MOFCAT

Functional Metal Organic Frameworks as Heterogeneous Catalysts

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Instrument type: STREP

Priority name: NMP

Publishable executive summary

Period covered: 2008-09-01 to 2010-02-28

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Duration: 42 months

Project coordinator name: Richard Blom

Project coordinator organisation name: SINTEF

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1. Publishable executive summary

Contractors involved:

Partic. Role*	Partic. no.	Participant name	Participant short name	Country	Date enter project	Date exit project
CO	1	Stiftelsen for Industriell og Teknisk Forskning ved Norges Tekniske Høyskole	SINTEF	Norway	1	42
CR	2	Università degli Studi di Torino – Dipartimento di Chimica IFM – Centre of Excellence Nanostructured Interfaces and Surfaces.	UNITO-NIS	Italy	1	42
CR	3	University of Oslo	UiO	Norway	1	42
CR	4	Ecole Supérieure de Chimie Physique Electronique de Lyon	ESPCE	France	1	42
CR	5	Eni S.p.A.	ENI	Italy	1	42
CR	6	Haldor Topsøe A/S	HTAS	Denmark	1	42
CR	7	Humboldt Universität zu Berlin	UBER	Germany	1	42

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Summary description of project objectives and work performed

Metal Organic Frameworks (MOFs) are novel organic-inorganic crystalline materials, which promise to become a powerful and flexible family for different industrial uses within catalysis, adsorption and sensor technology, overcoming many of the limitations of Zeolites, the porous crystalline solids which are conventionally used as catalysts: MOFs may display extreme porosity and surface areas, and their functionalities can be tailored by using functional precursors in their preparation or by post-functionalisation using standard techniques of organic- and organometallic chemistry. These features have been studied in the MOFCAT project for the development of new heterogeneous catalysts and gas adsorbents. The project aims have been to 1) develop reproducible and scalable synthesis procedures for known and new MOFs, and also using combinatorial techniques; 2) understand at the molecular level the interactions governing their stability, self-assembly and adsorption properties, by means of combined experimental and theoretical modelling efforts; 3) develop functionalisation routes to create MOF-based single-site catalysts for two emerging industrial processes; 4) exploit the functionalised MOFs as catalysts in two emerging industrial processes; 5) exploit Pt-functionalised MOFs as catalysts for C-H activation at moderate conditions; 6) exploit MOF materials for catalytic hydrodesulphurisation (HDS) of oil; and 7) exploit selected MOFs as adsorbent or storage media for non-condensable gases (hydrogen and methane). The work packages of the project comprise the synthesis, characterisation, modelling, and testing of the materials, as well as a technology implementation plan for their production and use.

The project has been split into 6 technical work packages that have worked in parallel: All materials synthesis has been carried out in WP1 (Synthesis) and WP2 (Functionalisation). In WP1 the aim has been to prepare open, porous and crystalline MOFs, both non-functionalised MOFs and MOFs having specific functionalities inside the pores that later can be made into active catalysts in WP2. Linkers that are not commercially available are synthesised and post-functionalisation of the MOFs prepared in WP1 are done by solution or gas phase techniques. In WP4 (Characterisation) deep understanding of selected materials have been gained through spectroscopic analyses of the material itself and its interaction with various gaseous molecules. To complement the experimental work and obtain a full understanding of the materials, quantum chemical modelling is carried out in WP3 (modelling). In cases where potential catalysts have been prepared, the catalyst will be tested in WP5 (Catalysis), while the most porous MOFs made will be evaluated for gas storage potentials in WP6 (Adsorption). Together the 6 work packages contain the complete work needed for a state-of-the-art development of novel MOF materials.

The main findings in the project can be summarized as follows:

Novel MOFs:

During the project period, a high number of new MOF materials have been prepared and for some of these their crystal structures have been determined. One MOF structure that was invented prior to the MOFCAT project,[1] has been further studied within the project resulting in a deep understanding on the material activation and the behaviour in the presence of various gases. The CPO-27-M family, M= Ni, Mg, Co, Mn, shows a very nice one-dimensional pore structure as shown in Figure 1 below. Actually, thermal treatment of the CPO-27–M materials leads to an open porous structure where each metal atom has on open coordination site. Thus, this is one of the rare MOF materials where the reactivity and effect of the different metals can be directly compared within the same framework structure. This effect has been studied in depth when evaluating the CPO-27-M materials for gas storage as described in the following sections. In addition, the CPO-27-M materials have been used as precursors for further post-functionalisation with the aim of making novel single-site catalysts.

