

SPECTROSCOPIC STUDY OF CATALYSIS BY ZINC CHLORIDE OF COAL DEPOLYMERIZATION

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ABSTRACT

Diffuse reflectance infrared spectroscopy was used to monitor in situ reactions which ether groups undergo during the depolymerization of $ZnCl_2$ -impregnated Wyodak coal at elevated temperatures. Subtraction procedures were used to obtain difference spectra that revealed small changes in IR band intensity between 2000 and 1000 cm^{-1} . Evidence was obtained indicating that the $ZnCl_2$ -impregnated coal samples could be depolymerized in an inert argon atmosphere. However, the degree of the cleavage of ether linkages catalyzed by $ZnCl_2$ in an inert atmosphere is about 30 % of that in a high pressure hydrogen atmosphere (68 atm). The effect of solvent on impregnation of $ZnCl_2$ in coal samples was also studied. A higher degree of cleavage of what appears to be a phenyl ether linkage was found for $ZnCl_2$ -impregnated coal prepared in methanol compared to similar preparations in water and in acetone.

INTRODUCTION

It is believed that ether oxygen plays an important role in linking the macromolecular units in coal. Wachowska and Pawlak [1] have indicated that ether groups represent the main linkages between aromatic clusters. Early works have shown that a catalyst such as $ZnCl_2$ will promote the liquefaction of coal at temperatures below those at which pyrolysis can occur [2]. Mobley and Bell [3] noted that $ZnCl_2$ may catalyze the cleavage of ether linkages and thereby promote a reduction in molecular weight.

The average chemical properties of coal have been widely studied using infrared spectroscopy. Recent improvements in the infrared techniques make it possible to measure the infrared spectra of coal powders in situ with the diffuse reflectance method. The present work was undertaken to determine the extent to which the cleavage of ether linkages is catalyzed by $ZnCl_2$. We have also applied this method to the study of the effect of solvent on impregnation of $ZnCl_2$ in coal samples.

EXPERIMENTAL

Reagent grade $ZnCl_2$ (used as received) was impregnated on the THF preextracted Wyodak Coal from different solvent media such as methanol, water, and acetone. The $ZnCl_2$ -impregnated coal samples (25% by weight of extracted Wyodak Coal) was then dried at 353 K overnight. Hydrotreatment of the coal samples were done in a tubing bomb reactor in high pressure hydrogen (68 atm) at 635 K.

Infrared spectra were recorded on a Digilab FT-IR spectrometer (FTS-40). For all spectra reported, a 64-scan data accumulation was obtained at a resolution of 4 cm^{-1} . In order to observe small changes in band intensity, subtraction procedures were used to obtain difference spectra that more effectively compare spectra measured under various conditions. Almost identical base lines for infrared spectra measurements were also obtainable which facilitated calculation of the small spectroscopic changes between different samples using the subtraction method.

About 50 mg of each coal sample was dried at 373 K for one hour in the flowing argon (30 ml/min.) in a controlled environmental chamber (Spectra Tech Inc., Model No.0030-025) which was designed for diffuse reflectance infrared spectroscopy (DRIFTS) at elevated temperatures. In situ infrared spectra of coal samples were measured at temperatures ranging up to 723 K.

RESULTS AND DISCUSSION

It is expected that the presence of the $ZnCl_2$ catalyst during coal liquefaction may accelerate the cleavage of ether linkages (depolymerization) in the coal matrix. The C-O stretching vibrations between 1265 and 1000 cm^{-1} [4] were investigated using in situ infrared spectroscopy. Figure 1 shows the difference infrared spectra obtained at three different temperatures in an inert argon atmosphere. Each spectrum is the difference between the infrared spectra obtained from the original and the $ZnCl_2$ -impregnated (from acetone media) coal samples. The negative features between 1265 and 1000 cm^{-1} in Figure 1 indicate that the cleavage of ether linkages (depolymerization) was catalyzed by $ZnCl_2$. The fact that the depolymerization occurred at a temperature as low as 493 K suggests the possibility of a low-temperature coal liquefaction process catalyzed by $ZnCl_2$. It should be noted that pyrolysis may occur at temperatures higher than 630 K. Furthermore, the negative features between 1350 and 1500 cm^{-1} are in part due to CH_2 and CH_3 bending [4]. The negative feature occurring near 1740 cm^{-1} is present because of the C=O stretching groups [4]. The present work focuses on the study of C-O stretchings in the infrared spectra measured since the formation of C-O bonding is not expected at our reaction conditions.

Generally, the objective of the pyrolysis of coal is to improve the tar/oil yield at the expense of char and gas formation. Thus it is important to study the redistribution of

the hydrogen available within the coal mass and the effect of the hydrotreatment on the depolymerization of coal. The depolymerization of coal samples was investigated in the presence of externally added hydrogen (68 atm). The comparison for the spectra of the depolymerization at 590 K between hydrotreated (573 K and 68 atm hydrogen) and non-hydrotreated coal samples (ZnCl₂ impregnated from acetone) is shown in Figure 2. Difference infrared spectra are used to reveal the net changes in the C-O stretching region. These spectra indicate that the degree of cleavage of ether linkages catalyzed by ZnCl₂ in an inert atmosphere is about 30% of that in a high pressure hydrogen atmosphere (68 atm).

