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Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction

Technical Progress Report

April - June 1996

(Approved)

Stephen R. Kirby, Shona C. Martin, Chunshan Song, and Harold H. Schobert

Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, Pennsylvania, PA 16802

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TABLE OF CONTENTS

ABSTRACT	1
TECHNICAL PROGRESS	2
HYDRODEOXYGENATION IN LOW-RANK COAL LIQUEFACTION SYSTEMS USING NOVEL ORGANOMETALLIC CATALYST PRECURSORS	
Introduction	2
Experimental Section	3
Results and Discussion	5
Conclusions	9
References cited	10
MINERAL MATTER EFFECTS IN LOW-TEMPERATURE LIQUEFACTION OF LOW-RANK COALS.	
Introduction	11
Experimental Section	12
Results and Discussion	13
Conclusions	18
References cited	19

ABSTRACT

This quarterly report describes our recent work on two related subjects: effect of using organometallic catalyst precursor on hydrodeoxygenation under coal liquefaction conditions, and the effect of mineral matters in liquefaction reactions of coals.

Oxygen functionalities, especially phenols, are undesirable components of coal derived liquids. Removal of these compounds from the products of coal liquefaction is required. A beneficial alternative would be the removal of these functionalities, or the prevention of their formation, during the liquefaction process. Organometallic precursors of Co, Ni and Mo have been studied as catalysts. To ascertain the hydrodeoxygenation properties of these catalysts under liquefaction conditions, model compounds were investigated. Anthrone, Dibutylmethyl phenol, dinaphthyl ether and xanthene were studied to provide a comparison of conversions to deoxygenated products. Studies of the deoxygenating abilities of these catalyst precursors in coal liquefaction systems have also been performed. Improvements in conversion and product quality are observed. Both these factors are dependent on the coal used.

It is also considered that some mineral matters in coal may have catalytic actions. Demineralization by successive HCl/HF treatments of a low rank coal has demonstrated that removal of the inherent mineral matter imparts no serious detrimental effect upon low temperature liquefaction. It appears that elimination of such species allows for better access for gaseous H_2 , as suggested by previous studies.

Technical Progress

1. HYDRODEOXYGENATION IN LOW-RANK COAL LIQUEFACTION SYSTEMS USING NOVEL ORGANOMETALLIC CATALYST PRECURSORS

ABSTRACT

Oxygen functionalities, especially phenols, are undesirable components of coal derived liquids. Removal of these compounds from the products of coal liquefaction is required. A beneficial alternative would be the removal of these functionalities, or the prevention of their formation, during the liquefaction process. Organometallic precursors of Co, Ni and Mo have been studied as catalysts. To ascertain the hydrodeoxygenation properties of these catalysts under liquefaction conditions, model compounds were investigated. Anthrone, Dibutylmethyl phenol, dinaphthyl ether and xanthene were studied to provide a comparison of conversions to deoxygenated products. Studies of the deoxygenating abilities of these catalyst precursors in coal liquefaction systems have also been performed. Improvements in conversion and product quality are observed. Both these factors are dependent on the coal used.

INTRODUCTION

The present consensus is that direct coal liquefaction will be a catalytic process. High conversions (>88%) have been achieved using "conventional" liquefaction catalysts of iron and molybdenum[1] . As we can achieve good conversions with regular catalysts, the main reason for considering "unconventional" catalysts must be to improve the product quality. A major concern with product quality is the abundant oxygen content. Phenols can comprise as much as ~40% of the liquefaction distillates in low-rank coals[2] .

Oxygen-containing functional groups are present in virtually all coals [3] . Ethers have been proposed as sites for depolymerization [4] , and together with carboxyls and phenolics, have been implicated in facilitating repolymerization reactions [5, 6] . Phenols have been identified as components of coal-derived distillates [2, 7], and oxygenated compounds have been connected to the instability of these distillates [8] .

