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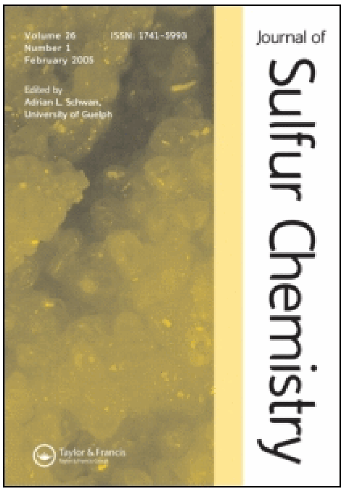

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Sulfur speciation in fluid coke and its activation products using K-edge X-ray absorption near edge structure spectroscopy

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Fluid coke is a by-product of bitumen upgrading process and a stockpiled industrial waste produced in large quantities in Alberta, Canada (overall 10,000 tonnes per day). It has been used as a raw material for manufacturing sulfur-impregnated activated carbon (SIAC). Properties of sulfur in the SIAC are critical to the effectiveness of SIAC in adsorbing mercury at ppb levels. K-edge X-ray absorption near edge structure (XANES) spectroscopy was employed to characterize sulfur in two fluid coke samples and their activation products. It was found that about 90% of sulfur in two coke samples is of organic nature, with over 50% of sulfur in the form of thiophene and the rest 40% being organic sulfide. About 10% of sulfur is in the form of oxides, *i.e.* sulfate. To simulate the coke samples and validate the analytical technique, a mixture of pure sulfur compounds and graphite was prepared and examined with XANES; the results showed good agreement between the actual and measured sulfur contents in specific forms. XANES results were found to be consistent with X-ray photoelectron spectroscopy (XPS) results. The two techniques are complementary to each other; XANES is capable of distinguishing sulfur species at low oxidation states whereas XPS is able to separate some sulfur species with higher oxidation state. The activation process with KOH and SO_2 affected the chemistry of sulfur in fluid coke. XANES surface analysis identified disulfide, sulfide, sulfonate, and sulfate in SIACs and found no thiophene, suggesting a complete removal of thiophene from carbon surface by KOH.

Keywords: XANES; sulfur characterization; fluid coke; sulfur-impregnated activated carbon; XPS

1. Introduction

Oil-sands fluid coke is a by-product of upgrading Athabasca oil sands bitumen. It is being produced in large quantities (>10,000 tonnes per day) and stockpiled onsite in Alberta. The high sulfur content of this type of petroleum coke (5–8 wt%) precludes it from being used as a direct energy source. For this reason, effort has been directed toward developing ways to utilize this type of coke. One of the most significant approaches is using the fluid coke to produce activated carbons which are potentially useful for water and air purification. Since fluid coke has high sulfur content, a carbon product that is particularly relevant is sulfur-impregnated activated carbon (SIAC). SIACs have been proven to be effective in removing mercury vapor from flue gases (*1*, *2*), where sulfur seems to play an enhancing role in capturing mercury.

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In order to understand the roles of sulfur in coke activation and in mercury capture, the forms of sulfur in both raw fluid coke and SIAC have to be identified. However, the characterization of sulfur within a carbon matrix is a challenging task, particularly when the sulfur is organic in nature. The commonly used wet chemistry methods, ASTM D 2492 and D 3177, can only determine the amount of total sulfur, pyrite, sulfate, and, by difference, the organic sulfur in coal or coke. Thus, there are significant errors in the quantification of organic sulfur, and the forms of organic sulfur cannot be identified (*3, 4*). X-ray photoelectron spectroscopy (XPS) has been used to characterize sulfur in coal and coke (*5, 6*). However, using XPS, it is difficult to distinguish sulfur species with similar oxidation states, such as sulfide and thiol. Despite the importance of sulfur speciation, the quantitative characterization of sulfur species in fluid coke and fluid coke-derived activate carbon has not been done.

X-ray absorption near edge structure (XANES) spectroscopy has been used by several groups of researchers as an aid to characterize sulfur in coal, soil, and activated carbon (*7–16*). It has been widely accepted that XANES is the most effective technique for determining organic sulfur in coal (*4*). However, XANES has not been applied to characterize sulfur species in fluid coke and its activation products. In this study, the sulfur K-edge XANES was used to identify and quantify sulfur species in fluid coke and their activation products, SIACs. This information will be used to better understand the transformation of sulfur during activation and the roles of sulfur in fluid coke activation and mercury uptake.

