Catalytic Fluorination of Organic Substrates

Modelling Fluorination Reactions in the Simons Process

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Figure 1: *Starting structure for the adsorption of CO on NiF_2 (001) surface and the resulting structure after ionic relaxation.*

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 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. Despite its wide usage on an industrial scale 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 these 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.

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

To start modelling the fluorination reactions we picked fairly simple substrates, carbon monoxide, methane and ethene. We have studied their adsorption on the twice oxidised NiF_2 (001) surface. Adsorption of CO resulted in readily formed COF_2 after ionic relaxation, showing no thermodynamic barrier for the reaction (see Figure 1). Adsorption of CH_4 on the twice oxidised (001) surface resulted in different outcomes depending on the position, orientation and proximity to the surface of the methane molecule. We have obtained the physisorbed, chemisorbed, once fluorinated CH_4 and twice fluorinated CH_4 (see Figure 2). Adsorption of ethene resulted in 6 groups of different products formed on the surface.

Because the Simons process is done in the liquid HF, we also so far studied co-adsorption of HF with CO and CH_4, respectively. For both the molecules the resulting structures after ionic relaxation depended on the initial position of the adsorbates on the surface, their orientation and their proximity to the surface. Furthermore we also studied the co-adsorption of two HF molecules.

To determine the transition states between our calculated structural minima (e.g. between each successive step in Figure 2), we have employed the climbing image nudged elastic band (CI-NEB). So far we have been able to locate a few possible transition states, however because of the slow convergence we had to reduce the accuracy of the calculations and, therefore, we were unable to perform the frequency analysis which would confirm the transition states. This part of the project is hence ongoing.

By studying the adsorption on the (001) NiF_2 surface we have developed a workflow of successive steps
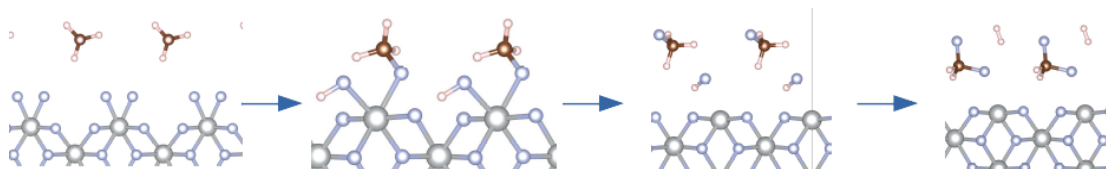
Figure 2: *Resulting structures of ionic relaxation of CH₄ on the twice oxidised NiF₂ surface (from left to right): physisorbed CH₄, dissociatively chemisorbed CH₄, physisorbed singly fluorinated CH₄ and physisorbed twice fluorinated CH₄.*

to study such systems, which we are now using to study the adsorption of CO, CH_4 and ethene on both the surfaces derived from NiF_3, namely $(01\bar{1}0)$ and $(11\bar{2}0)$ surfaces.

Our future work plan is divided into two main sections. First we want to improve on the accuracy of the CI-NEB calculations and find the transition states between different adsorbed structures with reliable accuracy. This will allow us to perform the calculation of vibrational frequencies and hence confirm whether the located structures are the true transition states (i.e. exactly one imaginary frequency).

Secondly, we plan to study the fluorination reactions in the Simons process by *ab-initio* molecular dynamics (AIMD) including electric field. This should further reveal possible reaction pathways, which could be overlooked by the standard static DFT calculations. By inclusion of electric field we hope to be able to simulate HF bond braking and hence determine how the surfaces get re-fluorinated and catalytically active again. We plan to pick the most stable calculated adsorbed structures and progressively add first one and two HF molecules per surface unit cell and then simulate a monolayer and a bilayer of HF. Because our aim is not to do a fully molecular dynamics study, we will restrict the simulation times to 9 ps, with a 1 fs time step. By doing this, we hope to determine different possible pathways of the fluorination reactions. As these calculations are computationally very demanding we will first focus on the twice oxidised NiF_2 (001) surface.

With all the above, we aim to be able to give an accurate description of transition states in the fluorination reaction happening in the Simons process and describe thermodynamics and kinetics of the reaction paths. Thus 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

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Project Partners

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