Low-rank coals include significantly more oxygen-containing groups than coals of higher rank [9, 10] . With the increase in the extraction of low-rank coals in the U.S. and research into their use as liquefaction feedstocks [5, 11, 12] , the ability to remove oxygen functional groups becomes even more important. Compounds containing these functional groups are usually removed down-stream in a catalytic hydrodeoxygenation step. Supported CoMo and NiMo catalysts facilitate oxygen removal in these processes [8, 13, 14] . However, the use of these catalysts increases complexity and cost of the process. An alternative is to extract the phenols from the distillates, but this would discard ~40% of the potential product [2] . Therefore, deoxygenation during the liquefaction process itself would be beneficial. Utilization of either a CoMo, or a NiMo, catalyst in a liquefaction stage has the potential to increase the quality of distillates, by combining hydrodeoxygenation and liquefaction in a single stage.

Sulfided metal catalysts have been considered desirable for liquefaction, because they are not readily poisoned by the heteroatom-containing compounds from the coal. Sulfided molybdenum catalysts are particularly active for liquefaction. Unfortunately, MoS_2 is insoluble in all common solvents, and is difficult to disperse onto the coal particles. A strategy to mitigate this problem is the use of catalyst precursors, soluble salts that presumably can be readily dispersed onto coal. The catalyst precursors may have little or no catalytic activity themselves, but decompose into an active form at the temperatures of the liquefaction reaction.

It would be neither easy nor efficient to obtain the promoting effect of nickel or cobalt by sequential dispersion of a molybdenum-containing catalyst precursor followed by application of a nickel or cobalt precursor. Instead, we hypothesized that this goal may be attainable with the use of bimetallic catalysts dispersed onto the coal using an appropriate precursor [15, 16] .

Model compound studies were performed to investigate the capabilities of these catalyst precursors. The model compounds selected represent a variety of oxygen functionalities, possibly present in coals of differing ranks [17-19]. They include a carbonyl; an aryl-aryl ether; a heterocyclic ether; and a substituted phenol. The reactions of these compounds in the presence of several catalyst precursors under liquefaction conditions give an indication of the hydrodeoxygenating abilities of these precursors.

Liquefaction studies were then performed on a selection of coals of varying rank and oxygen content. Here we report an investigation of the effect a bimetallic organometallic precursor (CoMo-T2) on conversion and product distribution of these coals under liquefaction conditions.

For comparison we have conducted the same reactions under non-catalytic conditions, and in the presence of ATTM, commonly used in liquefaction research.

EXPERIMENTAL

The model compounds studied were: anthrone, dinaphthyl ether (DNE), xanthene and 2,6-di-*t*-butyl-4-methyl phenol (DBMP). The coals studied were: DECS26 Wyodak (subB), DECS24 Illinois #6 (hvCb) and DECS23 Pittsburgh #8 (hvAb). These coals have oxygen contents (daf) of 16.92, 10.74 and 6.66, respectively.

All experiments were performed in 22 mL capacity microautoclave reactors made of stainless steel. A 0.5 g sample of the model compound, or a 4 g sample of coal (<60 , mesh), was loaded into the reactor. 1-Methylnaphthalene was added as solvent in a 1:2 weight ratio to reactant, and catalyst precursors were added at 2.5 mol% for the model compound studies and 1 wt% concentration for coal. The catalyst precursors used were $(\text{NH}_4)_2\text{MoS}_4$ (ATTM), and $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$, which for convenience we call CoMo-T2. (The symbol Cp represents the cyclopentadienyl group.) This precursor has a thiocubane structure. Air was removed by flushing the reactor three times with H_2 to 7 MPa. The reactor was then repressurized to 7 MPa H_2 (cold). Reactions were performed at 400°C for 30 minutes in a fluidized sand bath. At the end of the reaction the reactor was quenched in cold water.

For the reactions with coal, the reactor contents were removed to a porous thimble. The liquid and solid products were separated by sequential Soxhlet extraction with hexane, toluene and THF for approximately 24 hours. The THF insoluble residues were washed with acetone, then with pentane to remove THF completely, and subsequently dried before weighing. Products from the model compound studies were extracted from the reactor with acetone.

Capillary gas chromatography (GC) and gas chromatography / mass spectrometry were used for the quantitative and qualitative analysis of the hexane solubles.

