A Density Functional Theory Study of Fe(II)/Fe(III) Distribution in Single Layer Green Rust

W. SUN[1*], D. J. TOBELR[1] AND M. P. ANDERSSON[2]

[1]Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark([*]wsun@chem.ku.dk)
[2]Department of Chemical and Biochemical Engineering, Technical University of Denmark, Denmark

Green rust (GR) is a mixed-valent Fe(II)/Fe(III)-layered double hydroxide, it has been widely investigated for its reductive capacity towards various (in-)organic compounds (e.g., Cr, NO_3^-, nitroaromatics), particularly in terms of remediation application. The rates and products of these interactions are fairly well understood, but less is known about where on GR sheets, these interactions take place (edges vs. center). For this, we need to know the spatial distribution of Fe(II) and Fe(III) ions within GR sheets.

We constructed a cluster model of a single GR layer and analyzed its electronic properties using density functional theory(DFT). We analyzed the relationship between spin state and total electronic energy. We used an implicit solvent model to take into account the interlayer water between the GR hydroxide sheets. We found that high-spin electronic states are favored thermodynamically for the single layer GR model, which is consistent with Hund's rule for single atoms, and that to maintain the hexagonal shape of the single sheet model, the ratio of Fe(II)/Fe(III) needs to be between 0.2 to 5. Three different size models were constructed and analyzed, the results were consistent for different cluster sizes. The spin states of the outermost iron atoms, i.e. the edge atoms, are higher than the inner ones, which means that the edge Fe atoms are more Fe(III)-like than the inner Fe atoms. This suggest that reductive capacity is unevenly in the GR layer structure and that there is a Fe(II) to Fe(III) transition from the center of GR to the edges. Therefore, our DFT calculations predict that redox reactions which involve Fe(II) oxidation are more likely to occur in the central part of green rust.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675219.