AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

2.

DOE/PC/92531--75
11-2
1

HETERONUCLEAR PROBES OF COAL STRUCTURE AND REACTIVITY

John G. Verkade
Gilman Hall
Iowa State University
Quarterly Report
Due April 30, 1994

January - March 1994

92531

The highlights of the previous report were:

1. Donna Hill coal vacuum impregnated with PBU_3 releases 57.0% of its sulfur but by employing AlCl_3 as a catalyst, 70.0% of its sulfur is released.
2. Dibenzothiophene treated with PBU_3 in the presence of AlCl_3 gives up no sulfur whereas with FeCl_3 as a catalyst (but not with FeCl_2 or Fe) it gives up 100% of its sulfur.
3. Preliminary solid state NMR and analytical evidence was put forth for the participation of OH hydrogens in the desulfurization of Ill. #6 by PBU_3 .
4. Substantiating evidence was presented that the ^{31}P NMR peak at 3 ppm in solid coals treated with PBU_3 is due to $[(\text{coal})\text{C}-\text{O}]_3\text{P}=\text{O}$ species.
5. We confirmed our result that contrary to a Moessbauer study in the literature, the reaction of $\text{Bu}_3\text{SnOSnBu}_3$ with the OH groups in Ill. #6 gives tetracoordinate $-\text{OSnBu}_3$ species and not five-coordinate $\text{coal-OSnBu}_3 \cdot \text{HO-coal}$ species.

A. FeCl_3 as a desulfurization catalyst

1. **Spanish lignite.** Runs 1 and 2 in Table I show that FeCl_3 substantially augments the sulfur removal from this coal upon PBU_3 treatment. This further substantiates our conclusion in the last quarterly report that FeCl_3 catalyzes this reaction.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
DOE/PC/92531
92 APR 29 11:11:23
MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

2. **Ill. No. 6 coal.** Run 3 in Table I shows that the addition of FeCl_3 as a catalyst does not enhance sulfur removal upon PBU_3 treatment. This suggests that the Fe(III) in this coal is already available for desulfurization catalysis even though the iron content (0.8 %) is lower than that found in Spanish lignite (1.26 %).

B. Vacuum impregnation of PBU_3

1. **Spanish lignite.** Run 1 in Table I reveals no improvement of sulfur removal by PBU_3 using vacuum impregnation over that obtained earlier without impregnation. This suggests that Spanish lignite is more porous to PBU_3 than is Ill. No. 6.

C. On the Significance of the ~ 32 ppm ^{31}P NMR Peak in PBU_3 -Treated Coals

1. **Ill. No. 6 Pretreatment with MeI and Ionic Bases.** Impregnation of Ill. No. 6 with MeI followed by washing with aqueous $\text{Bu}_4\text{N}^+\text{OH}^-$ and treatment with PBU_3 produced a prominent peak at 33 ppm in the filtered residue (previous report). The same was true upon MeI/NaOH/ PBU_3 treatment. These puzzling results suggested that either MePBU_3^+ was produced or that protons were still present despite the methylation attempts. We then tried MeI/ PBU_3 /pyridine washing and found that a 32 peak appeared in the pyridine extract, and the 33 ppm peak disappeared from the solid-state spectrum. These peaks are likely to be due to MePBU_3^+ since addition of an authentic sample of this material ($\text{MePBU}_3^+\text{I}^-$) to the extract enhanced the 32 ppm peak intensity. A peak at 33 ppm of presently unknown origin also appeared in this extract.

2. **Ill. No. 6 Pretreatment with Et_3OBF_4 and a Non-ionic Strong Base.** To minimize proton sources even further we vacuum impregnated Ill. No. 6 with Et_3OBF_4 in ether, removed liberated protons with our (patented) superbase $\text{P}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$, and then treated the coal with PBU_3 . After filtration, the residue showed a prominent ^{31}P peak at 32 ppm. Washing the residue with

pyridine revealed the same peak in the extract, suggesting that in both cases EtPBU_3^+ is present, probably stemming from excess $\text{Et}_3\text{O}^+\text{BF}_4^-$ which then reacted with the PBU_3 .

D. On the Significance of the 3 ppm ^{31}P NMR Peak in PBU_3 -Treated Coals

It appears that acidic protons participate in the reaction that converts PBU_3 to $[\text{coal-O}]_3\text{P=O}$ species in coals treated with a wide variety of phosphorus compounds. Thus the residues from C.1. and C.2. all feature a low intensity of this peak in their solid state ^{31}P NMR spectra.