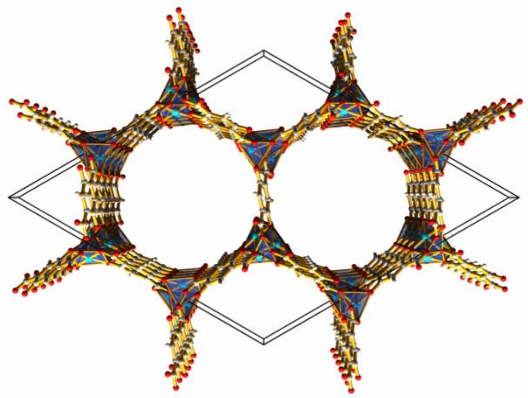

Figure 1: The CPO-27-M structure

A second family of novel MOF materials that has been developed through the MOFCAT project and that has gained much attention is the zirconium based UiO-66 family.[2] Variation of the organic linker gives an isoreticular family of ultra stable MOFs, some showing stable performance to temperatures above 400ºC! Increasing the length of the linker make pore size and –volume larger, which is of importance if the materials should be used to store or convert molecules of larger size.

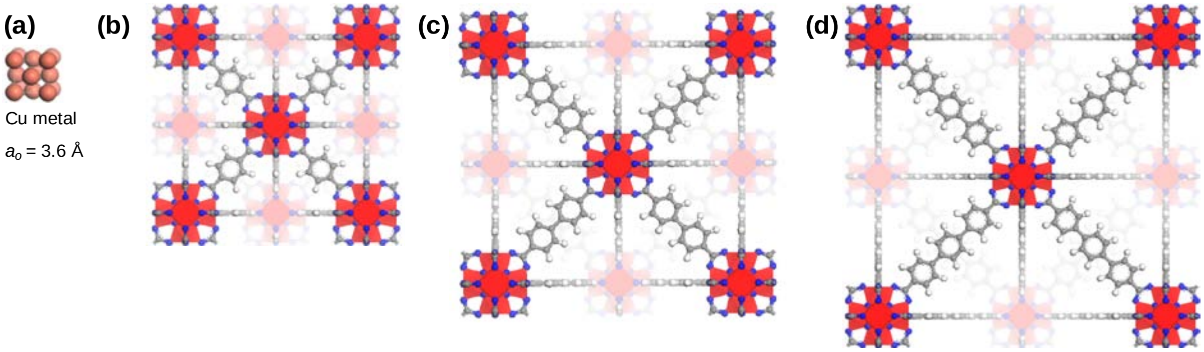

Figure 2: The UiO-66 family

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[1] Pascal D. C. Dietzel, Yusume Morita, Richard Blom, and Helmer Fjellvåg, ”In situ High Temperature Single Crystal Investigation of a Dehydrated Metal-organic Framework Compound and Field-induced Magnetization in a One-dimensional Metal-oxygen Chain”, *Angew. Chem. Int. Ed.*, **2005**, *44*, 6354

[2] Hafizovic Cavka, Jasmina; Jakobsen, Søren; Olsbye, Unni; Guillou, Nathalie; Lamberti, Carlo; Bordiga, Silvia; Lillerud, Karl Petter. “A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability.” *Journal of the American Chemical Society* (2008), *130*(42), 13850-13851

Further functionalities in the MOFs can be inserted either as part of the organic linker used, or by post-functionalisation. Both these approaches have been used throughout the MOFCAT project. For example, in the CPO.27-M system a second metal component has been introduced by sublimation of metal carbonyls such bas $Mo(CO)_6$ leading to pre-catalysts for industrial reactions such as hydrodesulphurisation (HDS). Using tagged linkers, special versions of UiO-66 bearing -amine, -nitro and -bromine functionalities have been made. Such materials can easily be converted into materials with selectivities towards specific gas or solvent molecules. Applications range from catalysis to selective adsorption.

Part of the material preparation part of MOFCAT has been devoted to synthesis up-scaling and particle formulation since both these aspects are of great importance when it comes to the application of these materials in real industrial processes. Both preparations of CPO-27-Ni and UiO-66 have been successfully up-scaled from gram to 100 gram scale. In addition, pelletising CPO-27-Ni shows only negligible reduction in pore volume and surface area.

Finally, a number of new MOF materials for which the preparation routes and detailed structures are still not finalised have appeared during the project. A number of these will be followed up in subsequent projects.

MOFs for gas storage

One on the main objectives of MOFCAT has been to develop novel MOFs for storage of non-condensable gases such as hydrogen and methane. For hydrogen storage we have not reached the 2010 target set by US DoE of 4.5 wt% H_2 for the total storage system running at ambient temperature. However, both the CPO-27-M family and the UiO-66 family can store significant amount of hydrogen at low temperature (77K). This has been shown in Figures 3 and 4 below.

