Sub-nanoscale characterization by XANES of vanadium speciation in oil sands fluid petroleum coke

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Oil sands deposits are increasingly being developed as an alternate petroleum resource. The potential environmental impact of related oil sands byproducts has also drawn extensive attention. Geochemical characterization of oil sands fluid petroleum coke has been performed, especially from the perspective of vanadium comportment, revealing that vanadyl porphyrins are the principal V-bearing species in petroleum coke [1]. X-ray absorption near edge structure (XANES) spectroscopy played a unique role in this characterization because of its distinct element specific, sub-nano scale local structural probing capability.

Vanadyl porphyrin typically has a vanadium centred O-N_4 pyramid type first shell coordination with one single oxygen as apex and four nitrogen constructing a pseudo square base of the pyramid. Theoretical XANES modeling revealed that subtle changes (0.01-0.02Å) to the overall first shell structure is clearly visible by XANES. The identified signature feature can differentiate two types of vanadyl porphyrin. XANES modeling further revealed that the pre-edge feature of V K edge carries structural and chemistry information, including the two types of the first shell local structural distortion for V-O bonding and V-N bonding, respectively, for nitrogen-sulphur replacement at the pyramid base of the first shell, and low limit of the size of the vanadium centred porphyrin nano particle as well. Both FDMNES and FEFF codes were used for modeling in this research.

[1] Nesbitt, Jake A.; Lindsay, Matthew B.J.; Chen, Ning (2017). Geochemical characteristics of oil sands fluid petroleum coke. Applied Geochemistry 76, 148-158.