

## 1. PhD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

### Project title:

Mechanistic studies on the interaction of nano-oxide particles at the interface of multiphase chemical processes

### 1.1. Project goals

-To investigate the modification of nano-oxide particles (in the solid state) via the interaction with strong nucleophiles (in solution) to produce modified nano-oxide particles at the interface of multiphase chemical processes.

-To investigate the role of homogeneous-heterogeneous interactions that can contribute to the efficiency of such reactions through a systematic variation of reaction conditions in terms of temperature, pH, ultrasound and solvent effects.

-To contribute to the mechanistic clarification of multiphase reactions and their ability to affect the redox potential of nano-oxide particles in applications dealing with redox cell biology.

-To study solvent exchange reactions on the surface of nano-oxide particles using  $^{17}\text{O}$ -NMR techniques at ambient and high pressure conditions

### 1.2. Outline

The mechanistic understanding of chemical reactions at the solid-liquid interface of chemical processes involving nano-oxide particles, has received little experimental attention and is mostly described by computational techniques.<sup>1</sup> Such knowledge is crucial to understand the advantages and disadvantages of the modification of nano-oxide particles. As far as we know, such processes have not been investigated in detail for nano-oxide particles before. In a recent study,<sup>2</sup> as proof of principle, we demonstrated that the surface of nano-oxide particles can be systematically modified by ligand substitution reactions at the solid-liquid interface. A reproducible method was developed with which nano-oxide particles can undergo ligand substitution reactions at the solid-liquid interface of a multiphase chemical reaction. The resulting particles were analyzed by a combination of SEM, TEM, DLS and EDX spectroscopy in the solid state, and their optical properties by UV/Vis spectroscopy in aqueous solution.

### 1.3. Work plan

-The activation of small molecules such as  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{NO}$  and  $\text{H}_2\text{O}_2$ , i.e. processes that are of fundamental interest to biology,<sup>3</sup> will be studied with the application of nano-oxide particles of  $\text{Fe(II/III)}$ ,  $\text{Mn(II/III/IV)}$  and  $\text{Cu(I/II/III)}$ .

-Water exchange reaction on the surface of nano-oxide particles will be studied with the help of  $^{17}\text{O}$ -NMR experiments as a function of temperature in the presence of different nucleophiles that can be expected to modify the surface of the nano-oxide particles.

-More fundamental studies on water exchange reactions of nano-oxide particles will be studied as a function of pressure in order to determine activation volumes from which more detailed mechanistic insight can be gained.

-Finally, redox reactions of nano-oxide particles with typical reducing reagents such as ascorbic acid, will be studied with suitable redox partners based on our earlier work in homogeneous solution.<sup>4</sup>

Such systematic studies will enable us to gain more insight into the mechanism of ligand substitution and electron transfer reactions at the solid-liquid interface of chemical processes dealing with nano-oxide particles.

#### **1.4. Literature**

1. J.R. Rustad, W.H. Casey, *Nature Mat.*, 11, 223-225 (2012). W.H. Casey, *Environm. Chem.* 12, 1-19 (2015). W.H. Casey, *Adv. Inorg. Chem.*, 69, 91-114 (2017).

2. D. Langford, M. Djurovic, M. Oszajca, J. Kuncewicz, R. van Eldik, *Angew. Chem. Int. Ed.*, 57, 663-667 (2018).

3. A. Franke, R. van Eldik, *Chem. Eur. J.*, 21, 15201-15210 (2015). M. Oszajca, A. Franke, M. Brindell, G. Stochel, R. van Eldik, *Coord. Chem. Rev.*, 306, 483-509 (2016).

4. O. Impert, A. Katafias, J. Fenska, M. Chrzanowska, S. Koter, C. Dücker-Benfer, R. van Eldik, *Eur. J. Inorg. Chem.*, 5380–5386 (2016). M. Chrzanowska, A. Katafias, O. Impert, A. Kozakiewicz, A. Surdykowski, P. Brzozowska, A. Franke, A. Zahl, R. Puchta, R. van Eldik, *Dalton Trans.*, 46, 10264–10280 (2017).

#### **1.5. Required initial knowledge and skills of the PhD candidate**

- Basic understanding of transition metal coordination chemistry
- Basic understanding of reaction kinetics in solution
- Keen to learn new techniques and instrumentation
- Eager to work hard and contribute to the success of the project
- Keen to be part of a dynamic research team

## **1.6. Expected development of the PhD candidate's knowledge and skills**

The candidate will receive a basic training in the following knowledge and skills:

- Detailed understanding of the complexity of solid-liquid interactions at the interface of solid submicron coordination complexes in solution.
- The application of a variety of spectroscopic techniques such as SEM, DLS and EDX spectroscopy in the solid state, and optical properties by UV/Vis and NIR spectroscopy in solution.
- Clarification of the underlying reaction mechanisms of ligand substitution processes in the solid state at the interface of the solid-liquid system.
- Presentation of the candidate's results at group meetings and at local and international meetings in the form of poster and oral presentations.