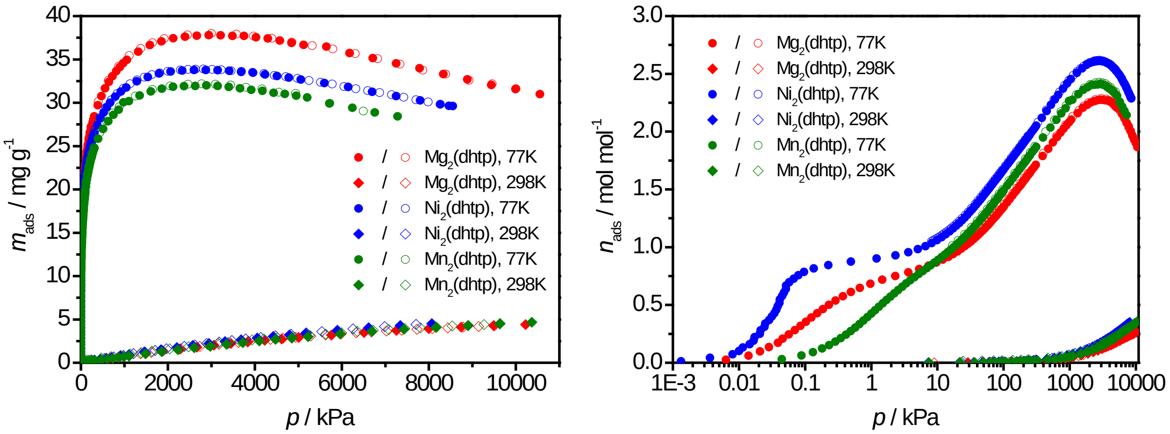

Figure 3: H_2 isotherms for a series of CPO-27-M materials. Logarithmic pressure scale to the right.

For the CPO-27-M system, the mechanism of adsorption can be visualized by plotting the isotherm on a logarithmic scale (Figure 3). A two step isotherm show first the adsorption of molecular hydrogen onto the open metal sites followed by adsorption on the rest of the pore walls. The initial adsorption energies determined are strongly dependent on the metal of the MOF, the highest being nickel with 12.4 kJ/mol (CPO-27-Ni) which is among the highest reported for MOF adsorbents. This observation is nicely complemented by spectroscopic results (Figure 5) showing a gradual reduction in H_2 adsorption energies through the series Ni>Co>Mg.[3]

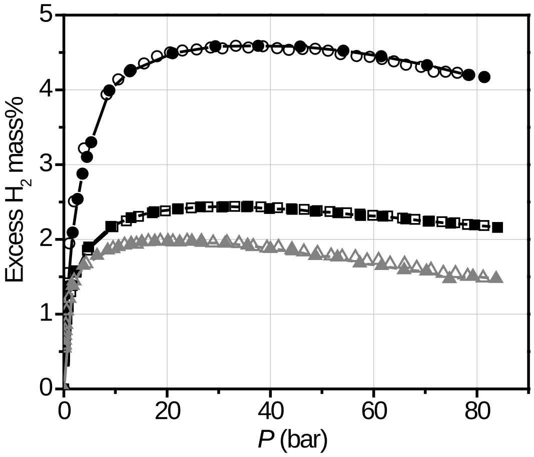

Figure 4: H_2 isotherms for UiO-66 family of materials.