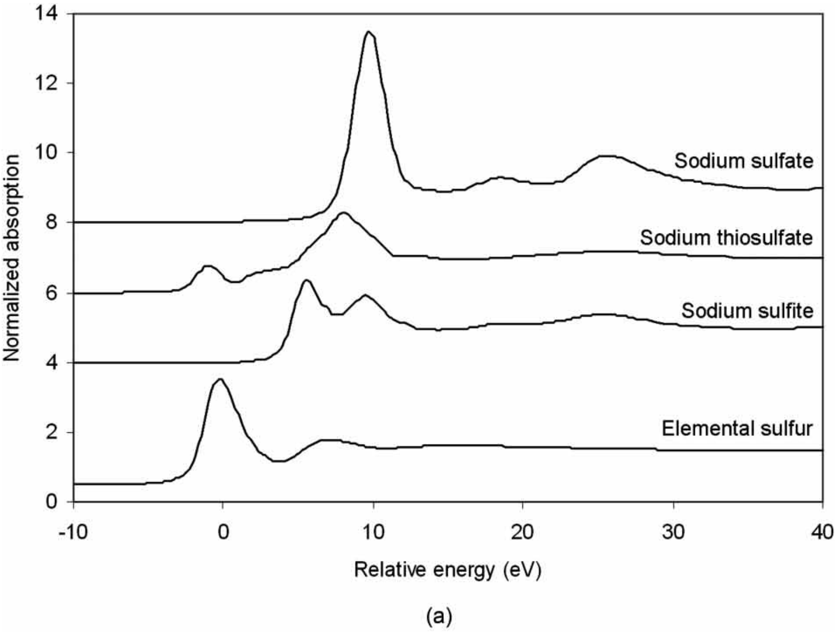
2. Results and discussion

2.1. *Model compounds*

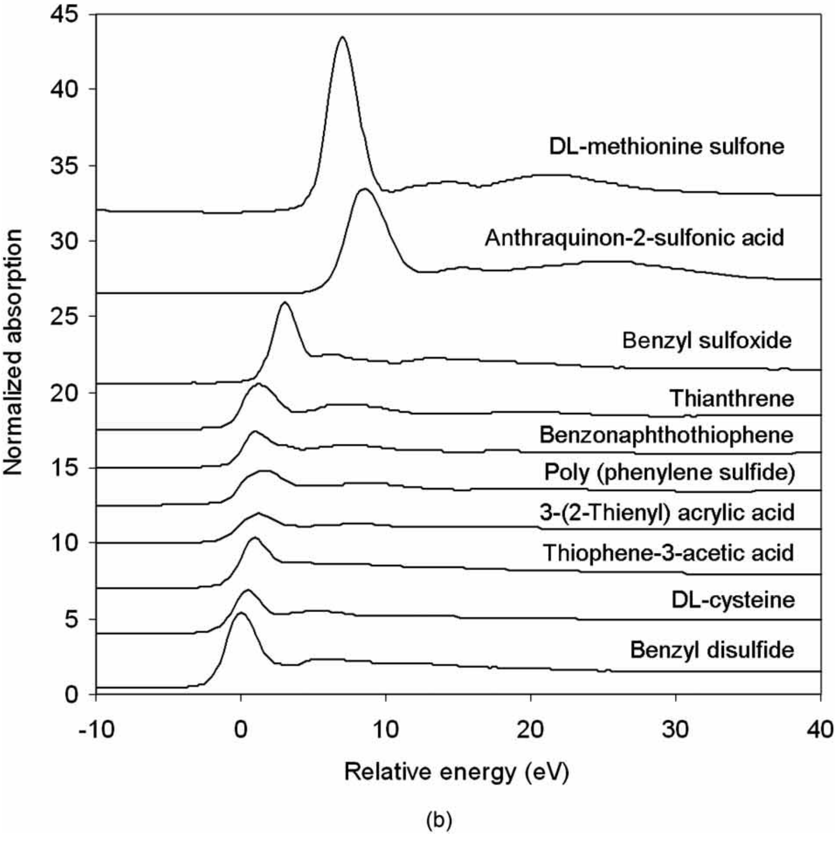
Among the 25 model compounds, 21 are organic sulfur compounds and belong to four categories– (i) alkyl and aryl sulfides, (ii) six-membered ring heterocyclic sulfur, (iii) thiophenic sulfur, and (iv) organic oxyanions. Inorganic model compounds include elemental sulfur, sodium thiosulfate, sulfite, and sulfate. Sulfur K-edge XANES of 25 model compounds was recorded in the total electron yield (TEY) mode, some of which are shown in Figure 1a and b. The TEY mode probes $\sim$50 nm, which means that it is surface sensitive (*17*). The zero of energy is taken at the first peak in the spectrum of elemental sulfur, and thus the relative energy is the absorption energy relative to elemental sulfur. The first large peak in the spectrum indicates the occurrence of an $s \rightarrow p$ transition (*i.e.* the edge, or 'white line'). The transition of the photoelectron from the 1s level to hybridized 3p level reflects the oxidation state of the sulfur compound. The subsequent broader and smaller peaks in the range of 5–30 eV above the edge are formed from low-energy scattering resonances, which are features of a specific molecular structure. Therefore, each sulfur compound has a unique spectrum which can be used as a fingerprint for the electronic nature of a sulfur compound, and for distinguishing sulfur forms in pure compounds.

Appendix 2 shows that the first inflections of oxidized sulfur compounds are notably higher than those of reduced sulfur, with a total energy span of 10.1 eV from 2471.7 (elemental sulfur) to 2481.8 eV (sodium sulfate). Based on the electronic oxidation states recorded in the present study, the sulfur species can be grouped into three major groups: (i) the most reduced sulfur (2471.7–2475.0 eV), including: elemental sulfur, sulfide, disulfide, thiol, and thiophene, (ii) intermediately oxidized sulfur (2475.0–2481.0 eV), which include sulfoxide, sulfone, sulfonate, sulfite, and thiosulfate, and (iii) highly oxidized sulfur (higher than 2481.0 eV), representing sulfates.

The first inflection energy can be readily used to distinguish the forms of sulfur in pure compounds. However, some sulfur compounds may have similar absorption energies. For instance, thiophene-3-acetic acid, benzonaphthothiophene, and 3-(2-thienyl)-DL-alanine have identical absorption energies of 2473.0 eV, since they are all thiophenic sulfur, despite their different atomic



(a)



(b)

Figure 1. (a) Sulfur K-edge XANES spectra of inorganic model compounds; (b) sulfur K-edge XANES spectra of organic sulfur model compounds.

environment. Elemental sulfur and L-cystine have the same absorption energy of 2471.7 eV, yet they have different sulfur forms. A chart was plotted based on data in the literature and from this study, which shows the overlapping of inflection energies (Figure 2). Therefore, from the first inflection energy, there is an uncertainty in distinguishing all sulfur forms. In this case, the complete XANES spectra of individual sulfur compounds have to be examined.

