron. The experimental results for the 5% H_2S partial pressure are very similar to those observed for the 1% H_2S case except for slightly lower 47.8 at. % iron. When the partial pressure of H_2S is increased to 10%, there are significant changes in the Mössbauer spectrum. The first observation is the almost total disappearance of Fe_3O_4 (some traces are still noticeable) as well as a significant change in the Mössbauer spectrum, especially in the central portion. Figure 5 shows a low-velocity scan. One notices the presence of three well-resolved lines (actually four since two overlap completely). One line around −0.01 mm/s corresponds to one of the internals lines of $Fe_{1-x}S$; line B with an IS = 0.25 ± 0.03 mm/s belongs to the phase we have identified as resulting from the reaction of iron with the compounds present in the reactor at high temperatures (austenitic-like iron). This iron species has a more negative IS in the presence of 10% H_2S than for lower pressures, suggesting some degree of interaction between sulfur, iron, and carbon on the surface. Still, the real structure of this species remains a puzzle. A remarkable result is the appearance of a doublet A with IS = 0.27 ± 0.03 mm/s and quadrupole splitting of 0.54 mm/s. The isomer shift and quadrupole splitting are very close to those

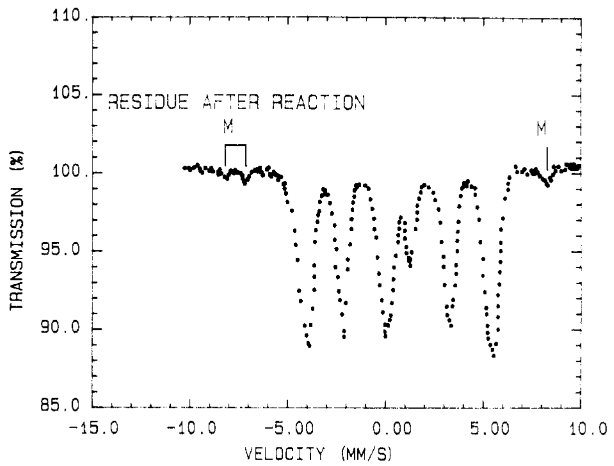

Figure 4. Mössbauer spectrum of the residue after the reaction. The magnetite peaks can be seen on the spectrum.

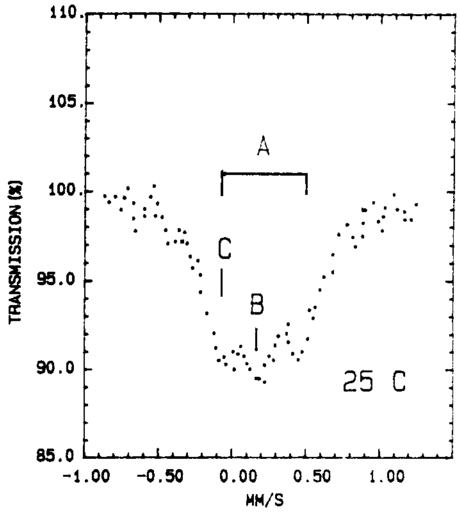

Figure 5. Mössbauer spectrum after reaction (10% H_2S; low-velocity scan). Peaks A indicated the position of FeS_2, peak C is part of the inner lines of $Fe_{1-x}S$, and peak B is a residue of the reaction of iron with the compounds in the reactor.

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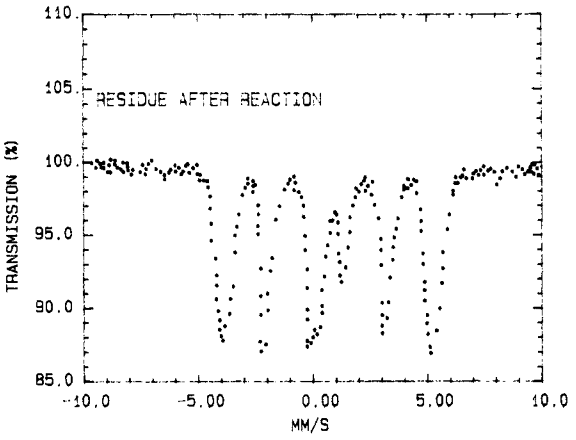

Figure 6. Full Mössbauer spectrum at room temperature of the residue of the hydrogenation of DPE in the presence of 10% H_2S.

