

Abstract:**Synthesis of bifunctional heterogeneous catalysts based on metal-organic frameworks****Co-supervisor 1: Prof. Dr. Arne Thomas, Functional Materials, TU Berlin****Co-supervisor 2: Dr. Frank Rosowski, BasCat, TU Berlin**

The chemical valorization of carbon dioxide in an economically feasible way is a challenging goal. Carbon dioxide can be hydrogenated to methanol, and methanol is an important intermediate e.g. for synthesis of dimethylether (DME) or olefins. The combination of methanol synthesis and its consecutive reaction to DME or olefins in one reactor is a promising concept. To facilitate this tandem reaction, bifunctional catalysts are needed. The goal of the present project is to explore a new synthetic route and combine two catalytic sites in a metal-organic framework (MOF) with one side located at the metal-organic nodes, while the second site is part of the organic linker molecules. Using such bifunctional MOFs, the conversion of carbon dioxide into the DME or olefins will be attempted.

Extended description version of the project:

Synthesis of bifunctional heterogeneous catalysts based on metal-organic frameworks

Co-supervisor 1: Prof. Dr. Arne Thomas, Functional Materials, TU Berlin

Co-supervisor 2: Dr. Frank Rosowski, BasCat, TU Berlin

1. Overall goal of the project

The focus of the proposed work is the synthesis of new materials based on a rational catalysts design concept. The concept aims at combining two catalytic sites that can be tuned individually within one catalyst, with the option to vary the distance between catalytic sites on a molecular level. This will be realized by using metal-organic frameworks (MOFs). The metal nodes within such a MOF can be used as catalytic site, a second site can be incorporated in the organic linker molecules connecting the metal nodes. The use of MOFs as catalysts requires relatively mild reaction conditions, i.e. rather reducing than oxidizing conditions and temperatures below 300°C. Methanol synthesis based on copper catalysts falls into this regime, as well as the reaction of methanol to dimethylether (DME). The coupling of these two reactions is already studied within UniSysCat, and suitable testing facilities are available at BasCat. Thus, methanol synthesis using synthesis gas rich in carbon dioxide coupled with DME synthesis is a suitable test reaction for our catalyst design concept. A very special MOF is a material named NU-1000, in which the nodes consist of Zr_6O_x clusters. These oxidic clusters can be used to support single metal atoms, which allows tuning of the metal site without changing the host structure of the MOF. Therefore, NU-1000 is a suitable starting point for the proposed study.

2. State of the art

The coupling of two reactions within a single reactor can yield increased reaction rates and improved selectivity. Other advantages are related to economic considerations and energy balances. In literature, several examples can be found regarding the combination of two catalysts into one reactor for the formation of DME via methanol from synthesis gas.^[1] In these examples, a metal (or metal oxide) catalyst is mostly combined with a solid acid zeolite catalyst. However, the catalytic sites in these combinations are separated on a macroscopic, i.e. μm or mm scale, while an example for a tandem catalyst with defined and tunable distances between catalytic sites on an atomic scale is still missing. Such a tandem catalyst could be based on metal organic frameworks (MOFs), with catalytic sites located at the nodes and the linkers, respectively. A suitable starting point for such a task are MOFs, which contain nodes of Zr_6O_x clusters connected via pyrene-based linkers, e.g. NU-1000.^[2] The OH groups located at the Zr_6O_x clusters can be used as anchor site for single metal atoms via Atomic Layer Deposition (ALD),^[3] with the possibility to mimic catalyst systems active for methanol synthesis, e.g. Cu/ZrO_2 . Modification of the organic linker molecules furthermore allows the introduction of additional catalytic sites.^[4] ALD is a well-established technique to deposit thin layers on flat substrates, and is industrially applied e.g. for semiconductors. The technique can also be used to modify the surface of particles, e.g. catalysts or catalyst supports. Within the network of UniSysCat, several ALD reactors were designed and build at BasCat.^[5] These reactors were successfully applied in order to synthesize and modify several catalysts, bulk catalysts as well as supported metal catalysts.^[6,7]

3. Specific aims and how they may be reached:

Within this work, a series of bifunctional MOF-based catalysts will be synthesized, fully characterized and the catalytic performance of selected catalysts will be studied. The aim is to investigate the impact of the distance between catalytic sites on the overall performance of the catalyst.

The starting point will be the synthesis of NU-1000, a MOF that contains oxidic Zr_6O_x clusters as metal nodes (Fig.1), via a solvothermal reactions of $ZrCl_4$, 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H4TBAPy), and benzoic acid in suitable solvents. This will yield single crystals of phase pure NU-1000 and can also be prepared at larger scales.

