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}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.[1] 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,[2] 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 O_2, CO_2, NO and H_2O_2, i.e. processes that are of fundamental interest to biology,[3] will be studied with the application of nano-oxide particles of Fe(II/III), Mn(II/III/IV) and Cu(I/II/III).

-Water exchange reaction on the surface of nano-oxide particles will be studied with the help of ^{17}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.[4]

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
- 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.