E. Hydrodesulfurization of Ill. No. 6

1. **Ni_2B as a Catalyst.** There is literature evidence that $\text{Ni}_2\text{B} + \text{H}_2$ effects HDS on oils. Our attempt to extend this chemistry to Ill. No. 6 by using PBU_3 as a carrier (i.e., as SPBU_3) failed (Run 4 in Table I). In fact, these conditions reduce the amount of sulfur removed compared with PBU_3 treatment only.

2. **AMOCAT 1A as a Catalyst.** Here we used no H_2 or coal but tried to determine if SPBU_3 would give up its sulfur to the catalyst. If this worked, a run with H_2 and coal could be set up to see if PBU_3 could act as a shuttle between the coal and the catalyst. This experiment failed at room temperature, 250 °C and at 320 °C.

3. **SHELL 324 as a Catalyst.** This catalyst with SPBU_3 at 320 °C does produce a new phosphorus species ($\delta^{31}\text{P}$ at 54.2 ppm) but it is not PBU_3 ($\delta^{31}\text{P}$ -31.8 ppm) and we do not know yet if the new species contains sulfur.

F. Solid State ^{31}P NMR Studies

1. **Donna Hill coal.** Impregnation with phenol followed by PBU_3 treatment gives a spectrum similar to that seen without phenol present (PETC51, Table II). PBU_3 treatment in the presence of AlCl_3 gives rise to two additional peaks at 48 and 32 ppm, and a relatively minor peak at 3 ppm (PETC52, Table II). PBU_3 treatment in

the presence of Ni_2B also gives the additional 48 ppm peak but not the 32 ppm peak (PETC56, Table II). More data will be required to interpret these results.

2. Spanish lignite. The spectrum for the PBu_3 impregnation experiment (PETC58, Table II) is the same as that for the unimpregnated sample done earlier. The spectrum is similar to that of Ill. No. 6 impregnated with PBu_3 except for a new peak at 38 ppm whose origin is presently unknown. This peak, as well as a relatively narrow one at 48 ppm, also shows up in the spectrum of Spanish lignite treated with PBu_3 in the presence of FeCl_3 (PETC59, Table II). The 48 ppm peak does not show up when PBu_3 is used alone and it may represent SPBu_3 with a different degree of mobility than that at 51 ppm. The 48 ppm peak may stem from sulfur liberated by the added FeCl_3 .

3. Illinois No. 6 coal. PBu_3 treatment following MeI impregnation and NaOH washing showed the peaks given in Table II (PETC57). After washing with pyridine, the peaks at 33, -33, 38, 49 and 73 ppm disappear, and a 31.5 ppm peak occurs which presumably was overlapped with the 33 ppm peak (PETC57.001). As mentioned earlier, the 33 ppm peak is assigned to MePBu_3^+ . Ill. No. 6 treated with PBu_3 in the presence of anhydrous FeCl_3 (PETC60) or Ni_2B (PETC61) gives a very similar spectrum to that observed without these additives. Similarly the presence of $\text{Ni}_2\text{B} + \text{H}_2$ makes little difference in the ^{31}P NMR spectrum (PETC55). Pretreatment of a sample with $\text{Et}_3\text{O}^+\text{BF}_4^-/\text{P}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$ followed by PBu_3 (see also above) gives the spectral data given in Table II (PETC62). As mentioned earlier, a ^{31}P spectrum of the pyridine extract reveals that the prominent 32 ppm peak is associated with EtPBu_3^+ .

G. HPLC Studies

Retention times of ca. 50 model phenols of a wide variety of types have been collected in order to be able to analyze coal liquids. These studies are being correlated with the phenol derivatization studies discussed in the next section.

H. ^{31}P NMR Studies of Derivatized Phenols

1. **Model Phenols.** One of the goals of the proposal is to employ solution ^{31}P NMR spectroscopy in tandem with HPLC to speciate and quantitate phenols in coal resid. As solution ^{31}P NMR tagging agents, we are using both 1 and 2 since the

^{31}P chemical shifts provided by each are different for identical phenols. This allows a cross-check on the identity of phenols (especially isomeric examples) as well as their concentration. By building a library of ^{31}P chemical shifts of a wide variety of phenols derivatized with 1 and 2, speciation of phenols in coal liquids, for example, can be accomplished. Using preparative HPLC, we can separate the phenols and also derivatize them with 1 and 2 for speciation.

Tables III and IV list chemical shifts for phenols derivatized with 1 and 2, respectively. In Table V we list the total phenol contents of three Consol coal resid using reagent 1 and a ^{31}P NMR procedure we reported earlier.¹ We are gratified to note how well our quantitations compare with those reported in the literature using FTIR spectroscopy.² Because sample 3 contained paramagnetic species, speciation of phenols was precluded, owing to peak breadth and overlap. However, samples 1 and 2 produced well-resolved signals. We are now in the process of identifying the phenols responsible for these peaks.

