

AN ESCA STUDY OF ALKALI-TREATED COAL SURFACES

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ABSTRACT

The surface interactions of alkali with coal and mineral matter have been studied by ESCA to establish a basis for predicting the relative reactivity of alkali with sulfur during coal beneficiation processes. The speciation of sulfur in several coals doped with various alkali salts was determined and quantified following heating of the samples to 375°C in air or N₂ and after washing them with water. Organic and pyritic sulfur react with the alkali cation when heated, after which the sulfide or oxidized sulfur product can be washed from the coal. The extent of reaction between the alkali salt and sulfur is governed by the size of the cation and the electronic properties of the anion; larger alkali cations are more reactive, as are anions with stronger nucleophilic properties.

INTRODUCTION

Over the years several processes employing alkali have been used for coal beneficiation (1). Presently the process for removing sulfur and ash from coal by treatment with molten caustics (MCL) is continuing to be developed as an alternative method for removing troublesome impurities from coal (1-4). Research has been conducted to determine the effects of process variables on the efficiency of the MCL system and to develop methods for analyzing and regenerating spent caustic (5-7). More fundamental studies have attempted to determine the mechanisms for interaction between the Na and K hydroxides and the components of coal, especially pyrite (8) and organosulfur (9,10).

This study focuses on the surface interactions of alkali with coal and mineral matter as studied by ESCA. Such interactions may be important in several processes in which coal and sulfur in coal are treated with alkali. Changes in the chemical state of the sulfur components of coal were monitored following deposition of various alkali hydroxides and sodium and potassium salts, and after subjecting the coals to various thermal treatments and washes.

EXPERIMENTAL

Preparation of Alkali-Doped Samples. A Pittsburgh No. 8 hvAb coal (2.2% pyrite, 0.4% sulfate, 1.6% organic sulfur) and Rasa lignite (Yugoslavia) (approximately 11% organic sulfur) were ground in air to minus 100 mesh. A 0.75-g sample of coal was mixed with 1 mL of an aqueous solution containing enough NaOH or KOH to produce the desired alkali concentration in the coal. The alkali-doped coals were placed in a ceramic boat and dried overnight at 60°C in a flow of N₂; coals were stored under air in a dessicator.

Four Pittsburgh No. 8 coal samples, the first containing 0.5% Na, the second containing 0.5% K, the third containing 0.25% Na and 0.25% K, and a fourth containing no added Na or K were analyzed after heating them to temperatures up to 375°C for one hour in flowing air or N₂.

A quantitative study of the effects of washing on sulfur removal was carried out on Na-doped and (Na + K)-doped Rasa lignite that had been heated at 375°C for one hour in air or N₂. The lignite samples were doped using the same procedure described above so that the final concentrations of alkali were approximately 5% Na and 5% Na plus 5% K, respectively. After heating, the samples were mixed with approximately 10% to 40% high-surface-area gamma alumina, which was used as an internal standard for monitoring changes in sulfur content during the wash procedure.

The Pittsburgh No. 8 coal was also doped with aqueous solutions of Na, K, Rb, and Cs hydroxides so that 0.75 g of coal contained 1.62×10^{-4} moles of one of the alkali metals. Another series of coal samples was impregnated with aqueous solutions of various Na and K salts (fluorides, chlorides, bromides, nitrates, acetates, and carbonates); the concentration of Na or K was 0.5% in each sample. All of the above samples were heated either in air or in nitrogen at 375°C for one hour.

Instrumentation. The coals were analyzed as powders mounted on double-sided sticky tape using a Leybold-Heraeus LHS-10 spectrometer. The magnesium anode was operated at 12 kV and 20 mA with the analysis chamber at a vacuum of 2×10^{-8} mbar or lower. The S 2p peaks were curve-fitted using the L-H DS-5 data system.

RESULTS AND DISCUSSION

Thermal Treatments. The S 2p region was curve-fitted with two peaks: one at 169.7 eV due to oxidized sulfur, S_(o), most likely in the form of SO₄²⁻; and another at 164.0 eV due to unoxidized sulfur, S_(u) (organic sulfur, pyrite, and elemental sulfur) (11). Table 1 shows the results of the curve-fitting analyses of the S 2p spectra for the non-doped, Na-doped, K-doped, and (Na + K)-doped coals after heating to various temperatures in air. It can be seen that heating the coal to higher temperatures in air resulted in the conversion of an increasing percentage of S_(u) to S_(o) ($\%S_{(u)} = 100 - S_{(o)}$); the amount of S_(o) was always greater for the alkali-doped coals. Higher S_(o) values for Na-doped coals compared to K-doped coals may be due to the somewhat greater Na concentration, on a molar basis.

