Ultradispersed catalysts for artificial photosynthesis based on transition metal sulphides

Catalyseurs ultradispersés pour la photosynthèse artificielle basés sur les sulfures de métaux de transition

Level : PhD thesis

Profile of the candidate: Master degree, specialized in catalysis and/or physical chemistry

Team(s) : ECI2D team, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS & Université Claude Bernard Lyon 1, University of Lyon, France

Contact(s): Pavel.Afanasiev@ircelyon.univ-lyon1.fr; Laurent.Piccolo@ircelyon.univ-lyon1.fr

Keyword(s): Single atom catalysts; sulphide; electrocatalyst; CO_2 reduction

Scientific context : Solar-to-fuel conversion is one of the most promising approaches to sustainable energy transition. The energy of solar photons might be directly converted to that of chemicals or, alternatively, solar-based electricity could be used to convert CO_2 and water into valuable products. Photo- and electrocatalytic CO_2 reduction reaction (CO2RR) and hydrogen evolution reaction (HER) are considered as candidate reactions for the “artificial photosynthesis” cycle.

A major challenge is to develop novel catalysts, combining high activity, selectivity, stability, and economy of precious metals. In this context, recently emerged “single-atom catalysts” and, more generally, ultradispersed catalysts, containing single atoms or small clusters of atoms of transition metals (TMs), stabilized on a support [2]. The properties of single atoms or few-atom clusters are very different from those of conventional nanoparticles of supported catalysts.

Natural enzymes such as hydrogenases or nitrogenases are 100 % selective and contain single atoms or small groups of atoms of TMs (Fe, Mo, Cu...), coordinated by N, O and S atoms of proteins. Ultradispersed catalysts strive to mimic the high activity and selectivity of enzymes while being more stable and scalable, as they do not contain a fragile organic part. While heterogeneous sulfide catalysts (e.g. lamellar MoS_2) are

well-known HER and carbon oxides hydrogenation catalysts, there are no current examples of sulfide clusters or single TM atoms in sulfur coordination for these reactions. Our project aims at the development of such systems.

Missions : Subnanometric metal species of controlled nuclearity will be incorporated into S-doped carbonaceous supports. The catalysts will be tested in HER and CO2RR as well as thermocatalytic reactions of thiophene HDS and CO2 hydrogenation. The catalytic properties will be studied as a function of the nuclearity and the chemical state of the TM sulfide species.

The supports will be based on S-doped carbon and carbon nitride. Currently there are several literature examples of S-doped carbon materials. We shall follow and optimize the literature preparations aiming at high-surface-area and open-porosity systems with S loadings sufficient to coordinate the TM ions. The electrical conductivity and stability of such supports will be other crucial properties to optimize.

TM single ions (Mo, Cu, Fe...), sulfide clusters and eventually some bimetallic combinations will be anchored on S-doped supports by means of impregnation or grafting in aqueous or non-aqueous media, depending on the precursor solubility. Molecular precursors containing TM species of known nuclearity will be employed. To determine the nature of supported species, XAS, STEM and DRIFTS characterizations will be carried out. The stability of the catalysts and their possible evolution will be studied using XRD, Raman spectroscopy, chemical analyses and temperature-programmed reaction. CO2RR products will be analyzed by NMR. DFT calculations will be performed to simulate DRIFTS spectra as well as XANES spectra of sulfide clusters. To access the state of TM species during the reaction, operando synchrotron hard X-ray absorption and emission spectroscopies (XAS / XES) will be applied.

Our group has a large experience on the use of synchrotron radiation for materials analysis, and we have developed several cells to implement such experimental techniques for operando characterization of catalysts, on several synchrotrons worldwide. Moreover, we have a long-standing experience and considerable track record in the field of TM sulfide-based heterogeneous catalysts. In addition, we currently lead a national funded project (ANR UltraCat) focused on ultradispersed metal-based catalysts for thermocatalytic CO2 hydrogenation.

References:

[1] Z. Yin, G. Tayhas, R. Palmore, S. Sun Trends in Chemistry 1 (2019) 739-750.

[2] B. C. Gates Trends in Chemistry 1, (2019) 99-110.

[3] U. Gupta, C. N. R. Rao Nano Energy 41 (2017) 49-65.

Application: Please send CV, motivation letter, copy of M1 and M2 grades, one or two recommendation letters including contact information **until May 20th, 2020.**