POM-BASICS Summer School

"Polyoxometalate Chemistry for Fundamentals and Applications"

La Rochelle-France, June 13-<u>15th 2022</u>

Session 4- POMs in catalysis

Catalysis for the activation of small molecules

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Abstract of the course:

The course will present catalytic processes for the activation and transformation of small molecules, relevant for green chemical processes and sustainable energy schemes. Among these are: activation of dioxygen, water oxidation, proton reduction to hydrogen, carbon dioxide reduction. Biological systems will be first discussed in terms of a mechanistic analysis, case studies involving POM-based systems will be then presented.

Contents:

GENERAL ASPECTS OF OXIDATION CHEMISTRY: Definition of oxidation, substrate, oxidant. O_2 as the oxidant , monooxygenase and dioxygenase .

OXYGEN TRANSFER in HYDROXYLATION AND EPOXIDATION: Cytochrome P450 and its mechanism. The role of cysteinate proximal ligand of Iron. Artificial analogs : ruthenium porphyrins; polyoxometalate complexes.

WATER OXIDATION: The water oxidation process. The natural Oxygen Evolving Centre. Artificial models. The advent of POMs in water oxidation. Dark cycles of water oxidation under homogeneous and heterogeneous conditions. Photoactivated cycles in homogeneous solution and in regenerative devices: photoelectrochemical cells.

PROTON AND CARBON DIOXIDE REDUCTION: Metal hydrides and hydricity. Perspectives in the use of POMs.