

AEROBIC ELECTROCHEMICAL OXYGENATION OF HYDROCARBONS

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Activation of molecular oxygen is one of the holy grails in catalysis. Without a catalyst, the reaction between O₂ and an organic substrate has a high activation barrier and it proceeds via a free radical mechanism bringing to complete oxidation.^[1] Nature inspires us with fascinating copper and iron metalloenzymes that utilize air at room temperature, paradoxically under reducing conditions. The mechanism of these enzymes has been widely investigated both in vivo or using complexes that mimic their active sites.^[2-9] Surprisingly, reduction via electrolysis of these enzymes or similar biomimetic catalysts has been only sparingly reported and do not lead to alkane oxidation.^[10-13] In our work an iron-tungsten porous capsule was used as catalyst to hydroxylate light alkanes and cleave C=C bonds in alkenes at room temperature. The first step of the catalysis is the reduction of the metal center via electrolysis, followed by O₂ activation and hydrocarbon oxidation. The experimental results as well as relevant mechanistic studies will be reported.

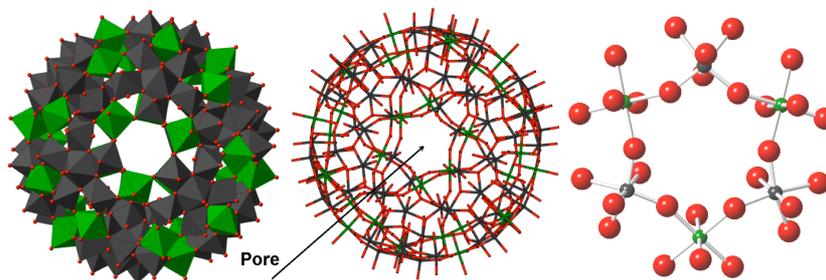


Figure. A polyhedral (left) and stick (middle) presentation of the iron-tungsten capsule, {Fe^{III}₃₀W^{VI}₇₂}. Iron-green, tungsten-black, oxygen-red. Not shown are the 25 disordered sulfate/bisulfate ligands coordinated to W and Fe within the capsule that supply a protic environment and NH₄⁺ cations on the outside of the capsule. The pore into the capsule is pointed to by the arrowed line, which is shown in more detail on the right.

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