RESULTS AND DISCUSSION

Model Compound Studies

Results of the model compound experiments are presented in Table 1. In the absence of a catalyst precursor no oxygen removal occurs in reactions of xanthene and DBMP. All products of the non-catalytic reaction of anthrone are deoxygenated (63.1 wt%). A large proportion of the

products formed from reaction of DNE, under non-catalytic conditions, are deoxygenated (22.9 wt%). For catalytic reactions with DNE and xanthene, CoMo-T2 shows a greater ability to facilitate deoxygenation than does ATTM. In the presence of ATTM, DBMP is deoxygenated to a greater extent than with CoMo-T2. Anthrone is deoxygenated completely in the presence of both precursors, although with differences in the product yields of the hydroaromatics.

CoMo-T2 shows a preference for ether cleavage facilitation, over the removal of phenolic oxygen. In the case of ATTM, the opposite appears true. In the context of coal conversion, it has been reported that ethers form a large proportion of the cross-links between aromatic moieties in mid-rank coals [4] and heterocyclic ethers have been proposed as a large contributor to the oxygen content of high rank coals [20]. The ability to remove these cross-links, without producing undesirable oxygenated products (phenols) should contribute greatly to coal conversion and product quality.

TABLE 1: Deoxygenation results of model compound studies at 400°C.

Catalyst Precursors		None	ATTM	CoMo-T2
Total Conversion	Anthrone	63.1	100	100
Yield of deoxygenates		63.1	100	100
Total Conversion	DNE	26.1	71.9	100
Yield of deoxygenates		22.9	69.9	95.2
Total Conversion	Xanthene	0	33	57.7
Yield of deoxygenates		0	12.4	14.1
Total Conversion	DBMP	100	100	100
Yield of deoxygenates		0	71.4	14.6

Phenols are present in almost all coals [20], and appear in great abundance in low-rank coals. From the non-catalytic reactions of DBMP, the refractory nature of the phenol hydroxy group is apparent. Great improvement in product quality may be achieved by removal of phenolic oxygens, or a reduction in their production from the reaction of other oxygen functional groups, as well as increases in conversion.

From these results ATTM should be the precursor better suited for conversion and desirable products from lower-ranked coals. Superior conversion and product distribution may be anticipated for coals of higher rank in the presence of the CoMo-T2 precursor.

Coal Liquefaction Studies

Figures 1-3 illustrate the conversion of the three coals to preasphaltenes (THF solubles), asphaltenes (toluene solubles), oils (hexane solubles) and gases. Total conversion to products is also shown.

Under non-catalytic conditions, great differences in reactivity can be observed. Wyodak exhibits a low reactivity relative to the two coals of higher rank. Illinois #6 forms increasing yields of preasphaltenes, asphaltenes and oils, whereas preasphaltenes are the most abundant products for Wyodak and Pittsburgh #8.

Total conversions are increased, in all cases, in the presence of either catalyst precursor, the most notable increase being that of the Wyodak coal using ATTm (26.6 wt% non-catalytic to 63.5 wt% ATTm). This difference is mainly attributed to greater yields of oil and gas. ATTm has very little effect on the total conversion of either the Illinois #6, or the Pittsburgh #8. Oil yields remain the same as the non-catalytic reactions, or decrease; the balance is achieved by increasing asphaltene and gas production.

Fig. 1. Conversion of three coals at 400°C for 30 minutes under 7 MPa H₂.

Fig. 2. Conversion of three coals with ATTM under the same conditions as Fig. 1.

A similar scenario is seen with CoMo-T2. Increases in conversion of the lower-rank coal are achieved through increased oil and gas. However, a difference is apparent when this precursor is utilized in the liquefaction of both Illinois #6 and Pittsburgh #8. Although presphaltenes yields increase slightly, these increases are accompanied by greater, or equal, yields of oils and no noticeable increases in gas production.

Comparison of the three coals indicates an increase in production of asphaltenes and preasphaltenes with increasing rank, under all three catalytic conditions. This is expected due to the increase in size and number of aromatic moieties observed with coals of higher rank.