To investigate the role of oxygen in the oxidation of alkali-doped coals, the coals were heated in a flow of N₂. Table 1 shows that little change in sulfur speciation occurred for the coal containing no alkali, in contrast to the decrease observed in the fraction of sulfur present as S_(o) on heating the alkali-doped coals under N₂. Bulk ASTM analyses showed no decrease in sulfur content on heating. The form of sulfur in the latter coals was hypothesized based on the results of subsequent experiments.

The percentages of S_(o) are higher for the mixed-alkali-doped coals heated in air when compared to either the Na- or K-doped coals (Table 1). The creation of a eutectic mixture of Na and K hydroxides may enhance their contact with sulfur and promote S_(o) formation.

Quantitative Determination of Sulfur Removal. Experiments employing Rasa lignite, which has a high sulfur content (approximately 11% S) that is almost exclusively organic, and Na or (Na + K) hydroxide were carried out to determine whether the alkali hydroxides were reactive toward organic sulfur and how much of the reaction products could be removed from the lignite by washing. The

percentages of $S_{(o)}$ and $S_{(u)}$ in the lignite before and after washing, and the S 2p/Al 2s intensity ratios, are reported in Table 2. There was a small increase in the percentage of $S_{(o)}$ and a 22% decrease in the S 2p/Al 2s intensity ratio following washing for the Na-doped lignite heated in N_2 . Therefore, heating of the Na-doped lignite in N_2 , followed by washing, led to the removal, or conversion to $S_{(o)}$, of 34% of the total sulfur in the starting lignite. If one were to assume that all of the Na was converted to Na_2S upon heating the lignite in N_2 , then 35% of the total sulfur in the lignite would have reacted. This would be in excellent agreement with the results obtained above if washing either oxidized the Na_2S to Na_2SO_4 or removed it from the lignite. Complementary reductions in sulfur content were obtained for air-heated coal (Table 2) and by increasing the fraction of alkali in the coal.

Rasa lignite must be doped with either NaOH or KOH in order to observe oxidation of sulfur during heating, thereby indicating the importance of the alkali hydroxide for sulfur reactivity. In studies of MCL reactions of alkali with model organosulfur compounds, such as benzothiophene, have shown that nucleophilic attack by OH^- can lead to ring opening and formation of the Na or K salt of the organosulfur fragment (9,10). To systematically evaluate the effect of the alkali cation and its associated anion on the reactivity of sulfur in coal, two sets of experiments were performed. In the first experiment, a Pittsburgh No. 8 coal was doped with various Na and K salts and heated in air or N_2 at 375°C for 1 hour. Coals doped with Na and K salts and heated in N_2 showed no significant difference in the percentages of $S_{(o)}$ and $S_{(u)}$ ($\%S_{(o)} = 14.3 \pm 2.4$) because formation of an alkali sulfide renders the reacted sulfur indistinguishable by ESCA from unreacted organosulfur and pyrite.

An easier comparison of the relative reactivity of alkali cations and anions towards sulfur, most importantly organic sulfur, in coal is achieved by heating the coals in air where the product is the alkali sulfate. Table 3 shows that for coals doped with Na salts and heated in air, F^- , NO_3^- , and CO_3^{2-} were least effective for conversion of $S_{(u)}$ to $S_{(o)}$, while the acetate salt was the most reactive. For coals doped with K salts, F^- , Cl^- , and NO_3^- were least effective for $S_{(o)}$ formation compared to acetate, which was most reactive. It is interesting to note that less conversion of $S_{(u)}$ to $S_{(o)}$ occurs in the presence of the small and highly electrophilic (less nucleophilic) anions, F^- and Cl^- (when associated with K) than in the presence of larger and less electrophilic Br^- and acetate anions. Studies of MCL employing model organosulfur compounds have shown that nucleophilic attack of the aromatic sulfur-containing ring is an important step in sulfur elimination (9,10). Therefore, while reactions between Br^- or acetate anions and the sulfur-containing moieties of coal may be sterically hindered, the stronger nucleophilic properties of these anions may play an important role in the overall reaction that leads to sulfur oxidation.

