Catalytic Fluorination of Organic Substrates

Modelling Fluorination Reactions in the Simons Process

***B. Paulus, T. Lindic**, Institut für Chemie und Biochemie, Freie Universität Berlin*

In Short

- Surface catalysis
- Fluorination reactions
- Simons process
- Periodic DFT

Fluorinated organic compounds play a big role in our everyday lives, as pharmaceuticals, agrochemicals, battery materials or in another important area.[1] Therefore, the research into the possible ways of fluorination is attracting a lot of attention. One of the main pathways towards fluorinated compounds is electrochemical fluorination (ECF). The most widely used ECF method is the Simons process, which has been around for more than half a century.[2] The process usually consists of a nickel anode which is immersed in the anhydrous HF, which acts as a fluorine source and as a solvent at the same time. Driving force for the reaction is the applied potential, which is usually around 5-6 V in the industrial setup. The cathode material is not as important because it only facilitates hydrogen gas evolution and the fluorination reaction takes place on the anode. Even though the Simons process is widely used on industrial scale, as already said it has been around for a long time, its mechanism is not completely understood. It has been proposed to consist of two main steps: (1) oxidation of Ni anode under external potential and formation of high valent Ni_xF_y films and (2) reaction of these films with an organic substrate yielding the fluorinated products.[3] Formation of Ni_xF_y films on the nickel anode was studied in our group with the support of HLRN in the project bec00154. It was shown that a possible description of Ni_xF_y films formed on the Ni anode are surfaces of NiF_2 and NiF_3.[4][5] In our project we want to model the second proposed step in the Simons process, that is the fluorination reaction of organic substrates itself.

We have identified three different surfaces with Ni(IV) centres and a $[F_2]^-$ moiety (cf. figure 1) on the surface. We believe that this fluorines are readily accessible for the fluorination reactions. Among the NiF_2 surfaces there is one such surface, namely the twice oxidised (001) surface. Among the NiF_3 there are two such surfaces, $(01\bar{1}0)$ and $(11\bar{2}0)$. Structures of all these surfaces were previously calculated in our group.

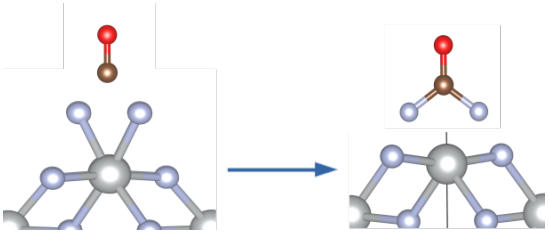

***Figure 1:** Schematic depiction of proposed fluorination of CO on NiF_2 (001) surface.*

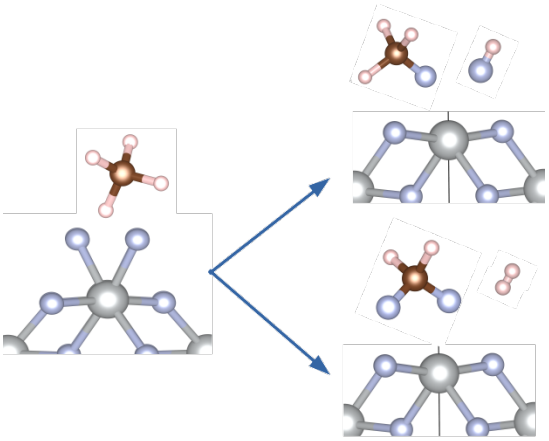

***Figure 2:** Schematic depiction of proposed fluorination of CH_4 on NiF_2 (001) surface.*

To start modelling the fluorination reactions we picked two fairly simple substrates, carbon dioxide and methane. The product of the fluorination of carbon monoxide is COF_2 (cf. figure 1), which is the simplest perfluorinated carbonyl compound. Fluorination of methane can give two different products (assuming that it is reacting only with one $[F_2]^-$ unit on the surface): CH_3F or CH_2F_2 with the formation of HF or H_2 as by-products, respectively (cf. figure 2).

To model the reactions we will use periodic DFT as implemented in Vienna Ab Initio Simulation Package (VASP). [6] As exchange correlation functional we will use PBE, with the Hubbard U correction for localised d electron of Ni and Grimme's D3 dispersion correction to account for long range interactions. For the transition state search we will use climbing image nudged elastic band method (CI-NEB).[7]

Our workplan is mainly divided into two different sections. First we will simulate the adsorption of reactants on Ni(IV) and products on the clean surfaces. After we will find the most stable adsorbed

structures, we will perform CI-NEB transition state search between the starting and final structures. On top of transition state structures and the adsorbed structures we will calculate vibrational frequencies to confirm that the structures are indeed either transition states (with exactly one imaginary frequency) or minima (with no imaginary frequencies). Furthermore we also intend to investigate adsorption of HF molecule on all the surfaces, since in the Simons process which is the motivation behind our research, the reactions occur in an anhydrous HF. This will give us some insight into the role and importance of HF in the fluorination reactions.
With all the above we will be able to give an accurate description of transition states in the fluorination reaction and describe thermodynamics and kinetics of the reaction path. With this we hope to add another piece in the puzzle of underlying chemistry of the reactions in the Simons process.

WWW

https://www.bcp.fu-berlin.de/chemie/index.html

More Information

[1] A.M. Thayer, *Chemical & engineering news*, **84**, 15, (2006).

[2] J. H. Simons, W. J. Harland, *Journal of The Electrochemical Society*, **95**, 55 (1949). doi:10.1149/1.2776733

[3] P. Sartori, N. Ignat'ev, *Journal of fluorine chemistry*, **87**, 157 (1998) doi:10.1016/S0022-1139(97)00139-5

[4] S. Mattsson, G. Senges, S. Riedel, B. Paulus, *Chemistry - A European Journal* (2020). doi:10.1002/chem.202000881

[5] S. Mattsson, B. Paulus, *Physical Chemistry Chemical Physics* **22**, 4407 (2020). doi:10.1039/C9CP06348J

[6] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **54**, 11169 (1996). doi:10.1103/PhysRevB.54.11169

[7] G. Henkelman, B. P. Uberuaga, H. Jonsson, *The Journal of chemical physics* **113**, 9901 (2000). doi:10.1063/1.1329672

Project Partners

AG Riedel, FU Berlin, Institut für Chemie und Biochemie

Funding

SFB 1349 Fluor-Spezifische Wechselwirkungen