The spectra of standards show some evidence of oxidation. For example, the spectrum of sodium sulfite shows a shoulder (at 2482 eV) which is normally absent in the sulfite spectrum. Since sodium sulfite is readily oxidized in air, this suggests the presence of sulfate. This cannot be avoided when TEY detection is used, due to the surface sensitivity of the method. Other methods may be used to reduce the oxidation effect, such as the fluorescence yield (FY) mode, although self-absorption will be another issue for the FY mode. SIAC is mainly used as an adsorbent material and the adsorption mainly takes place on its surface. Thus, surface chemistry is most important, and consequently, the TEY mode was used in this study.

2.2. *Mixture of sulfur compounds*

In order to evaluate the reliability and accuracy of the XANES method for determination of sulfur forms in carbonaceous materials, a mixture of pure sulfur compounds with graphite was prepared and its sulfur forms were analyzed using XANES. Least-squares peak fitting was used to fit the spectra and the detailed fitting procedure is shown in Section 4.2. Briefly, the spectrum was first normalized by calibrating absorption energy and subtracting the background. It was then fitted with four Gaussian peaks and two arctangent steps. By varying the height and area of Gaussian peaks and arctangent steps, a fitting with χ^2 of 1.96 was reached. The probability calculated from the χ^2 was higher than 0.99, which suggested a good fit. Figure 3 shows the least-squares peak fit of XANES spectrum for the mixture of DL-methionine, sodium thiosulfate, sodium sulfate, and graphite (code: M-1). The spectrum is fitted using four Gaussian curves and two arctangent step functions. According to the absorption energy, the peaks can be assigned to: 2472.6 eV for sulfide or thiol, 2480.1 eV for sodium thiosulfate, and 2481.7 eV for sodium sulfate. There is a small peak at 2471.2 eV that does not match the first inflection energy of any model compounds. By checking the spectra of model compounds, it is found that it could be the pre-edge peak of sodium thiosulfate (Figure 1a). In the least-squares method, only the primary peak of the standard spectrum is considered. Therefore, the influence of secondary peaks in standard spectra is neglected, although these small peaks may significantly affect the degree of fitting.

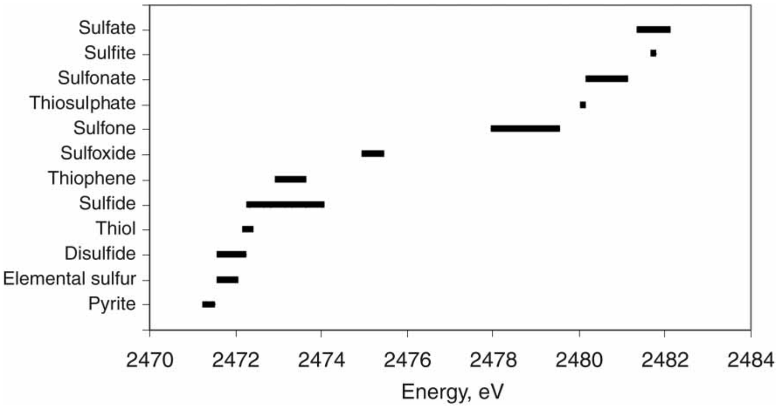


Figure 2. Energy range of specific sulfur compounds.

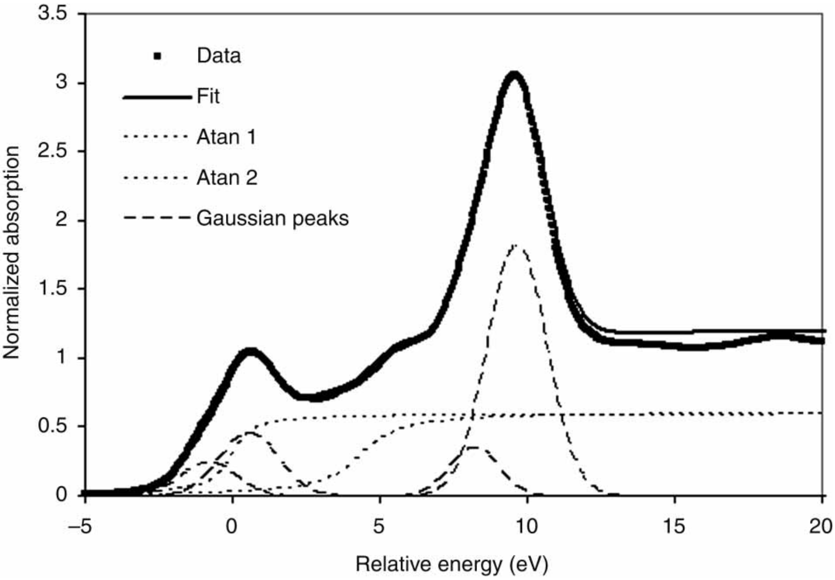


Figure 3. Least-squares peak fitting of sulfur K-edge XANES TEY spectrum of sulfur model compound M-1.

Linear combination fitting is another method to analyze XANES spectra, which uses the entire spectrum of each standard sulfur compound to fit the sample spectrum using the linear combination principle. This method is ideal for quantifying the amount of known components in a sample. Therefore, when using this method, prior knowledge about the types of compounds is required in order to choose appropriate standard sulfur compounds. Based on peak positions in the least-squares peak fitted spectrum, several sulfur standards, including several organic sulfide, thiol, sodium thiosulfate, and sodium sulfate, were chosen to perform a linear combination fit of the spectrum. Figure 4 shows the linear combination fitting curve of M-1 with these components.

