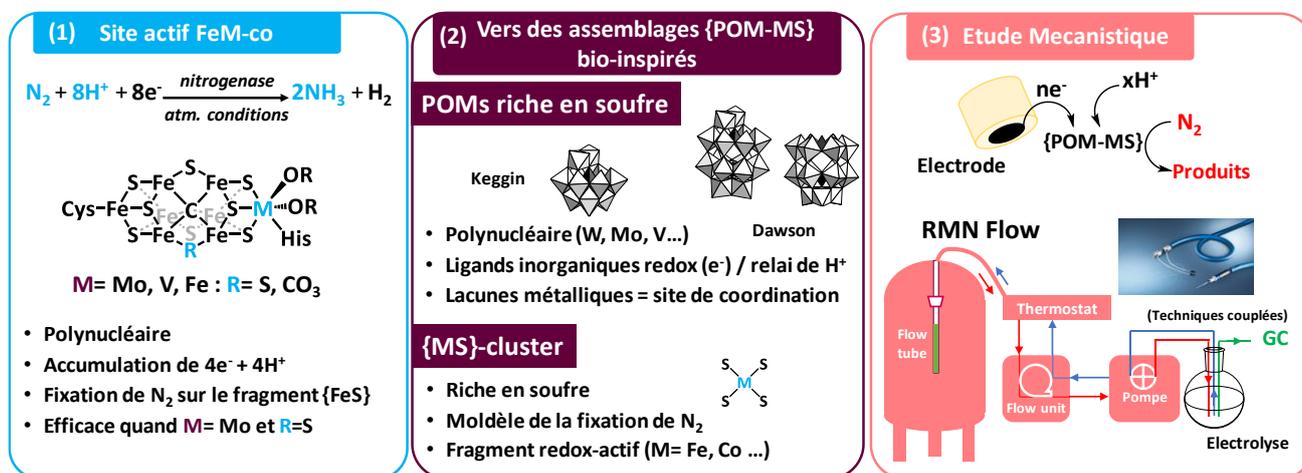


Development of sulfur-rich polyoxometalates (POMs) containing 3d metals for the activation of small molecules for energy transition

Keywords: Inorganic molecular chemistry, electrocatalysis, NMR spectroscopy, electrochemistry

Ammonia NH_3 is the chemical product, prepared using the Haber-Bosch industrial process, with the highest carbon footprint, responsible for 1% of global CO_2 emissions each year. To meet this environmental challenge, more eco-friendly NH_3 production, particularly through the electro-activation of atmospheric nitrogen N_2 , is desirable. In this context, nature is a source of inspiration for chemists. Nitrogenases are the only enzymes capable of reducing N_2 to ammonia at atmospheric pressure and ambient temperature thanks to their recently identified polymetallic "FeM-co" (M= Mo, V or Fe) active sites (Figure 1).¹ Biochemical studies of these enzymes have provided valuable guidance for the design of molecular catalysts², but no polymetallic complex has yet shown satisfactory efficiency.³ We propose to develop a new class of organic-inorganic hybrid compounds that combine metals in a bio-inspired, sulfur-rich environment with POMs.⁴ The latter are soluble polymetallic oxides known for their electron and proton transfer properties. We hypothesize that the molecular assemblies will be able to accumulate enough electrons and protons to activate N_2 (Figure 2). Mechanistic studies will be conducted using an innovative flow NMR device, unique in the Paris region, enabling *in operando* studies, the principle of which is shown in Figure 3. **This thesis project aims to develop synthesis methodologies for the preparation of new polymetallic complexes that combine POMs and 3d metals in a sulfur-rich environment and to study their electrocatalytic properties. The candidate will be responsible for developing procedures for the synthesis and physicochemical characterization of molecular assemblies. In addition, he/she will be heavily involved in studying their electrocatalytic properties using coupled techniques.** As such, he/she will develop strong skills in synthesis as well as in various spectroscopies (NMR, IR, Raman, etc.) and electrochemistry. In particular, he/she will use an innovative approach combining NMR with other complementary analytical techniques, such as gas chromatography.



(1) C. Van Stappen et al. Chem. Rev. **2020**, 120, 5005–5081 ; (2) D.F. Harris et al. Biochemistry **2019**, 58, 3293–3301 ; (3) K.Tanifuji et al. Chem. Rev. **2020**, 120,5194-5251; (4) K. Yonesato et al. Chem. Sci. **2024**,15, 11267-11271

Profile. The candidate must have a strong interest in the subject area and experience in coordination chemistry and/or the activation of small molecules (CO_2 , N_2 , etc.) with skills in spectroscopic characterization and/or electrochemistry.

Salary: approximately €1,800 net per month (possibility of additional pay if teaching duties are included).

Duration: 36 months starting October 1, 2026.

Supervision/contacts if you are candidate : Dr Maxime Laurans (maxime.laurans@uvsq.fr), Dr Nada Savic (nada.savic@uvsq.fr) Dr Mohamed Haouas (mohamed.haouas@uvsq.fr), Pr. Sébastien Floquet (sebastien.floquet@uvsq.fr).