Fig. 3. Conversion of three coals with CoMo-T2 under the same conditions as Fig. 1.

Conversion to oils is the most desirable result for liquefaction. However, if a large portion of these low molecular weight products are detrimental to the total product (i.e. reduction of oil stability), then a large oil yield becomes worthless. Analysis of the hexane-solubles fraction provides an estimation of the portion of the product that may be undesirable. Figure 4 illustrates the size of the phenolic fraction of the hexane-solubles. No trends are immediately. Phenol concentration increases with increasing rank, in the presence of ATTM. However, this is accompanied by a reduction in oil formation, making the amount of hexane soluble phenols produced approximately constant across the range of coal ranks.

The presence of a catalyst precursor reduces the phenol concentration of the oil yield for the higher rank coals, but increase the yield with Wyodak. However, a smaller proportion of hexane soluble phenols is observed for the lower-ranked coal under all conditions.

CONCLUSIONS

Improvement of liquefaction product quality may be achieved by the removal of oxygen functional groups. Phenols are undesirable products of liquefaction. Therefore, their removal, or prevention of their formation, during liquefaction would be beneficial.

Model compound studies indicated that different oxygen functional groups will react differently under liquefaction conditions. The catalyst precursors under investigation facilitate deoxygenation of some model compounds to a greater extent than others. ATTM showed a preference toward phenolic oxygen removal, whereas CoMo-T2 demonstrated greater facilitation of ether cleavage.

It was predicted from the model compound results that ATTM should improve the product quality of coals with high phenol contents, by phenolic oxygen removal, and that CoMo-T2 would increase the conversion of coals with high proportions of ether linkages, or ethers within aromatic systems, and reduce formation of phenols from the reaction of these linkages.

Liquefaction studies were performed on coals of differing rank and oxygen content. ATTM improved the conversion of all the coals. Product quality from Wyodak was also improved, by increasing oil yields without a significant increase in the proportion of phenols in the oil fraction. CoMo-T2 also improved conversion of all the coals. Improvement of product quality was achieved for Illinois #6 and the Pittsburgh #8, by increasing oil formation and reducing the phenolic fraction within the oils.

Fig. 4. Wt% of phenols in the hexane soluble fraction of the liquefaction products.

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2. MINERAL MATTER EFFECTS IN LOW-TEMPERATURE LIQUEFACTION OF LOW-RANK COALS

ABSTRACT

Demineralization by successive HCl/HF treatments of a low rank coal has demonstrated that removal of the inherent mineral matter imparts no serious detrimental effect upon low temperature liquefaction. It appears that elimination of such species allows for better access for gaseous H_2 , as suggested by previous studies.

INTRODUCTION

The pathways by which coal macromolecules can be depolymerised to give lighter products have long been sought by coal scientists and the precise roles of individual functional groups in the reactions which occur during liquefaction are still not clear. Depending on reaction conditions, the mineral and inorganic species present in coals can act as catalysts or poisons during liquefaction [1,2]. For example, clays, the dominant mineral species in many coals, may be possible acid cracking catalysts and pyrite, the predominant sulphide form, is a well-documented hydrogenation catalyst; however cations, common in low rank coals, block access to pores or reaction sites. Several authors have observed a favorable influence of demineralization on coal depolymerization, specifically upon removal of naturally occurring cations such as Na^+ , Ca^{2+} and K^+ [3,4]. Shams et al. [5] reported that treatment of coals with methanol and HCl removes virtually all of the calcium species, leading to retardation of the retrogressive reactions Ca was proposed to catalyze.

The aim of this work was to evaluate the nature and distribution of mineral matter in both untreated and treated (demineralized) samples of Wyodak coal, and consider the influence of these compounds by assessing their possible catalytic effect. A series of experiments has been undertaken to compare the effect of demineralization on coal conversion at low temperatures (*ca* 300-350°C), where preliminary results indicated that conversions were comparable upon pretreatment.