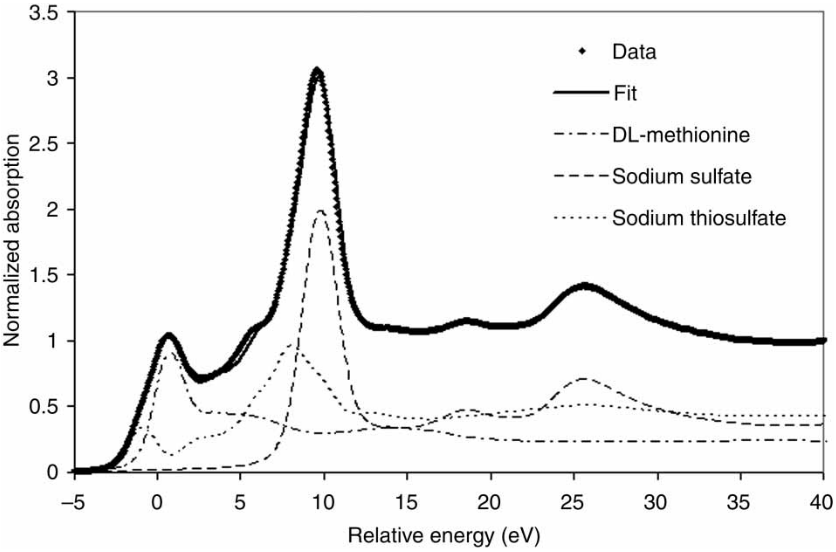


Figure 4. Linear combination fit of sulfur K-edge XANES TEY spectrum of sulfur model compound M-1.

Table 1. Composition of the mixture of sulfur model compounds, M-1.

		S wt% in specific form			
Component	Amount (g)	S form	Actual (by calculation)	By measurement	Relative difference (%)
DL-Methionine	0.1	Sulfide	25.4	25.5	0.4
Sodium thiosulfate	0.1	Thiosulfate	47.9	44.9	6.3
Sodium sulfate	0.1	Sulfate	26.6	29.4	10.5
Graphite	0.1				
Average difference					5.7

The fitting result is given in Table 1, indicating a good agreement between the actual and measured compositions of the mixture (~10%).

Comparing the least-squares peak fit and linear combination fit, it seems that the linear combination fit is not as good as the other one, which may be caused by the fact that the small features of each standard spectrum can significantly affect linear combination fitting and make it more complicated. Moreover, the Gaussian and step functions in least-squares peak fitting are independent of each other, thus the heights, widths, and positions can all be adjusted. In the linear combination fitting, everything changes together. For example, the ratio of the peak height and the step height does not change. This results in more spectra being needed to obtain the same number of degrees of freedom as in the least-squares peak fit. However, since linear combination fitting incorporates the small features of each spectrum, it is more accurate when there is preliminary knowledge of the sample.

2.3. *Fluid coke samples*

Figure 5 shows the spectra of two fluid cokes: Syncrude fluid coke (FC-S), provided by Syncrude Canada Ltd, and Imperial Oil fluid coke (FC-I), provided by Imperial Oil Ltd. Two major peaks

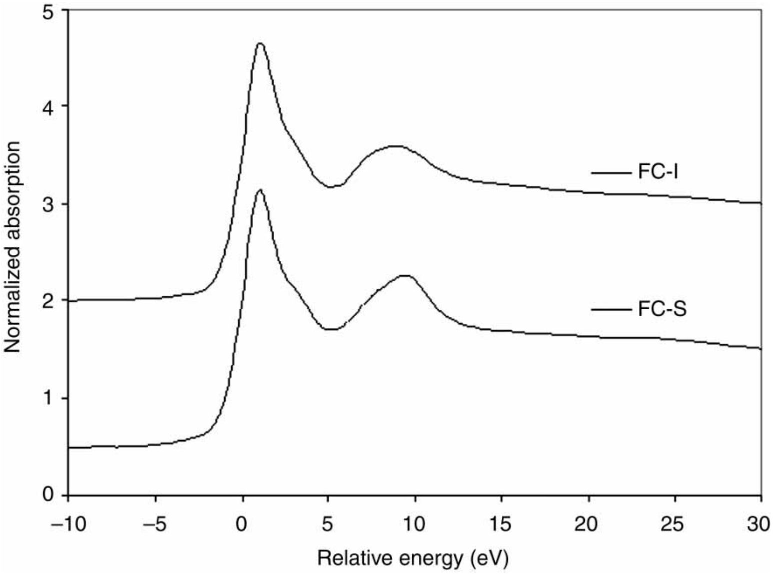


Figure 5. Sulfur K-edge XANES TEY spectra of FC-S and FC-I.

were found in these spectra: one for reduced sulfur and the other one for oxidized sulfur. From the second peaks in these coke spectra, it can be seen that FC-S has a slightly higher oxidized state than FC-I. The small shoulder on the first peak indicates that there may be another reduced sulfur form in these cokes. The spectra were analyzed using both least-squares peak fitting and linear combination fitting. Three types of sulfur were identified in these raw cokes: thiophene, sulfide, and sulfate. Their quantities are summarized in Table 2. The total sulfur contents were determined using an elemental analyzer (Vario EL III).

Similarities were expected since both samples are fluid coke, which is a bitumen upgrading by-product made by fluid cokers. The difference in total sulfur content is also justifiable. Sample FC-I was produced from a fluid coker that treats a blend feed with lower sulfur content, while sample FC-S was produced from a coker which feed was from a single source and had higher sulfur content. It should be pointed out that sample FC-S was collected 2 years earlier than FC-I, which may explain its relatively high sulfate content.

Table 2. Composition of sulfur compounds in FC-S and FC-I.