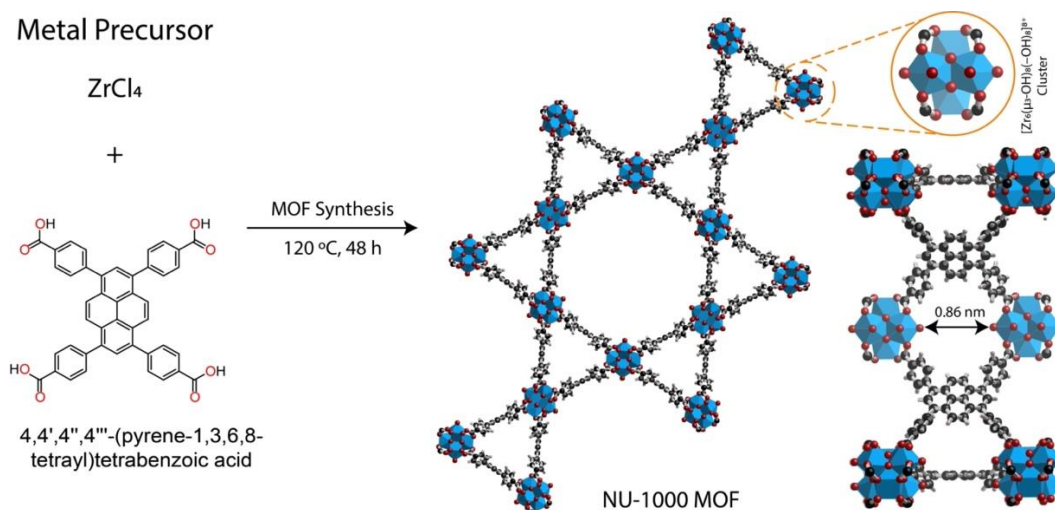


Figure 1: Synthesis and structural features of the metal organic framework NU-1000 showing the nodes consisting of an octahedral Zr_6 cluster capped by eight μ_3 -OH ligands.

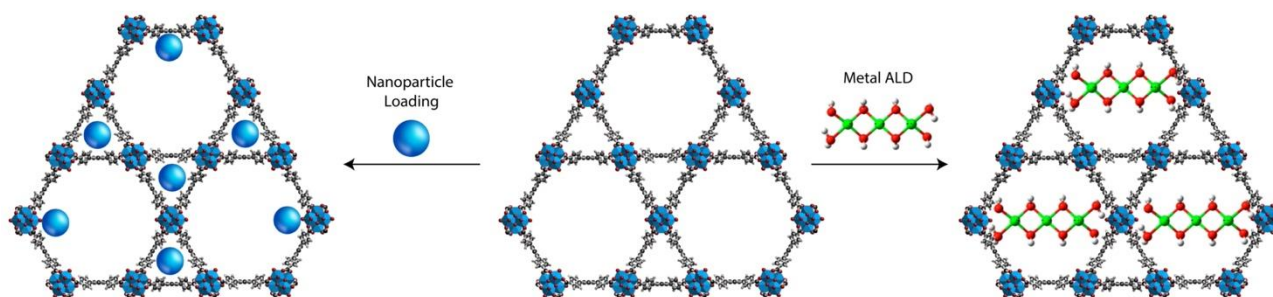
The $Zr_6(\mu_3-OH)_8(OH)_8^{8-}$ nodes can be used as support for single metal atoms, e.g. copper, palladium or platinum, which can be incorporated by ALD (Fig. 2a). Introduction of single metals or small metal nanoparticles can also be achieved using other synthetic methods. The next step will then be to modify the organic linker molecules of the NU-1000 structure to introduce acidic sites suitable for dehydration of methanol to DME (Fig. 2b). Finally, further variation of the linker molecules will allow to vary the distance between the catalytic sites on an atomic scale.

The work plan includes three large work packages: synthesis, characterization, and catalytic studies. Synthesis work includes production of standard NU-1000 following literature reports in quantities of about 10 g per batch. The next step is then the development of procedures to deposit homogeneously metal sites on the Zr_6O_x nodes. The final step will be the modification of the linker molecules, in order to change the acid strength and distances between catalytic sites.

The characterization will involve single crystal and powder XRD, nitrogen physisorption, XPS, FTIR, spectroscopy (including chemisorption experiments), TPD of CO and NH_3 , and electron microscopy. Experiments will be performed at AK Thomas, BasCat and Fritz-Haber-Institut (ChemiT_{EM}).

Finally, catalytic performance will be tested at BasCat in a fourfold parallel testing set-up suitable for methanol synthesis and Fischer Tropsch chemistry.

a) Doping of metals in NU-1000



b) Creating the acidic sites in NU-1000

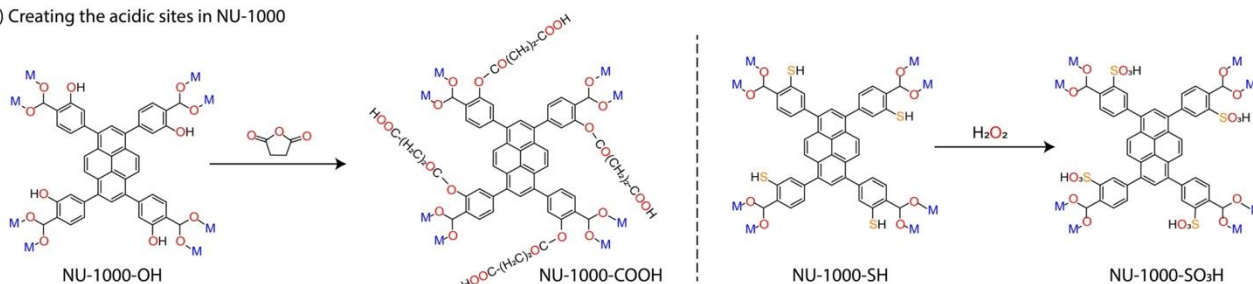


Figure 2: Post synthetic modification of NU-1000 to create bifunctional catalysts. a) Modifications in $Zr_6(\mu_3\text{-OH})_8(\text{OH})^8$ -nodes via ALD or doping of metal atoms/nanoparticles. b) Creating the acidic sites in NU-1000 through post-synthetic modifications of hydroxy and thiol-functionalized MOFs.

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