METHODS

Demineralization

Wyodak coal (DECS-8) , ≤ 60 mesh, was obtained from the Penn State Coal Sample Bank; proximate and ultimate analyses are as follows [6]. Proximate analysis (as received) 32.4% vol. matter, 29.3% fixed carbon, 9.9% ash, 28.4% moisture; ultimate analysis (wt%, dmmf basis) 75.8% C, 5.2% H, 1.0% N, 0.5% S, 17.5% O. Demineralization was facilitated by successive acid treatments. The first stage was an HCl wash (10 ml per gram of coal) to remove alkaline earths which would form insoluble fluorides at the HF wash stage. This was stirred at 60°C for 1h, filtered and washed. In the second stage, a 40% HF solution (10 ml per gram of coal) was digested at 60°C for 1 hour. The final sample was thoroughly washed with distilled water to ensure removal of residual HF. The filtrate was tested with AgNO_3 to indicate the presence of any residual chloride ions.

Determination of Inorganic and Mineral Phase Distribution

Both coal samples were analyzed by ICP-AAS and CCSEM to more clearly identify the changes in inorganic element and mineralogical phase distribution upon acid. Samples were ashed at 950°C and the ash dissolved using lithium metaborate fusion. Solutions were then analyzed using an inductively coupled plasma spectrophotometer (ICP). For CCSEM, coals were ground to -200mesh and the samples mounted in an epoxy resin. The sample is scanned with an electron beam to locate bright spots which correspond to mineral or ash species. Integrated software classifies the minerals into categories based on size and composition.

Liquefaction

Demineralised coal samples were vacuum dried at 110°C for 2h prior to use. Liquefaction was carried out in a 25 ml stainless steel microautoclave with *ca* 4g coal, at 300 and 350°C, 1000 psi H_2 or N_2 for 30 min. When solvent was present, the coal:solvent ratio was 1:1 w/w; both H-donor (tetralin) and non-donor solvents (1-methylnaphthalene) were utilized. Gaseous products were collected and analyzed by GC; liquid and solid products were recovered and separated by sequential Soxhlet extraction into *n*-hexane solubles (oils), toluene solubles (asphaltenes) and THF solubles (preasphaltenes). The THF-insoluble residue was washed with acetone followed by *n*-pentane to remove residual THF. All products were dried under vacuum at 110°C for *ca*

10h. The conversion of coal into soluble products and gases was calculated on the basis of recovered THF-insoluble residue and reported on a dmmf basis.

¹³C NMR

Solid state ¹³C NMR spectra of the normal and demineralized coal samples and their associated THF-insoluble residues were recorded on a Chemagnetics M-100 NMR spectrometer using the cross polarization magic angle spinning (CP-MAS) technique. The measurements were carried out at a carbon frequency of 25.1 MHz.

FTIR

Fourier transform infrared (FTIR) spectra of the demineralised coal and liquefaction residues were recorded on a Digilab FTS-60 spectrometer by co-adding 400 scans at a resolution of 2 cm⁻¹. The samples were prepared as KBr discs; predried sample (3 mg) was mixed with KBr (300 mg). All spectra were baseline corrected.

RESULTS AND DISCUSSION

ICP-AAS

As summarised in Table 1, metal concentration was determined by ICP-AAS in the normal and demineralised Wyodak coal samples. Ash concentration was determined as 8.94 wt%, falling to *ca* 0.37 wt% upon demineralization, with the corresponding metal concentrations as indicated. All values are expressed in weight percent on an coal basis.

CCSEM

Table 2 summarises the mineral phase distribution in both the normal and acid digested coal samples. Results are expressed on a weight % coal basis. As anticipated, clays were the predominant mineral phase in the initial coal sample. Upon acid treatment, all mineral species concentrations were significantly reduced.

Liquefaction Data

Results for the reactions conducted at 350 °C, both in the presence and absence of solvent, are reported in Table 3. These will be discussed with respect to data with untreated Wyodak coal [7]. Clearly, demineralization imparts no seriously detrimental effects on liquefaction under such conditions.