		Sulfur content in specific form (% in total S)		
Raw coke	Total S (wt%)	Thiophene	Sulfide	Sulfate
FC-S	7.37	53	38	9
FC-I	5.61	52	43	5

2.4. *Sulfur-impregnated activated carbons*

Sulfur forms in fluid coke activation products, *i.e.* SIACs, were also characterized using XANES analysis. It was found that sulfur forms changed after activation, and the changes were strongly dependent on the activation conditions. After activation, the sulfur composition became more complex. As an example, Figure 6 shows the spectra of raw coke FC-S and its activation product, SIAC-S. SIAC-S was produced from FC-S with KOH and SO_2 activation. The total sulfur content of SIAC-S is 5.14%, which was determined using a sulfur analyzer. There are two major peaks present in the spectrum of SIAC-S. The first one represents a low oxidization state sulfur compound, and the second peak with a small feature is an oxidized sulfur peak. After activation,

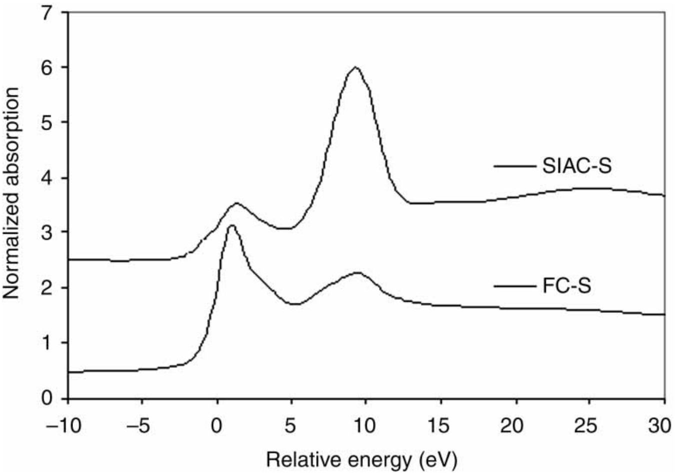


Figure 6. Sulfur K-edge XANES TEY spectra of FC-S and SIAC-S (produced from FC-S with KOH and SO_2).

the first peak of FC-S diminished in size, while the second peak grew much larger. Apparently, the activation process has resulted in a conversion of the sulfur in low oxidation states to that in high oxidation states, *i.e.* the oxidation of sulfur. Fitting the spectrum of SIAC-S suggests that four sulfur compounds exist in the sample: disulfide (7% of total S), sulfide (30%), sulfonate (6%), and sulfate (57%).

Another example shown in Figure 7 is the change of sulfur forms in a SIAC sample (SIAC-I) produced from FC-I. SIAC-I was produced with KOH activation and followed sequentially by SO_2 treatment, which was a different process from SIAC-S production. Fitting the spectrum of SIAC-I using model compound spectra suggests that three sulfur compounds exist in the sample: disulfide (58% of total sulfur), sulfonate (29%), and sulfate (13%).

In fluid coke activation, sulfur transformation may play an important role. Therefore, the changes in sulfur forms were studied by activating FC-S under different activation conditions, and sulfur forms in activated FC-S were characterized using XANES. Figure 8 shows the sulfur K-edge XANES spectra of SIACs produced using KOH and SO_2 activation with different temperatures

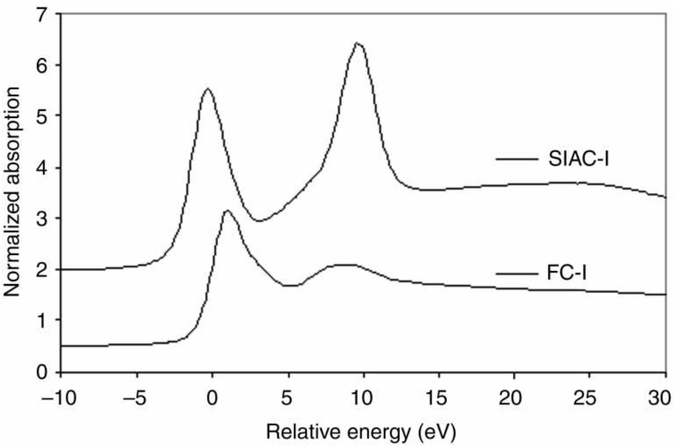


Figure 7. Sulfur K-edge XANES TEY spectra of FC-I and SIAC-I (produced from FC-I with KOH activation and SO_2 treatment).

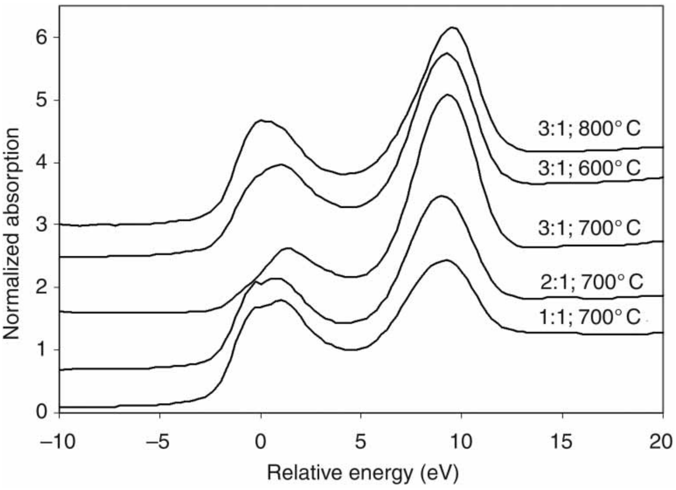


Figure 8. Spectra of SIACs produced from KOH–SO_2 activation at different activation conditions.

and KOH/coke ratios. Since these SIACs were produced with the same process but various conditions, there is not much difference in sulfur oxidation states, yet the amount of each sulfur form changes. Therefore, using the SixPACK software package, the XANES spectra were analyzed by applying the principal component analysis (PCA) which can reduce the multidimensional data sets to lower dimensions for analysis. It was found that five specific components could provide the set of spectra with the cumulative percentage of total variance over 99.5%. Therefore, a maximum of five components were used for each spectrum in XANES analysis. By applying the linear combination technique, the relative ratio of different sulfur species can be obtained from the spectra. With the total sulfur content measured using a sulfur analyzer, the sulfur content in each specific form can be obtained. For samples shown in Figure 8, elemental sulfur, sulfide, disulfide, sulfonate, and sulfate were found. Studies of sulfur transformation are not within the scope of this paper, but will be reported in future work.

