Full Length Article

Identification of sulphur, oxygen and nitrogen species in heavy oils by X-ray photoelectron spectroscopy

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HIGHLIGHTS

- XPS "cold" mode for the speciation of chemical environments of heteroelements.
- Database of sulphur, nitrogen and oxygen species contained in oils.
- Follow-up of the sulphur compounds at different steps of the hydrotreatment.

ARTICLE INFO

ABSTRACT

The removal of heteroelements issued from petroleum products is an important problematic in the developments of the refining processes, in particular for the refining of the unconventional oils for which it is necessary to better understand and quantify the chemical environments of those heteroelements. The aim of this work was to evaluate how the speciation of sulphur, nitrogen and oxygen in oils with the X-ray photoelectron spectroscopy in the "cold" mode could be the appropriate technique. The characterization of liquids and solids with low melting point, has been possible thanks to the use of the liquid nitrogen cooling system, for which the temperature can reach −135 °C on the sample holder in the analysis chamber.

The S 2p high resolution spectra recorded for the sulphur organic compounds has allowed establishing a valuable database for sulphur environments where six classes can be distinguished. The methodology developed in this work has been applied to the analysis of a straight run atmospheric residue for which thiol and thiophenic/sulfide environment has been identified. The relative concentration of those two chemical classes has been evaluated. 70% of the whole sulphur is present in thiophenic/sulfide group whereas the rest is thiol chemical class. The analyses performed on hydrotreated effluents highlight larger reactivity of the thiol compounds. But, we are facing a quite high detection limit of the XPS technique estimated at 0.1 at.% not permitting the detection of sulphur in the highly desulphurised effluents. This is still a main limitation for deep hydrotreatment applications but this technique can be used to investigate visbreaking, deasphalting or combustion processes where the heteroelement removing is less severe. Developments on the XPS technique have to be continued in order to reduce its detection limit. The whole quantitative analysis must be considered carefully as hydrogen is not detected by XPS. However, the S/C, N/C and O/C atomic ratio of the reference samples are relatively consistent with combustion techniques.

1. Introduction

The rarefaction of light conventional crude oils implies new challenges for the refining industry. Unconventional oils such as extra-heavy crude, oil shales, oil sands, coal-based liquids and biomass-based liquid, which begin to flood the market, have properties and chemical compositions different from conventional crude oils. The unconventional products contain up to several % of sulphur, nitrogen, and oxygen. The challenge is to refine these unconventional oils into technically and commercially valuable organic products such as fuels. However, regulations related to sulphur content in fuel are becoming more and more stringent, for example the European specification limit on sulphur content of

10 ppm in gasoline and diesel and 0.1% in bunker fuels used in SO_x emission control areas [1,2]. Therefore, the strategies of desulphurisation become important steps in the petroleum refining [3].

An effort has to be made towards the efficiency of hydrotreatment process in order to remove heteroelements and especially the hydrodesulphurisation process. As a previous step to the heteroatom elimination planning, it is necessary to make a speciation of heteroelements in order to obtain precise knowledge on the chemical nature of the structures in which these heteroatoms are included. Indeed, the desulphurisation reactivity in conventional petroleum products depends on the sulphur chemistry specificity [4]. The aliphatic sulphur compounds such as thiols and disulfides are highly reactive and can be removed under very mild conditions. The saturated cyclic sulphur compounds and aromatic systems, in which sulphur is present in six-membered rings, are also highly reactive. However, compounds in which the sulphur atom is incorporated into a five-membered aromatic ring structure are much less reactive and the reactivity decreases as the ring structure becomes increasingly condensed [5]. Thus, the speciation of heteroelements allows to understand the reactions involved and to identify the less reactive species. This knowledge is needed to optimize the selectivity of heterogeneous catalysts and therefore improve hydrotreatment processes.

The routine direct speciation and quantification of organic heteroelement forms in oils has not yet been accomplished. For the time being, speciation is commonly made by gas chromatography [6], but this technique cannot be used for non-volatile fractions such as distillation residues. Progress in heteroelement speciation in heavy fractions has been made using X-ray absorption near edge structure (XANES) spectroscopy for understanding the chemistry of sulphur in coal and heavy hydrocarbons [7–11]. However, this technique needs a synchrotron light and cannot be routinely employed. More recently, high resolution mass spectrometry FT-ICR/MS has been used to characterize heteroelement in oils [12,13], but the relative intensity of species depends highly on the analytical conditions [14–16]. Therefore, the quantification aspect of this technique is debatable and has to be taken with care. Because of the complexity of these speciation methods, usual characterization approach such as combustion techniques are used, but provide access only to total sulphur content. A routine analytical method which allows the discrimination and the quantification of the sulphur, oxygen and nitrogen atoms in different chemical environments and applied for oils with heavy fractions has to be developed.