The overall conversions and liquid product distribution indicate that the most significant changes occur in the presence of solvent, both H-donor and non-donor. In the absence of solvent, conversion is solely due to pyrolysis, i.e. there are no solvent dissolution or H donation contributions. Higher conversion is the result of increased gas yield rather than liquid yield. This may be derived from two contributions. If the reduction in Fe concentration, as highlighted by ICP, also comprises pyrite, this would account for the decrease in liquid yield. Moreover, as the increased gas make is due to CO_2 , removal of the mineral matter may be considered to promote more facile pyrolysis of $-\text{COOH}$ versus $-\text{COO}^-\text{M}^+$. This confirms model compound studies conducted by Eskay et al. [8] who reported that the salts of carboxylic acids do not readily undergo decarboxylation at 400°C and should therefore be stable at the reaction temperature of 350°C used here.

Reaction in the presence of the non-donor solvent, 1-methylnaphthalene (1-MN), results in increases in both gas and liquid yield relative to the no-solvent situation. With "normal" coal and 1-MN, the increase in liquid yield for the raw coal is 5.1%. Presumably this increase is the "extra" liquid dissolved out by the solvent. With demineralised coal and 1-MN, the increased liquid yield is 12.4%. The solvent is better able to dissolve material from the demineralised coal. This suggests that there is improved access of the solvent to the coal interior upon removal of mineral species. Swelling of the samples in pyridine provided confirmation of this; the swelling ratios of the normal and demineralised samples in pyridine were 2.18 and 2.9, respectively.

The best liquid conversion, defined by oil concentration as a fraction of the total liquid yield, occurs upon reaction with tetralin. This is not surprising given that tetralin is an H donor, thus any enhancement in tetralin conversion relative to 1-MN can be attributed to H donation. The increase in liquid yield for normal coal in tetralin, relative to 1-MN, is 7.4%; the increase for demineralised coal is 8.6%. The difference in these numbers is within experimental error, $\pm 3\%$, hence demineralization has no effect on H transfer from tetralin and there is no mineral matter catalysis of H donation.

Table 4 summarises the results of liquefaction conducted under N_2 and those in H_2 . No significant deviation in overall conversion or product distribution was observed, even in the presence of solvent.

TABLE 1. Inorganic Elemental Analysis of Normal and Demineralised Wyodak Coal Samples by ICP-AAS.

Sample	Ash	Metal Concentration (wt%, coal basis)				
		Fe	Ca	Mg	Na	K
Normal	8.94	0.49	1.18	0.27	0.10	0.07
Demineralised	0.37	0.21	0.03	0.006	7×10^{-4}	9×10^{-4}

TABLE 2. Mineral Concentrations of Normal and Demineralised Wyodak Coal Samples by CCSEM.

Mineral	Composition (wt%, coal basis)	
	Wyodak	Wyodak (demin)
Montmorillonite	4.15	-
Na Al silicate	2.20	0.0016
Aluminosilicate	1.32	0.07
Kaolinite	0.92	0.014
Barite	0.8	0.006
Quartz	0.78	0.012
Pyrite	0.58	0.018

TABLE 3. Results of Non-Catalytic Liquefaction of Normal and Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H₂.

Pretreatment	Solvent	Product Distribution (% dmmf basis)				
		Gas	Oil	Asph	Preasph	% Conv.
-	-	3.3	2.1	2.6	4.5	12.5
demineralised	-	10.0	0.8	0.4	5.3	16.6
-	Tetralin	4.2	4.1	7.6	10.0	25.9
demineralised	"	12.0	7.1	6.3	14.4	40.3
-	1-MN	4.0	1.1	5.8	7.4	18.3
demineralised	"	7.7	5.6	3.3	10.3	26.9

TABLE 4. Results of Non-Catalytic Liquefaction of Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H₂ and N₂.