2.5. *Comparison of XANES and XPS results*

XPS has been widely used to reveal the chemical states of sulfur on the carbon surface (*4*–*6*). Although using this method is convenient to characterize the sulfur oxidation states on sample surfaces, it is difficult to distinguish certain sulfur forms with similar oxidation state, such as thiophene and elemental sulfur (*18*). In this study, XPS was used to verify the XANES findings. High resolution XPS spectra of the S 2p region were recorded, and they were analyzed by peak fitting using Gaussian functions. Figures 9 and 10 show the XPS S 2p spectra of samples FC-S and FC-I. The sharp peak at 163.7 eV can be assigned to sulfide, disulfide, thiol, or thiophene with a binding energy (BE) of S 2p3/2 in the range of 163.6–163.8 eV, while the second one matches sulfoxide with a BE around 166.0 eV. The small peak of oxidized sulfur species with a BE around 168.8 eV could be sulfate (*18*, *19*). As shown in Table 3, XPS analysis suggests that in FC-S 91% of sulfur was in the form of sulfide, disulfide, thiol, or thiophene. The XANES result

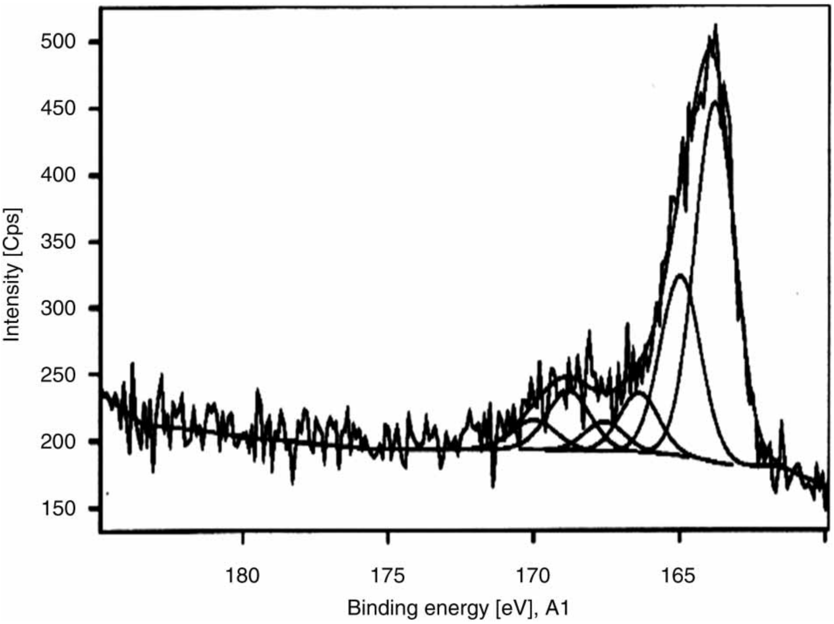


Figure 9. The XPS spectrum of S 2p region for FC-S.

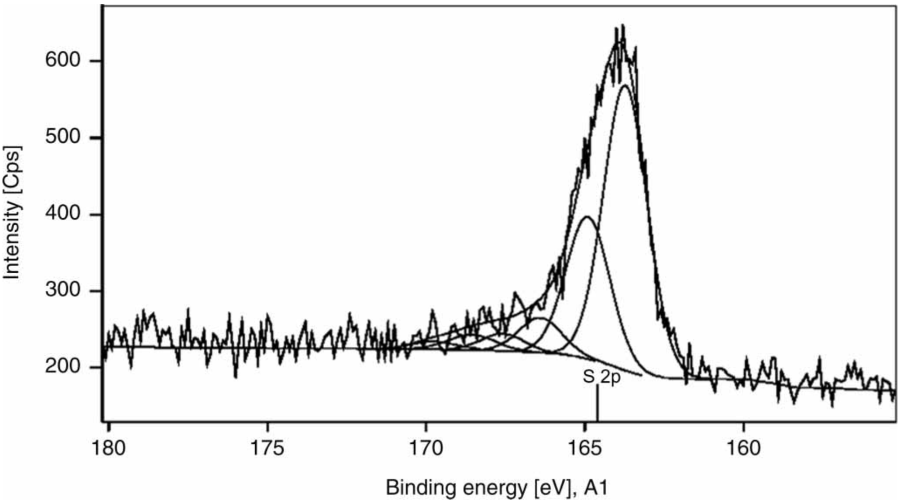


Figure 10. The XPS spectrum of S 2p region for FC-I.

Table 3. Results of XPS analysis of samples FC-S and FC-I.

	Sulfur content in specific form (% in total S)		
Raw coke	Sulfide/thiophene	Sulfoxide	Sulfate
FC-S	91	4	5
FC-I	85	10	5

(Table 2) indicates that 91% of sulfur in FC-S was in the form of sulfide and thiophene. On the other hand, the sum of sulfoxide and sulfate obtained from XPS analysis ($4\% + 5\% = 9\%$) is the same as the sulfate amount obtained from XANES analysis, which indicates that the XANES analysis may not be able to distinguish sulfur in sulfate and sulfoxide forms in this case. For FC-I, the agreement between XPS and XANES is reasonable but not as good as FC-S. However, it is encouraging to see that XANES and XPS results are consistent and complementary to each other.

