Photo-catalysis on metal nanoclusters: mechanisms and in-situ reactivity

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**Scientific Context:**

The last decade has seen the explosion of coinage metals as catalysts[1]. The key challenge for robust catalyst design and optimization is to reach beyond the well identified limitations: “there is usually more speculation than true knowledge about the mechanisms of catalytic processes” and “the identity of the catalytically active species is frequently not known”[2]. This is particularly true for the development of inexpensive and efficient catalysts composed of earth-abundant transition metals. This project aims at contributing to the pressing need for fundamental research into these latter reactive species.

Recently, molybdenum (Mo) clusters were reported in the context of photo-catalysis. Based on prior results, octahedral Mo6 clusters will be taken as principal model photo-catalytic systems: we will focus on face-capped \([\text{Mo}6\text{X}_1\text{X}_8\text{X}_6]^2- (\text{X} = \text{Cl, Br or I})\) and edge-bridged \([\text{M}_6\text{X}_1\text{X}_6\text{X}_6]^2- (\text{M} = \text{Nb, Ta}; \text{X} = \text{Cl, Br or I})\) clusters prepared by our partners from ISCR in Rennes.

Two prototypical photo-catalytic reactions will be studied: (1) the photo-reduction of CO2 into methanol[3], and (2) the photo-production of H2 from water[4]. Reaction schemes have been proposed but none confirmed. Can we detect reaction intermediates? Can we characterize the catalytic cycle?

Ion trap approaches are particularly relevant to study homogeneous catalysis systems since they are “molecular” systems that can thus be isolated by mass spectrometry. Additionally, most of the proposed catalytic cycles involve intrinsically charged reaction intermediates, which ionic state - and associated reactivity - will thus not differ between gas phase and solution.

**Missions:**

After an initial stage dedicated to the implementation of an ion-molecule reaction setup, we will focus on performing ion-molecule reactions under irradiation: the metal clusters will be transferred to the gas-phase and mass selected/isolated. Then cluster ions will be irradiated with a laser at selected wavelength and put in contact with neutral molecules (CO2, H2O ...). Reaction products will appear on the mass spectrum and may be in turn mass selected for further reactivity study. This project aims at understanding step-by-step a photo-catalytic cycle by observing the successive reactive intermediates using cutting-edge experimental tools, namely multi-stage mass spectrometry using a modified LTQ ion trap coupled to multiple light sources[5].

**Outlooks:**

**IN BRIEF:** investigate experimentally the reaction mechanisms of photo-catalytic processes (CO2 reduction, H2 generation from water) involving transition metal clusters as photo-catalytic centers. Implement the ion-molecule reaction setup on a LTQ ion trap mass spectrometer (the laser coupling exists already). Monitor the reactivity of mass selected cluster ions after irradiation and identify reactive intermediates.

It will be possible to extend the training towards a PhD: ANR proposal was submitted, otherwise specific funding (MENRT) will have to be applied for.

**Bibliography:**

2 Frenking, G. Topics in Organometallic Chemistry (12), Theoretical Aspects of Transition Metal Catalysis, Springer 2005  