Gas	Solvent	Product Distribution (% dmmf basis)				
		Gas	Oil	Asph	Preasph	% Conv.
H ₂	-	10.0	0.8	0.4	5.3	16.6
N ₂	-	10.7	1.2	0.7	5.2	17.8
H ₂	Tetralin	12.0	7.1	6.3	14.4	40.3
N ₂	"	10.4	10.3	3.6	17.8	42.1
H ₂	1-MN	7.7	5.6	3.3	10.3	26.9
N ₂	"	8.7	5.8	1.4	8.4	24.4

There are similarities between the results presented here and those of other studies, not necessarily limited to demineralised samples. Tomic and Schobert [9] also observed solvent effects under mild liquefaction conditions of subbituminous coals; solvent addition enhanced conversion relative to the reaction with no solvent, similar to the results in Table 3. If pyrite concentration has been reduced, the results in Table 4 confirm those reported by Tomic and Schobert [9], Artok [10] and Huang [11] who similarly reported that utilization of H₂(g) is ineffective without a good hydrogenation catalyst, as illustrated by the similarities in the comparative H₂ and N₂ runs. Serio et al. [3], also reported enhanced conversion for low rank coals following demineralization. This raises questions as to possible contribution of mineral species to low temperature liquefaction mechanisms. Joseph [4] ascribed this phenomenon to cations inhibiting hydrogen transfer from donor solvent/gaseous hydrogen to free radicals, in effect promoting retrogressive reactions. It could be that the absence of these species allows for better access to reactive sites in the coal interior.

Solid State ¹³C NMR

The ¹³C CPMAS spectra of the normal and demineralised coal are shown in Figure 1. The ¹³C CPMAS spectrum of the demineralised Wyodak displays many similarities to that of the untreated coal. The region between 0 and 80 ppm consists primarily of aliphatic carbons, e.g. methoxy groups. The second region of interest between 90 and 170 ppm is due to aromatic carbon. The shoulders on the side of the aromatic band may be attributed to specific functionalities, e.g. catechol groups (at 142 ppm) and phenolic groups (at 152 ppm) [7]. The carboxylic functionality is prominent at 180 ppm, similarly for the carbonyl at *ca* 210 ppm. In the aliphatic band, the symmetry observed for the parent coal is lost, and the appearance of a shoulder at ~25 ppm is observed. This may be attributed to a number of groups, including CH₃-Ar side chains (20-21 ppm). Furthermore, the distinct shoulders observed in the aromatic region have virtually disappeared, indicating a loss of oxygen functionalities.

Figure 1. ^{13}C CP-MAS Spectra of (a) Normal and (b) Demineralised Wyodak Coal.

Figure 2. FTIR Spectra of THF-Insoluble Residue from Reaction of Demineralised Wyodak Coal in (a) Absence of Solvent, (b) Presence of Tetralin and (c) Presence of 1-MN.

FTIR

Comparative FTIR spectra of the normal and demineralised coal and associated residues from reaction at 350°C under H₂ are shown in Figure 2. After reaction under H₂ at 350°C, the most notable feature of the whole product spectrum is a decrease in hydroxyl concentration, in part attributed to a loss of H₂O. Further examination of the THF-insoluble residues from these experiments indicates little difference between the composition of the residues, from both the normal and demineralized samples reacted under H₂ in the presence and absence of solvent. The FTIR spectrum of the THF-insoluble residue from the reaction conducted with tetralin displays somewhat contrasting features. The carboxyl stretching region is much broader; moreover, the ester shoulder is more pronounced and the carbonyl region is much more defined. Similarly, the FTIR spectra of the THF-extracted raw coal and the residues from the runs conducted at under N₂ demonstrated that under all conditions, i.e. both in the presence and absence of solvent, no marked changes were observed.

CONCLUSIONS

Relative to runs at 350°C with untreated coal, demineralization affords higher overall conversions; . this increase in conversion is the result of increased gas make over soluble products. This trend becomes more apparent when either an H-donor (tetralin) or non-donor (1-MN) solvent are used. Specifically, there is no evident mineral matter effect on solvent H donation acting only in solvent capacity. Comparison of the two sets of data suggests that the reactions undergone at 350°C are not mineral matter catalyzed. Indeed, the main effect of the acid treatments reported here is to open the coal structure, thus promoting more intimate contact between the solvent and the coal interior.

The residue from these sets of experiments is currently undergoing further analysis by Py-GC-MS, to evaluate in more detail the fundamental differences in speciation resulting from non-catalytic treatment under different regimes. If, indeed, there has been any catalytic behaviour by clays, this will be seen by examination of the residues and comparison between the two coal samples.

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