3. Conclusion

The K-edge XANES TEY technique was examined for use as a tool to characterize the sulfur forms in fluid coke and its activation products. Least-squares peak fitting and linear combination fitting were combined to analyze the spectra. A mixture of pure sulfur compounds and graphite was used to simulate the coke samples, and the results showed good agreement between the actual and measured contents of sulfur forms in the mixture. XANES results are consistent with XPS results. The two techniques are complementary to each other; XANES is capable of distinguishing sulfur species at low oxidation states while XPS is able to separate some sulfur oxides at higher oxidation state.

XANES was used to characterize sulfur in two fluid coke samples and their activation products. It was found that about 90% of sulfur in two coke samples is of organic nature, with over 50% of sulfur is in the form of thiophene while the rest is organic sulfide. About 10% of sulfur is in the form of oxides, *i.e.* sulfate.

The activation process with KOH and SO_2 affected the chemistry of sulfur in fluid coke. XANES surface analysis identified disulfide, sulfide, sulfonate, and sulfate in the activated products and found no thiophene, suggesting a complete removal of thiophene from the surface carbon matrix by KOH. Detailed studies of sulfur transformation during KOH and SO_2 activation will be reported in the future.

4. Experimental

4.1. *Materials, model sulfur compounds and SIAC sample preparation*

Two types of fluid coke were used: FC-S and FC-I. Fluid coke activation products (*i.e.* SIACs) were produced using two processes: (i) KOH and SO_2 sequential activation (*e.g.* SIAC-I) and (ii) KOH and SO_2 simultaneous activation (*e.g.* SIAC-S). Table 4 shows the activation conditions of these samples. In the first process, the fluid coke was mixed with KOH and activated at certain temperature for 1 h. After that, SO_2 was used to add sulfur to the KOH-activated fluid coke. In the second process, fluid coke was mixed with KOH and activated with SO_2 flowing through the reactor. A more detailed production process has been described elsewhere (*20*).

In total, 25 model sulfur compounds were used. Some of them were provided by the Canadian Synchrotron Radiation Facility (CSRF), while others were purchased from Sigma. The structures of these compounds are shown in Appendix 1. All the sulfur compounds were in the highest purity available and used without further treatment.

A model sulfur compound mixture was prepared to simulate the sulfur forms in fluid coke and SIACs. The mixture was prepared by mixing certain amounts of pure sulfur compounds and graphite in deionized water. After the compounds were mixed well, the solution was dried at room temperature in nitrogen, after which, it was ground to fine particles with particle size less than 200 mesh.

Table 4. Activation processes and conditions of SIAC samples.

SIAC	Raw coke	Temperature (°C)	KOH/Coke	Time (h)	Total S (%)
SIAC-S	FC-S	700	3:1	1	5.14
SIAC-I	FC-I	700	3:1	$1 + 1^a$	11.14

Note: [a] Sample prepared by KOH activation (1 h) followed by SO_2 treatment (1 h).

4.2. *XANES data acquisition and analysis*

XANES analyses were conducted at the CSRF situated on the 1 GeV electron storage ring, at Aladdin, University of Wisconsin. X-ray absorption spectra of TEY at the sulfur K-edge were recorded. The TEY mode probes ~50 nm, which is surface sensitive (*17*). The K-edge data were recorded using the double-crystal monochromator beamline with a photon resolution of ~0.7 eV. The resolution is relatively low compared with that in some newly built facilities. The low resolution may result in the loss of small features of the spectra. However, small features generally represent species with small amounts. In this study, only major sulfur forms were studied due to the extremely complex system. Therefore, the current beamline is satisfactory for this study. The TEY spectra at the S K-edge were recorded directly by monitoring the current from the sample. At least two individual scans were recorded for each sample and digitally combined.

All spectra were analyzed using the software, Athena, following the suggested procedure (*21*) with some conditions and constraints in order to obtain meaningful fits. First, for all spectra, the energy scale at the K-edge was calibrated by setting the strong absorption peak of elemental sulfur at 2472.0 eV. Second, the background was subtracted from all spectra using a linear fit of pre- and post- XANES contributions. The spectra were then normalized with respect to the individual step heights. Each spectrum was then fitted with a number of Gaussian peaks and arctangent steps. The Gaussian peaks represent the s → p electronic transitions and arctangent step functions represent the transition of ejected photoelectrons to the continuum. In practice, it was found that two arctangent steps were needed to obtain an adequate fit for all the spectra. The lower energy step represents the transition to the continuum for the sulfur bonded to carbon and the other step may represent the corresponding transition for sulfur bonded to oxygen (*22*). The least-squares peak fitting is fairly straightforward in providing the information of peak composition in XANES spectra, yet it is necessary to use a number of conditions and constraints to obtain meaningful fits. The justifications and assumptions of least-squares peak fitting process were given elsewhere (*23*).

Based on the position of the peaks fitted in the sample, a number of appropriate model compounds were chosen to perform linear combination fitting. The linear combination was applied to construct synthetic spectra using the model compound spectra, which were then compared with that of the sample. The software calculated all combinations of these possible candidate spectra, and the fitting with lowest R-factor was considered.

For SIAC samples produced from the same procedure under different conditions, PCA was conducted prior to linear combination fitting using software SixPACK, developed by Sam Webb at the Stanford Synchrotron Radiation Laboratory.