I. Plans for Future Work

1. Vacuum impregnate Ill. No. 6, Donna Hill and Spanish coals with a mixture of $\text{PBu}_3/\text{FeCl}_3$ to determine if premixing of these impregnation components elicits greater sulfur removal, or in the case of Ill. No. 6, complete sulfur removal in a shorter amount of time.
2. Heat $\text{Me}_2\text{NSn}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ with Ill. No. 6 to obtain coal-O-Sn(CH₂CH₂CH₂)₃N species and see if the ^{119}Sn chemical shift is indeed in the five-coordinate region as it should be in this case.
3. Impregnate Ill. No. 6 with $\text{Et}_3\text{O}^+\text{BF}_4^-$, wash with pyridine to remove excess reagent and HBF_4 , then treat with PBu_3 to see if the 32 ppm peak decreases in intensity.
4. Impregnate Ill. No. 6 with $(\text{Me}_3\text{Si})_2\text{NH}$, wash, then treat with PBu_3 . Any $\text{Me}_3\text{SiPBu}_3$ that forms should not have a 32 ppm resonance.
5. Does Ill. No. 6 impregnated with a PhOH/PBu_3 mixture followed by a pyridine wash show an enhanced 3 ppm peak?
6. Oxidized DBT (i.e., the sulfoxide and sulfone) should be treated with $\text{PBu}_3/\text{FeCl}_3$ to see if OPBu_3 and SPBu_3 is formed. This would tell us if weathered coals could be desulfurized with PBu_3 .

References

1. Mohan, T.; Verkade, J. G. *Energy and Fuels* **1993**, 7, 222.
2. a) Robbins, G. A.; Winschel, R. A.; Burke, F. P. *Prepr. Pap-Am. Chem. Soc. Div. Fuel Chem.* **1985**, 30, 155. b) Winschel, R. A.; Robbins, G. A.; Burke, F. P. *Technical Progress Report, July-Sept. 1985*, DOE/PC 70018-13, December 1985.

Table I. Reactions of Bu₃P with coal samples.

run #	coal samples	reaction conditions	solution	% sulfur
			³¹ P chemical shifts ^a (ppm)	(relative)
1	Spanish coal	250 °C, reflux, 2 d, prior vac. impreg.	48.48, 44.22	18.31
2	Spanish coal with FeCl ₃	250 °C, reflux, 2 d	— ^b	41.10 ^b
3	Ill. #6 coal with FeCl ₃	250 °C, reflux, 2 d	— ^b	90.32 ^b
4	Ill. #6 with Ni ₂ B	250 °C, reflux, 2 d	48.34, 44.09	35.39

^aPeaks due to the internal standard, Ph₃PMeI and the unreacted Bu₃P are also seen. ^bParamagnetism of the PBu₃ extract (owing to the FeCl₃) precluded resolved ³¹P NMR spectra. Thus the extracts were subjected to elemental analysis.

Table II. Solid state ^{31}P NMR Results for PBu_3 Treated Coals.

sample	sample treatment	$\delta^{31}\text{P}$ (ppm)
PETC51	Donna Hill, impregnated w/PhOH, then treated with Bu_3P^a	$3 \gg -33 > -5$
PETC52	Donna Hill, AlCl_3 , Bu_3P^a	$48 > -33 > 32 > 3$
PETC56	Donna Hill, Ni_2B , Bu_3P	$3 \gg -34 \approx 48$
PETC58	Spanish coal, impregnated and derivatized with Bu_3P	$51 > 32 > -33 > 3 \gg 38$
PETC59	Spanish coal, FeCl_3 , Bu_3P	$51 > 48 \approx 32 > 3 > 38$
PETC57	Ill. No. 6, CH_3I by impregnation, washed w/ NaOH , then treated w/ Bu_3P	$33 \gg 46 > 49 \approx -33 \approx 73 > 38 \approx 40 > 23 \approx 25 \approx 3$
PETC57.001	PETC57 washed with pyridine	$31.5 \gg 3 > 23.3 \approx 25.6 \approx 39.8 \approx 45.8$
PETC60	Ill. No. 6, FeCl_3 , Bu_3P	$50 > 32.5 \approx 3 \approx -33$
PETC61	Ill. No. 6, Ni_2B , H_2 , Bu_3P	$50 > 3 > 32.5 \approx -33$
PETC55	Ill. No. 6, Ni_2B , Bu_3P	$50 > 31 \approx 3 \approx -33$
PETC62	Ill. No. 6, $\text{Et}_3\text{O}^+\text{BF}_4^-$, $\text{P}(\text{MeNCH}_2\text{CH}_2)_3\text{N}$, PBu_3	$32 \gg 23 \approx -11 > 3$

^aRepeated measurement.