of pyrite.[4] Actually, they are almost identical with the pyrite dimorph marcasite.[18] We identify this doublet as FeS_2. However, the parameters are not those of the cubic-phase pyrite. We believe we have obtained an iron disulfide, but the crystallographic structure is not that of pyrite and is closer to that of orthorhombic FeS_2. X-ray diffraction was not sufficiently sensitive to detect this phase. It is reemphasized that this phase is absent when the partial pressure of H_2S is reduced. The full Mössbauer spectrum of the residues of this reaction is shown in Figure 6. The conversion of DPE to benzene and phenol is not reduced by the presence of FeS_2 in the reactor. This is in contrast to our earlier observation in the study of hydrocracking of diphenylmethane.[11] This is perhaps not so surprising since all iron sulfides show great reactivity toward oxygen.[15]

The present results suggest that the presence of a nonstoichiometric iron sulfide surface is necessary in order to obtain a higher conversion of DPE. The presence of H_2S in the reactor is necessary in order to maintain such a nonstoichiometric surface. It is noted that in the absence of pyrrhotite and in the presence of H_2S the conversion of DPE is dramatically reduced (less than 20%). The fact that some conversion occurs in the presence of H_2S and in the absence of the catalyst is related to the presence of iron sulfides formed on the stainless steel reactor walls, a fact often ignored in the literature.

It is interesting to compare the IS observed in the present experiments with those obtained in the in situ Mössbauer measurements in coal.[4,12] The IS is significantly more negative than for runs carried out with pure FeS_2 or pyrrhotite (no other compound present). Similar results are observed here; however, in the present study we were able to identify two phases—one with an IS around 0.21 mm/s at 440 °C and the other with parameters close to those of FeS_2. The last phase appears only when the hydrogen sulfide partial pressure in the reactor is high. It is clear that a great degree of interaction is taking place on the iron sulfide surfaces. In a model compound study such as the one reported here, it is more feasible to identify some of the species present. In a complex material such as coal, it is very difficult to identify the roles of vastly differing organic functional groups and their interaction with pyrrhotite or H_2S. Still, in general, we can propose that maintaining a nonstoichiometric surface enhances the reactivity of the iron sulfides. There is evidence of a synergistic effect of the pyrrhotite and H_2S in the catalytic hydrogenation of diphenyl ether, very similar to the results obtained for diphenylmethane.

In summary, pyrrhotites are shown to play a catalytic role in the hydrogenation of diphenyl ether. The present results are indicative of a probable catalytic role of iron sulfides in the cleavage of oxygen bonds in coal. The only real problem presently encountered with the use of these catalysts is their low surface area. One can try to support the catalyst on standard oxide materials (alumina, silica); however, care must be taken not to oxidize the catalysts during preparation. The second problem is more fundamental. The pyrrhotites have a rather complicated crystallographic structure,[18] consisting of a large unit cell with many molecules. Consequently, stabilizing such a structure on a support, as well as being a high dispersion, is an extremely difficult task. However, we hope that new ideas for special supports which retain the activity of the sulfides will make this compound more attractive in industrial applications, specifically in direct coal liquefaction.

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Registry No. DPE, 101-84-8; Fe_7S_8, 12063-67-1; H_2S, 7783-06-4; iron sulfide, 11126-12-8; pyrrhotite, 1310-50-5.

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Rate Constant and Branching Ratio for the Reaction of OH with ClO

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The rate constant and branching ratio for the reaction OH + ClO → products [HO_2 + Cl (1a) and HCl + O_2 (1b)] have been measured in a discharge flow system at 298 K. OH was monitored via the laser-induced fluorescence technique. ClO and HCl were analyzed by means of a modulated molecular beam mass spectrometer. The results are $k_1 = (1.94 \pm 0.38) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k_{1a}/k_1 = 0.98 \pm 0.12$. This implies that channel 1b cannot be a significant process for converting ClO into inactive HCl in stratospheric ozone–chlorine chemistry.

Introduction

The reaction between OH and ClO radicals can play an important role in stratospheric chlorine chemistry since one of its two possible channels converts the active species ClO into the reservoir molecule HCl. Such a sink would reduce the catalytic effect of the ClO_x chain carriers in the ozone destruction cycles. The two possible branches of this reaction are

$$\mathrm{OH + ClO \rightarrow HO_2 + Cl} \qquad (1a)$$

$$\Delta H^\circ_{298\ \mathrm{K}} \simeq -1.7\ \mathrm{kcal\ mol^{-1}}$$

$$\mathrm{OH + ClO \rightarrow HCl + O_2} \qquad (1b)$$

$$\Delta H^\circ_{298\ \mathrm{K}} \simeq -55.6\ \mathrm{kcal\ mol^{-1}}$$