X-ray photoelectron spectroscopy (XPS) has been applied [3,4,15–17] to the direct speciation and approximate quantification of organically bound forms of heteroatoms such as N, O, and S. In this respect, different carbonaceous materials, such as coals and their chemical or thermal derivates [7–11,17,18] have been investigated. As the binding energy of the core peaks is correlated with the chemical environment of an atom, X-ray photoelectron spectroscopy seems to be well adapted for that purpose, but under controlled conditions. Indeed, the core electron binding energy correlates with the atomic charge parameter estimated by using concepts of electronegativity and ionic character of bond. Among those rare publications [18,19], one can cite those of Siegbahn[209], who reported the binding energy of the S 2p core peak for a vast number of sulphur species. In addition, he indicated that the binding energy of S 2p obtained by XPS technique depends almost perfectly with the net charge carried by the sulphur atom and for all compounds. Descostes et al. [21] reported an XPS coherent binding energy database for iron and sulphur reference compounds. It is therefore possible according to the literature to discern the different families of sulphur compounds with based on XPS binding energies of S 2p core peak. As with sulphur, the chemical environment of oxygen into organic compounds strongly influences the

binding energy of the electrons from the O 1s core level, allowing their identification [22]. Several other studies also refer to energies characteristic of N 1s core peaks link to pyridine and pyrrole compounds.[3,10,16,23] However, not any paper deal with the samples preparation and the analyses conditions of those organic compounds which possess low melting points, although standard XPS analyses are usually carried out on compounds which are in the solid state at room temperature and ambient pressure.

In this work, the first part will be devoted to the speciation of sulphur, oxygen, and nitrogen organic references by XPS under controlled conditions, especially for solid and liquid with low melting points. Thus, a core peaks BE scale for these three elements according to their environments in model compounds will be elaborated. Then, this database will be applied to the direct speciation and quantification of sulphur, oxygen and nitrogen species in petroleum products and vacuum residue resulting from hydrotreatment in order to study the catalysts reactivity toward these species. By this way, an evaluation of the catalytic conversion of the hydrotreatment process could be providing. Throughout this report, we will focus on a comparative study of the quantitative results obtained by XPS analysis and combustion technology. The objective was to develop the XPS "cold" mode for the speciation and relative quantification of chemical environments of sulphur, nitrogen, and oxygen in heavy cuts.

2. Material and methods

2.1. Reference samples

2.1.1. Sulphur compounds

Thiophene (C_4H_4S, 99%), benzothiophene (C_8H_6S, 99%), dibenzothiophene ($C_{12}H_8S$, 99%), 1-octadecanethiol ($C_{18}H_{38}S$), diphenylsulfide ($C_{12}H_{10}S$, 98%), diphenylsulfone ($C_{12}H_{10}O_2S$, 97%), diphenylsulfoxide ($C_{12}H_{10}OS$, 97%), dimethylsulfite ($C_2H_6O_3S$, 99%), dipropylsulfate ($C_6H_{14}O_4S$, 97%), and sulphur (S_8, 99.98%) are all commercial products provided by Sigma Aldrich and were selected as standard samples which might be found in petroleum fraction with sulphur in different oxidation states.

2.1.2. Oxygen compounds

Benzoic acid ($C_7H_6O_2$, 99.5%), biphenol ($C_{12}H_{10}O_2$, 99%), dibenzofurane ($C_{12}H_8O$, 98%), and indanedione ($C_9H_6O_2$, 97%) from Sigma Aldrich were used as oxygen model compounds where oxygen is setting in four kind of chemical environment.

2.1.3. Nitrogen compounds

Acridine ($C_{13}H_9N$, 97%), diphenylamine ($C_{12}H_{11}N$, 99%), and benzanilide ($C_{13}H_{11}NO$, 98%) are all commercial products (Sigma Aldrich) which contain a unique nitrogen atom in different chemical environment.

2.2. Petroleum samples

An Arabian straight run atmospheric residue, i.e. the atmospheric distillation residue of a crude oil, and three of its hydrotreated effluents with different level of heteroelement removal, were used as real samples.

2.3. Elemental analyses

Carbon, Hydrogen, Nitrogen and Sulphur elemental quantification was achieved by a catalytic combustion method inspired from ASTM D5291 method. It consists of burning a sample under an oxygen atmosphere at about 1000 °C. Combustion products are quantified by gas chromatography with thermal conductivity detection