TITLE: Understanding the photoactivity of Ru/CeO_2 for ammonia production

Summary: The PhD student will computationally study Ru/CeO_2 for its photocatalytic properties in ammonia production. Ruthenium has been recognised as the leader in the second-generation catalysts for this reaction and CeO_2 has been shown to perform well as a support for photocatalysts. Thus, the student will focus on Ru/CeO_2, which is active for ammonia photosynthesis. First, the student will identify the most stable catalyst structure: the exposed facet, surface termination, Ru/CeO_2 interface etc. using ab initio modelling (DFT). Stability will be checked using AIMD. Subsequently, the effect of excitation under irradiation will be computed using TD-DFT. Once this is established, the entire reaction mechanism (associate, dissociative, distal route) will be theoretically studied at the excited conditions, which has not been done before (only ground state has), although the tools and approaches exist. The results will give a detailed microscopic insight, including the predominant reaction pathway, kinetics, electronic structure and catalyst changes upon irradiation. The kinetics will be simulated using KMC. In parallel, the catalyst will be synthesized at D13 and the experimental work at D09 will be carried out, providing information on the catalyst surface, coverage, reaction rate and selectivity to steer the modelling. Lastly, a microkinetic model will be constructed using the experimental parameters (reactor) and theoretical results (mechanism, energetics). Such a model will allow us to predict the optimum reaction conditions for ammonia production.

Research techniques used: The PhD student will use the state-of-the computational techniques, which are now feasible due to the large computational power available by the new supercomputer facility HPC Vega in Maribor, Slovenia (10 PFLOPS): plane-wave DFT with hybrid functionals (catalyst geometry and electronic structure), AIMD (stability of the catalyst), time-dependent DFT (excited states, photocatalysis, electronic transitions), CI-NEB, dimer (reaction parameters, activation barriers), reactive MD (effect of the surroundings on activation barriers), kinetic Monte Carlo (reaction kinetics, surface evolution during reaction) and microkinetic modelling (macroscopic reactor performance).

The reason why the topic is innovative: The topic is innovative two-fold: the problem being solved is pertinent to the modern society and the methods used have only recently become useful. Ammonia production costs 2 % of the global energy consumption (high T, pressure, H_2 required). Photocatalysis is a novel approach, using solar energy to carry out the reaction at ambient conditions. Such ammonia a chemical storage of hydrogen to which it can be easily converted, being a pillar of the hydrogen economy. From the scientific point of view, photocatalysis has so far theoretically only been described at a rudimentary level (electronic structure, adsorption, spectra) usually omitting excited states. No successful attempts at theoretically describing the excited-state kinetics exist. With the newly developed tools (such as support for TDDFT) and available computational power (HPC Vega, Maribor), this is finally possible.

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