ANALYSIS OF SULFUR X-RAY ABSORPTION NEAR-EDGE SPECTROSCOPY IN ASPHALTENES, RESINS, AND MALTENES OF TWO DIFFERENT CRUDE OILS

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Sulfur chemical structures present in crude oil products such as petroleum asphaltenes, resins, and maltenes obtained from two different oils have been determined using X-ray absorption near-edge structure (XANES) spectroscopy. Maltenes are pentane soluble portions, resins are pentane insoluble and heptane soluble portions, and asphaltenes are heptane insoluble portions of crude oil. The sulfur forms in these six fossil fuel samples are predominately organic; of them thiophene, sulfide and sulfoxide are the main contributors. One of the crude oils is known to have a high sulfoxide content; results from this study showed that there is a considerable amount of sulfoxide present in its asphaltene, resin, and maltene fractions. In spite of the fact that asphaltenes are known to be more polar than the other two fractions, and also that sulfoxide is a very polar chemical moiety, this structure is present in considerable amounts also in the resin and the maltene fractions of this particular crude oil. The second oil, lower in oxygen content, showed consistently less amount of sulfoxide in all its asphaltene, resin, and maltene fractions. Furthermore, no evidence for higher oxides such as sulfones, sulfonates, and sulfates are found in the three fractions of either of the crude oils.

INTRODUCTION

Asphaltenes, resins, and maltenes are some of the components of crude oil, and are of considerable interest.[1-3] The usual definition of these fractions are: maltenes are pentane soluble portions, resins are pentane insoluble and heptane soluble portions, and asphaltenes are heptane insoluble portions of crude oil. Asphaltenes are the heaviest, the next are resins, and the lightest parts of a crude oil are the maltenes. These fractions contain undesired heteroatoms; these heteroatoms are an issue in atmospheric pollution in the utilization of the resources. The study of heteroatoms, such as sulfur, in these components obtained from a particular crude oil is therefore of much interest, also in order to better understand the complex processes of crude oil formation.

Non-destructive and direct XANES spectroscopy methods have been very promising in analyzing the heteroatom structures of complex fossil-fuel samples. XANES spectroscopy has been recently employed to probe the chemical nature of sulfur in different fossil-fuel components[3] such as asphaltenes,[4-6] crude oils[7] and coal[8]. In asphaltenes the sulfur is found in mostly thiophenic and sulfidic forms, and the oxidized sulfur component in sulfoxide forms. In coal, sulfur exists in both organic and inorganic forms. Nitrogen XANES studies[9] on asphaltenes have shown that nitrogen occurs mostly in aromatic forms in pyrrolic and pyridinic forms.

In this study we present preliminary results of sulfur XANES spectroscopy on asphaltenes, resins, and maltenes obtained from two different crude oils. Several sulfur model compounds have been studied, and it is found that consistent with earlier results,[7] the s→p electronic transition peak in the XANES spectra vary in energies as the formal oxidation number of sulfur changes. The sulfoxide signature is well separated from the thiophenic signature, by about 3.00 eV. The organic sulfide peak also is separated from thiophenic peak by about 1.00 eV. The asphaltene fraction of one of the crude oils, CAL, is known to have a high sulfoxide content; the resin, and maltene fractions from this oil also consistently show much higher sulfoxide content than the three fractions from the other crude oil. In spite of the fact that asphaltenes are known to be more polar than the other two fractions, and also that sulfoxide is a very polar chemical moiety, this structure is present in considerable amounts also in the resin and the maltene fractions of this particular crude oil. Other forms of oxidized sulfur are not prominent in any of these samples.

EXPERIMENTAL

Our sulfur data have been collected at beamline X-19A at National Synchrotron Light Source at Brookhaven National Laboratory. We used a double crystal monochromator of Si (111) crystals. The model samples were first diluted in boric acid, finely ground, and then smeared on sulfur-free Mylar film; the fossil fuel samples were either ground and mounted on the film, or diluted in CCl_4 and smeared to dry on the film.

All sulfur models were obtained from Aldrich Chemical Company; they were dibenzyl sulfide, dibenzothiophene, thianaphthene, dibenzyl sulfoxide, iron(II) sulfide, potassium sulfate, and sodium thiosulfate. The fossil-fuel samples were asphaltenes, resins, and maltenes, obtained from CAL and KUW crude oils.

RESULTS AND DISCUSSIONS

Figure 1 plots the sulfur XANES of the asphaltene, maltene, and resin fractions obtained from CAL, KUW crude oils. Among the CAL suite, the most prominent region is around 2475.1 eV; the shoulder of this peak at around 2472.1 eV is quite prominent in all these samples. From the KUW suite, the most prominent feature occurs at 2472.1 eV, and the feature at 2475.1 eV is much less prominent. Thus from raw data it is evident that the structure with its s⇒p transition peak at 2475.1 eV is more abundant in the CAL suite than in the KUW suite. This trend is present in all the three fractions belonging to the same oil.
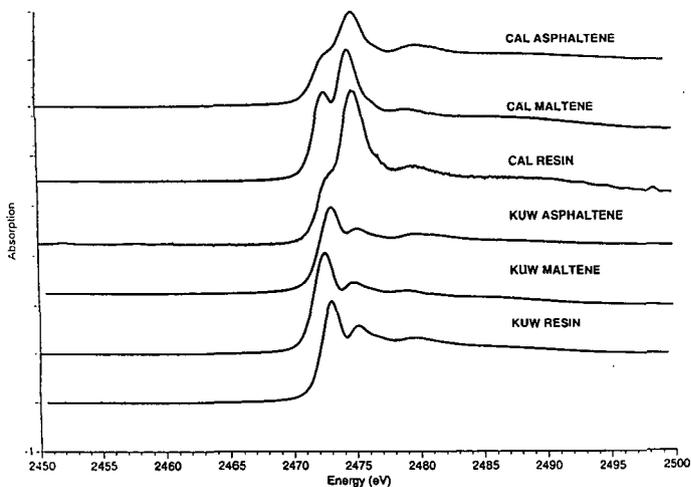

Figure 1: Sulfur XANES spectra of the asphaltene, maltene and resin fractions of CAL and KUW crude oils.