The effect of solvent media used in the ZnCl₂ impregnation on depolymerization of coal samples is shown in Figure 3. The difference spectra were calculated by subtraction of the infrared spectrum of original coal measured at 590 K in the flowing argon from those of ZnCl₂-impregnated coal samples prepared in media such as water, acetone, and methanol. A high degree of cleavage of what appears to be a phenyl ether linkage Ph-O-CH₂-R (~1030 cm⁻¹) was found for ZnCl₂-impregnated coal prepared in methanol compared to similar preparations in water and in acetone. It seems that the dispersion of ZnCl₂ in the coal matrix depends on the media used in impregnation of the catalyst. Thus one should not underestimate the effect of the interactions between solvent media and functional groups of coal on the catalytic depolymerization process.

SUMMARY

The following conclusions have been reached on the basis of this work.

1. The subtraction routines used to obtain difference spectra can reveal small changes in the highly complex infrared spectra of coal.
2. ZnCl₂-impregnated coal samples could be partially depolymerized in an inert argon gas atmosphere.
3. The degree of cleavage of ether linkages catalyzed by ZnCl₂ in an inert atmosphere is about 30% of that in a high pressure hydrogen atmosphere.
4. A higher selectivity in cleavage of a phenyl ether linkage was found for ZnCl₂-impregnated coal prepared in methanol compared to similar preparations in water and acetone.

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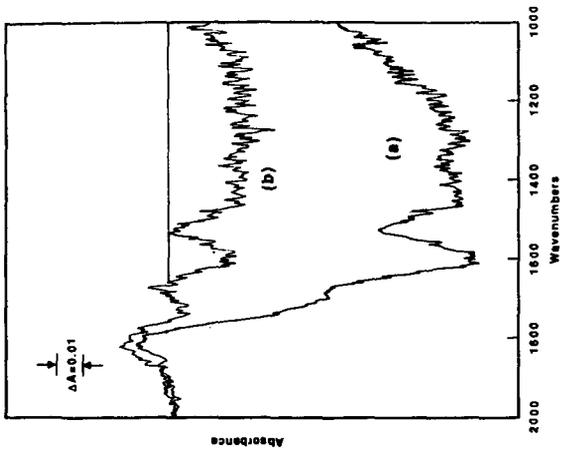


Figure 2
Effect of Hydrotreatment on coal depolymerization.
Difference spectra between original and hydrotreated (a)
and non-hydrotreated (b) $ZnCl_2$ -impregnated coal samples.

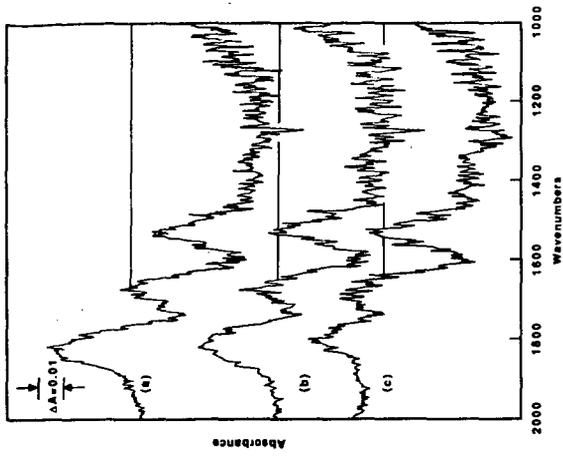


Figure 1
Infrared difference spectra for coal depolymerization
catalyzed by $ZnCl_2$. Difference spectra measured
between original and $ZnCl_2$ -impregnated wyodak coal at
(a) 675 K, (b) 590 K, and (c) 493 K.

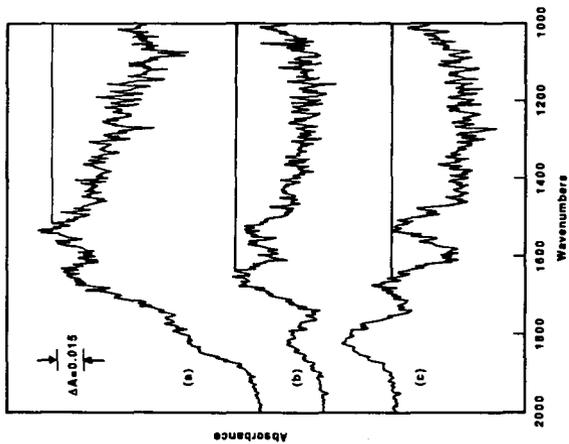


Figure 3
Effect of solvent media used in impregnation of ZnCl₂ in coal samples on the coal depolymerization. Difference spectra between original and ZnCl₂-impregnated coal (a) in methanol, (b) in water, and (c) in acetone.