Acknowledgements

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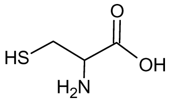
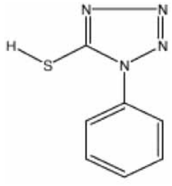
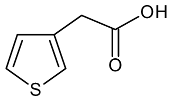
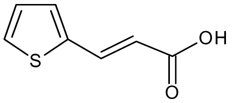
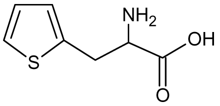
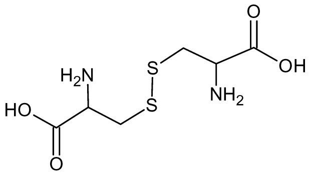
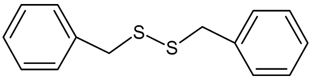
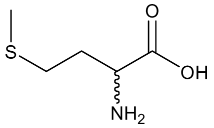
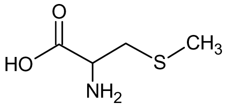
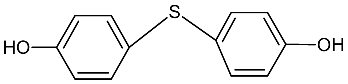
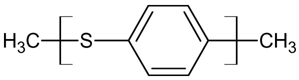
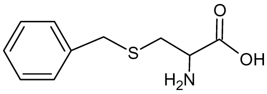
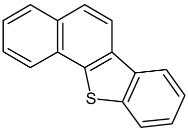
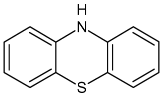
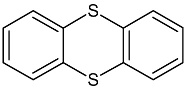
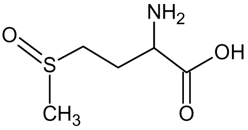
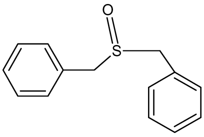
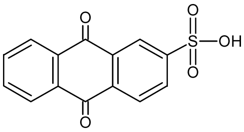
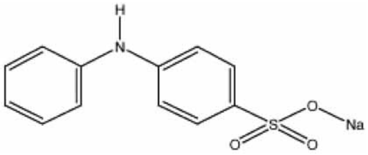
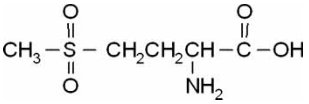
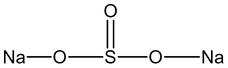
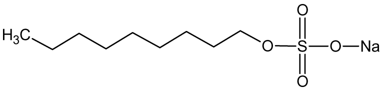
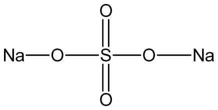
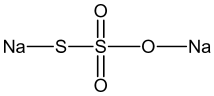
Appendix 1. Structures of sulfur model compounds which were used in this study

Name	Formula	Structure
Elemental sulfur	S	S_2 or S_8
DL-Cysteine	$C_3H_7NO_2S$	
1-Phenyl-1H-tetrazole-5-thiol	$C_7H_6N_4S$	
Thiophene-3-acetic acid	$C_6H_6O_2S$	
3-(2-Thienyl) acrylic acid	$C_7H_6O_2S$	
3-(2-Thienyl)-DL-alanine	$C_7H_9NO_2S$	
L-Cystine	$C_6H_{12}N_2O_4S_2$	
Benzyl disulfide	$C_{14}H_{14}S_2$	
DL-Methionine	$C_5H_{11}NO_2S$	
S-methyl-L-cysteine	$C_4H_9NO_2S$	
4,4′-Thiodiphenol	$C_{12}H_{10}O_2S$	
Poly (phenylene sulfide)	Poly (C_6H_4S)	

(*Continued*)

Appendix 1. Continued.

Name	Formula	Structure
S-benzyl-L-cysteine	$C_{10}H_{13}NO_2S$	
1,2-Benzodiphenylene sulfide	$C_{16}H_{10}S$	
Phenothiazine	$C_{12}H_9NS$	
Thianthrene	$C_{12}H_8S_2$	
DL-Methionine sulfoxide	$C_5H_{11}NO_3S$	
Benzyl sulfoxide	$C_{14}H_{14}OS$	
Anthraquinon-2- sulfonic acid	$C_{14}H_8O_5S$	
Diphenylamine-4-sulfonic acid, sodium salt	$NaC_{12}H_{10}NO_3S$	
DL-Methionine sulfone	$C_5H_{11}NO_4S$	 $CH_3-S(=O)_2-CH_2CH_2CH(NH_2)-C(=O)-OH$
Sodium sulfite	Na_2SO_3	 $Na-O-S(=O)-O-Na$
Sodium n-dodecyl sulfate	$C_{12}H_{25}NaO_4S$	
Sodium sulfate	Na_2SO_4	 $Na-O-S(=O)_2-O-Na$
Sodium thiosulfate	$Na_2S_2O_3$	 $Na-S-S(=O)_2-O-Na$

Appendix 2. K-edge first inflection energies of sulfur model compounds

Compound	First inflection energy (eV)
Elemental sulfur	2471.7
L-Cysteine	2471.7
Benzyl disulfide	2472.0
1-Phenyl-1H-tetrazole-5-thiol	2472.2
S-Benzyl-L-cysteine	2472.3
DL-Cysteine	2472.3
DL-Methionine	2472.7
S-Methyl-L-cysteine	2472.8
Thiophene-3-acetic acid	2473.0
Benzonaphthothiophene	2473.0
3-(2-Thienyl)-DL-alanine	2473.0
Thianthrene	2473.2
3-(2-Thienyl)acrylic acid	2473.2
Phenothiazine	2473.4
Poly (phenylene sulfide)	2473.7
4,4′-Thiodiphenol	2474.0
Benzyl sulfoxide	2475.0
DL-Methionine sulfoxide	2475.4
Sodium sulfite	2477.6
DL-Methionine sulfone	2479.0
Sodium thiosulfate	2480.1
Diphenylamine-4-sulfonic acid	2480.2
Anthraquinon-2-sulfonic acid	2480.4
Sodium n-dodecyl sulfate	2481.4
Sodium sulfate	2481.8