Figure 2 shows the XANES plots of several sulfur model compounds, studied by Waldo et al.[7] As mentioned earlier, the most prominent peak of a structure represents the s⇒p electronic transition peak. This figure shows that the different sulfur structures have s⇒p peaks located at different energies; these peaks shift to higher energies as the formal oxidation number of sulfur in the structure increases. As the formal oxidation number of sulfur in a structure increases, the electronics in the atom are more tightly bound to the nucleus, and it takes a larger energy to make the s⇒p transition. Our calibration procedure has resulted in a shift from these data by a few eV, but both the data sets show the same relative energy differences between the different sulfur structures. Dibenzyl sulfide, which has a formal oxidation number of zero, shows its prominent peak at 2474 eV (2471.1 eV in our case). Thiophene also has a formal oxidation number of zero, but the signature peak is shifted slightly from that of the sulfide, and occurs at 2475 eV (2472 eV in our case). The sulfoxide structure has a formal oxidation number of +2, and shows its signature peak much separated from the other two, at 2478 eV (2475.1 eV in our case).

XANES spectra of a maltene from the two different oils are shown in Figure 3. It is seen that the first peak of the KUW maltene appears at 2472.1 eV, the same energy as the main peak of our dibenzothiophene spectrum, and this feature appears only as a shoulder in the spectrum of CAL asphaltene. This leads one to the obvious conclusion that sulfoxide is present in larger percentage in CAL asphaltene than in the KUW sample.

A least-squares fitting program has been used in order to quantitatively analyze all the sulfur data. All the spectra of models and the fossil-fuels were first normalized with respect to the respective step heights, and then fit to a sum of several Lorentzian peaks and an arctangent step. The peaks specify bound to bound electrnic transitions, whereas the step signifies electronic transition tot he continuum. In order to be consistent, we held the width and the position of the steo function constant

420

till the very end of the fitting procedure. We subtracted from the fossil-fuel spectra any secondary contribution from a structure appearing at the same energy as the s→p transition from a different structure.
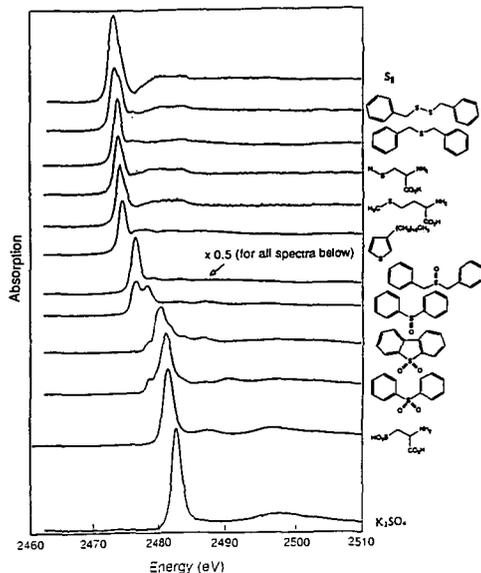

Figure 2: Sulfur XANES spectra of several model compounds[7]. The s→p transition peaks are blue shifted as the formal oxidation number of the structure increases.
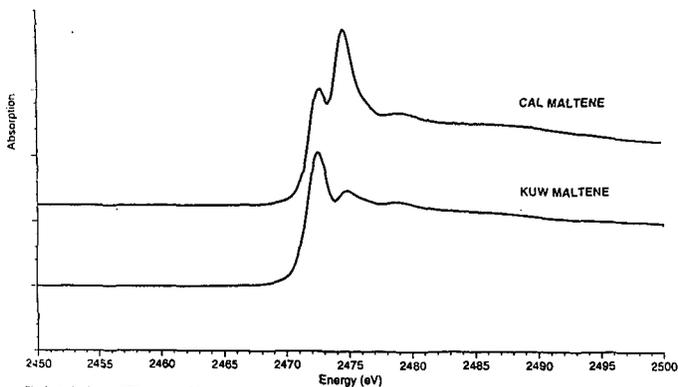

Figure 3: Sulfur XANES spectra of the maltene fractions from CAL and KUW. The differences in the resonance structures are very prominent.

Preliminary results of the sulfidic, thiophenic, and suloxide content of the asphaltenes, resins, and maltenes obtained from CAL and KUW crude oils show that the sulfoxide percentage in the CAL samples are higher not just in its asphaltene fraction, but also in the resin and maltene fractions. Asphaltene is known to be more polar than resin and maltene, and sulfoxide also has a very polar structure. It is interesting to note that in spute of this, all the CAL fractions showed higher sulfoxide percentages. Presence of high oxides, such as sulfone, and sulfate, in any of these samples was insignificant. There was no evidence of any inorganic sulfur structures in these samples.

421

CONCLUSIONS

Sulfur XANES spectroscopy is a very powerful way to ascertain the different chemical structures present in a complex material both qualitatively and quantitatively. Asphaltene, maltene, and resin extracted from CAL, which has a high sulfoxide content, all show consistently high sulfoxide percentages. Higher oxides of sulfur, such as sulfones, and sulfates are not present in significant quantities in any of these samples.

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