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Identification of vanadyl complexes structure in asphaltene molecules present in petroleum residues by pulsed EPR spectroscopy

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The increasing demand for petroleum products will require the production and the upgrading of heavy and extra-heavy oils. Hence, the petroleum industry is confronted with many issues in production, transportation, and refining. Indeed, petroleum residues are complex mixtures of high molecular weight compounds containing high amounts of impurities such as sulfur, nitrogen and metallic species. These elements need to be removed in hydro-processing units through hydro-desulfuration, hydro-denitrogenation and hydro-demetallation reactions before these oil fractions can be used. The most abundant metals in heavy feedstocks, vanadium and nickel, are mainly concentrated in the asphaltenes fraction, a petroleum fraction which precipitates in presence of paraffinic solvents. Characterization of vanadium and nickel complexes is therefore important to the development of demetallation and conversion strategies used to process heavy crudes. The dependence of vanadyl structures on the geographic origin of feedstocks and their evolution during hydroprocessing in an ebullated-bed pilot unit were studied. The aim of this contribution is to assess the possibilities of the EPR spectroscopy to provide information on the structure of the vanadyl species. Two Venezuelan Straight Run Vacuum Residues (SR VR), and one Russian SR VR, were hydroconverted at 410°C in an ebullated-bed pilot plant. By comparing the spectrum of VOTPP (vanadyl tetraphenyl porphyrin) reference with those of C₇ asphaltenes, it seems that nitrogen ridges are composed of two types of signatures which are attributed to nitrogens chelating the vanadium or are very close: one of them corresponds to nitrogen nuclei that are very close to the signal of the VOTPP nitrogen (noted N₁), but the other one has not been attributed (noted N₂). This work shows that pulsed EPR spectroscopy is a powerful technique that allows to distinguish several types of environments of vanadium species, amongst which are porphyrinic ligands, even in very complex samples such as C₇ asphaltenes from heavy feedstocks. It was shown that the relative proportions of vanadium species vary from one feed to another depending on its geological origin, and that the porphyrinic species in asphaltenes from hydroconverted effluents are more refractory to conversion. It will be very interesting to characterize more hydroconverted effluents to confirm the refractory character of porphyrinic species and to see whether pulsed EPR is able to follow the evolution of the second coordination sphere to better understand the mechanisms of hydrodemetallization.

Biography

Karima Ben Tayeb has completed his PhD from Lille University and Post-doctoral studies from Poitiers University. His field of competence in the application of EPR spectroscopy in the catalysis domain.

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