Table III. ^{31}P NMR Chemical Shifts of Phenols Derivatized with Reagent 1.

Phenols	$\delta^{31}\text{P}$ (ppm) ^a
1-indanol	147.17
2,7-dihydroxynaphthalene	138.15
4-methoxy-1-naphthol	139.05
3-phenylphenol	138.87
1,3-dihydroxynaphthalene	138.34, 137.95
4-phenylphenol	138.75
2,6-dihydroxynaphthalene	138.48
1,2-dihydroxynaphthalene	140.97, 140.73 ^b
1,5-dihydroxynaphthalene	138.64
2,4-ditertiarybutylphenol	138.16
2,3-dihydroxynaphthalene	138.86
3-tertiarybutylphenol	138.63
4-secondarybutylphenol	138.70
7-methoxy-2-naphthol	138.20
4,4'-biphenol	138.76
2-methoxy-4-methylphenol	140.79
1-methoxy-2-indanol	147.00
2-phenylphenol	139.39
3,5-dimethoxyphenol	138.10
2-tertiarybutyl-5-methylphenol	138.53
2-tertiarybutyl-4-methylphenol	138.51
3,5-ditertiarybutylphenol	138.56
thymol	139.25
3,4,5-trimethoxyphenol	138.60
2-tertiarybutyl-6-methylphenol	145.69

2,6-diisopropylphenol	143.62
4-tertiarybutylphenol	138.68
2-isopropylphenol	139.30
2-secondary butyl phenol	139.55
2,3-dimethoxyphenol	140.28
1,6-naphthalenediol	138.43
5-isopropyl-2-methylphenol	139.32
2-ethylphenol	139.30
3-isopropylphenol	138.70
1,7-naphthalenediol	139.21, 138.39
1,4-naphthalenediol	138.85
2-tertiarybutylphenol	138.64
2-methyl-1-naphthol	144.39
2-allylphenol	139.19
4-teritarybutyl-2-methylphenol	138.01

^aδ³¹P for reagent 1: 175.90 ppm. ^bJ_{PP} = 9.96 Hz.

Table IV. ^{31}P Chemical Shifts of Phenols Derivatized with Reagent 2.

Phenols	$\delta^{31}\text{P}$ (ppm) ^a
3-isopropylphenol	152.22
2-ethylphenol	155.52
4-isopropylphenol	153.38
2-tertiarybutyl-5-methylphenol	155.94
2-methoxy-4-methylphenol	159.90
2,6-diisopropylphenol	164.01
2-tertiarybutyl-4-methylphenol	166.96
4-methylcatechol	162.17, 161.13 ^b
thymol	156.57
3-methylcatechol	166.43, 160.86
phluoroglucinol	153.33
4-tertiarybutyl-2-methylphenol	154.34
5-isopropyl-2-methylphenol	154.11
3,5-dimethoxyphenol	155.59
2,3-dimethoxyphenol	162.13
3,4,5-trimethoxyphenol	155.64
2,6-dimethoxyphenol	167.30
2-tertiarybutylphenol	156.68
3,5-ditertiarybutylphenol	150.78
2,4-ditertiarybutylphenol	156.69
3-tertiarybutylphenol	151.99
4-tertiarybutylphenol	153.37
3-phenylphenol	154.47
4-secondarybutylphenol	152.47
4-phenylphenol	154.32

2-secondarybutylphenol 156.11

2-allylphenol 156.45

³¹P for reagent 2: 169.00 ppm. ^bJ_{PP} = 9.1 Hz. ^cJ_{PP} = 13.0 Hz.

Table V. Quantitation of Phenolic Content in Coal Liquefaction Resids from CONSOL Inc.

sample No.	source & processing	wt. of liquid (gm)	wt. of l-menthol <u>meg/g of phenolic oxygen</u>		
			(mg) ^a	³¹ P NMR	FT-IR
1	Separator overhead oil, HRI, CTSL Run CC-16. Burning Star #2 Mine, Ill. #6 coal.	0.4940	20.7	0.088	0.08
2	Atmospheric still overhead oil, HRI Run CC-16. Burning Star #2 Mine. Ill. #6 coal.	0.4428	11.9	0.15	0.14
3	Recycle Distillate (V-1074), Wilsonville run 262. Black Thunder Mine, Wyoming Subbituminous coal.	0.3654	12.1	0.39	0.44

^al-Menthol is used as an internal standard.

DATE

FILMED

7/13/94

END