The effects of alkali cation size on the reactivity of the sulfur-containing components of coal can be seen in Table 4, which shows that as the size of the cation increases ($Na^+ \rightarrow Cs^+$), the conversion of $S_{(u)}$ to $S_{(o)}$ for coal heated in air also increases. The extent of reaction of model organosulfur compounds under MCL conditions has been found to increase with cation size (9,10,12). The earlier studies proposed that the increased size of the cation may help to stabilize a reaction intermediate prior to sulfur elimination, thereby promoting the overall reaction.

CONCLUSIONS

These experiments have shown that removal of sulfur from coal may be accomplished by doping with alkali hydroxides followed by heating to moderate temperatures and washing. The types of alkali salts used for treating coal surfaces are important in determining the nature and extent of sulfur reactivity.

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Table 1. Percentages of $S_{(o)}$ as Determined by ESCA for a Pittsburgh No. 8 Coal Heated for 1 Hour at Various Temperatures.

<u>Temperature</u>	<u>Non-Doped Coal</u>	<u>Na-Doped Coal</u>	<u>K-Doped Coal</u>	<u>(Na + K)-Doped Coal</u>
Not Heated	30.7	37.5	32.6	45.8
100°C ^a	33.6	36.8	37.5	49.2
150°C ^a	38.0	43.1	43.1	57.2
250°C ^a	46.7	71.4	60.9	81.0
350°C ^a	58.6	82.7	77.0	84.5
375°C ^a	67.4	87.2	80.6	88.2
375°C ^b	31.5	14.6	15.9	23.5

^aHeated in air.

^bHeated in N_2 .

Table 2. Percentages of $S_{(o)}$ and $S_{(u)}$ and S 2p/Al 2s Intensity Ratios as Determined by ESCA for a Heated-Treated^a Rasa Lignite Before and After Washing.

	<u>Heated In Air</u>			<u>Heated In N_2</u>		
	<u>$S_{(o)}$</u>	<u>$S_{(u)}$</u>	<u>S 2p/Al 2S</u>	<u>%$S_{(o)}$</u>	<u>%$S_{(u)}$</u>	<u>S 2p/Al 2S</u>
<u>Na-Doped (5% Na)</u>						
Before Washing	57.2	42.8	0.796 ^b	8.6	91.4	1.40 ^c
After Washing	15.5	84.5	0.584 ^b	16.0	84.0	1.09 ^c

^aHeated at 375°C for 1 hour.

^bMixed with approximately 20% Al_2O_3 .

^cMixed with approximately 10% Al_2O_3 .

Table 3. Percentages of $S_{(o)}$ and $S_{(u)}$ as Determined by ESCA for Air-Heated,^a Alkali-Doped Pittsburgh No. 8 Coal.

Anion	Na ⁺ Cation		K ⁺ Cation	
	%S _(o)	%S _(u)	%S _(o)	%S _(u)
OH ⁻	87.2	12.8	80.6	19.4
F ⁻	76.7	23.3	71.0	29.0
Cl ⁻	85.3	14.7	74.4	25.6
Br ⁻	88.2	11.8	82.7	17.3
NO ₃ ⁻	80.1	19.9	77.5	22.5
(C ₂ H ₃ O ₂) ⁻	94.9	5.1	89.9	10.1
CO ₃ ²⁻	81.1	18.9	78.9	21.1

^aHeated at 375°C for 1 hour.

Table 4. Percentages of $S_{(o)}$ and $S_{(u)}$ as Determined by ESCA for Heat-Treated,^a Alkali-Doped Pittsburgh No. 8 Coal.

Cation	Heated In Air		Heated In N ₂	
	%S _(o)	%S _(u)	%S _(o)	%S _(u)
None	67.4	32.6	31.5	68.5
Na ⁺	87.2	12.8	14.6	85.4
K ⁺	87.2	12.8	15.9	84.1
Rb ⁺	91.4	8.6	26.4	73.6
Cs ⁺	100.0	0.0	22.4	77.6

^aHeated at 375°C for 1 hour.