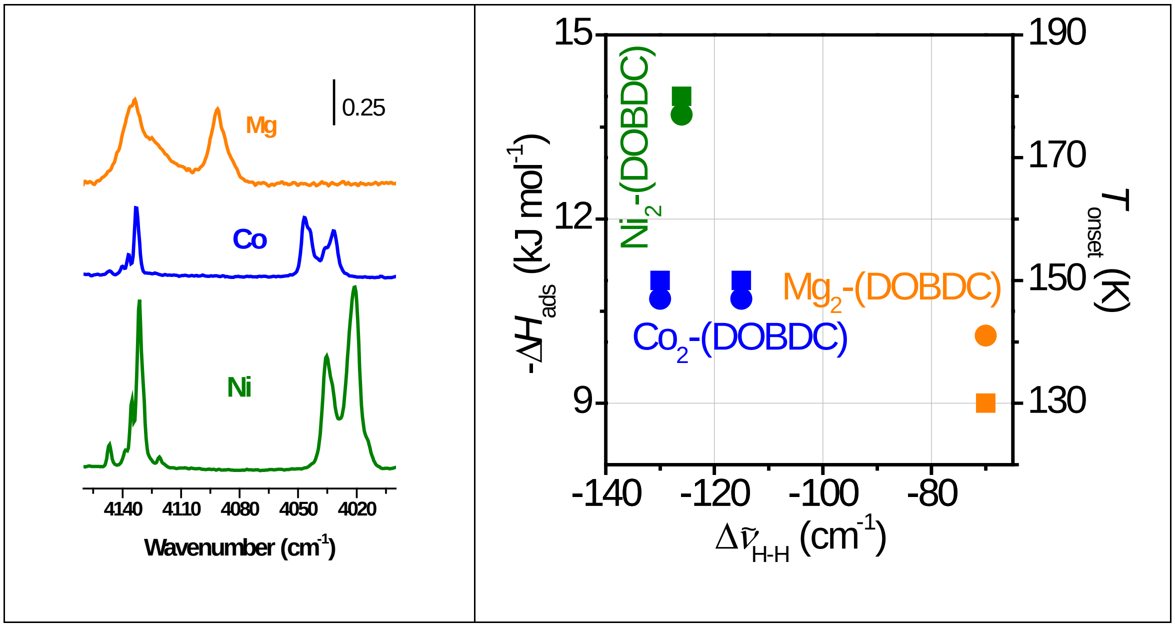

Figure 5: a) FTIR spectra of H_2 adsorption at 20K and high coverage on CPO-27- M. b) Dependence of the adsorption, $-\Delta H_{ads}$ (Circle) and of T_{onset} (square) on the corresponding shift of the (H-H) frequency on CPO-27-M. (For CPO-27-Ni Green, CPO-27-Co Blue and CPO-27-Mg Orange)

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[3] Jenny G. Vitillo, Laura Regli, Sachin Chavan, Gabriele Ricchiardi, Giuseppe Spoto, Pascal D. C. Dietzel, Silvia Bordiga and Adriano Zecchina. "Role of Exposed Metal Sites in Hydrogen Storage in MOFs." *J. Am. Chem. Soc.*, **2008**, 130 (26), pp 8386–8396

For the UiO-66 family, highest H_2 storage capacity is obtained with the material prepared with the dicarboxylic acid biphenyl linker (the middle structure in Figure 2 above) since this material have the highest specific surface area and pore volume. Future evaluation of the UiO-66 systems prepared with larger linkers might give even higher storage capacities.

Methane storage in the CPO-27-M materials show the same trend as with H_2: a similar two step adsorption is observed due to the initial strong adsorption on the metal sites. For the CPO-27-Ni material significant storage potential is observed, exceeding the volumetric storage density at room temperature set by US DoE (Figure 6).[4]

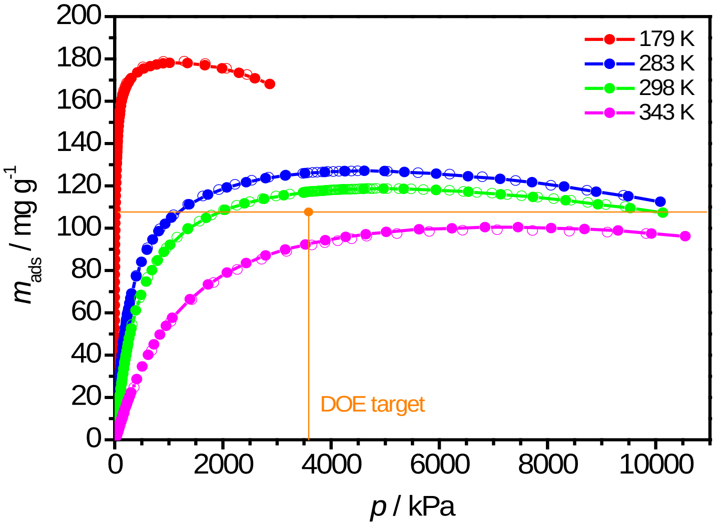

Figure 6. Excess methane adsorption at selected temperatures in CPO-27- Ni. The DOE target of 180 v/v at 298 K and 35 bar is indicated

From quantum chemical modelling the adsorption of methane inside the materials has been analysed. As for hydrogen, the shape of the methane isotherm can be explained by two contributions: one from the direct interaction of methane with the metal sites and another weaker contribution from the interaction of methane with the organic parts within the pores. This has been visualised in Figure 7 on the next page.

The high methane storage capacity has also been reproduced using pellettised CPO-27-Ni showing that real applications of MOFs for methane storage might be feasible.[5]

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[4] P. D. C. Dietzel, V. Besikiotis, R. Blom, “Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide”, *J. Mater. Chem.* **2009**, *19*, 7362-7370

[5] Marco Tagliabue, Caterina Rizzo, Roberto Millini, Pascal D. C. Dietzel, Richard Blom, Stefano Zanardi. "Methane Storage on CPO-27-Ni Pellets.” *J. Por. Mat.*, **2010**, DOI: 10.1007/s10934-010-9378-0

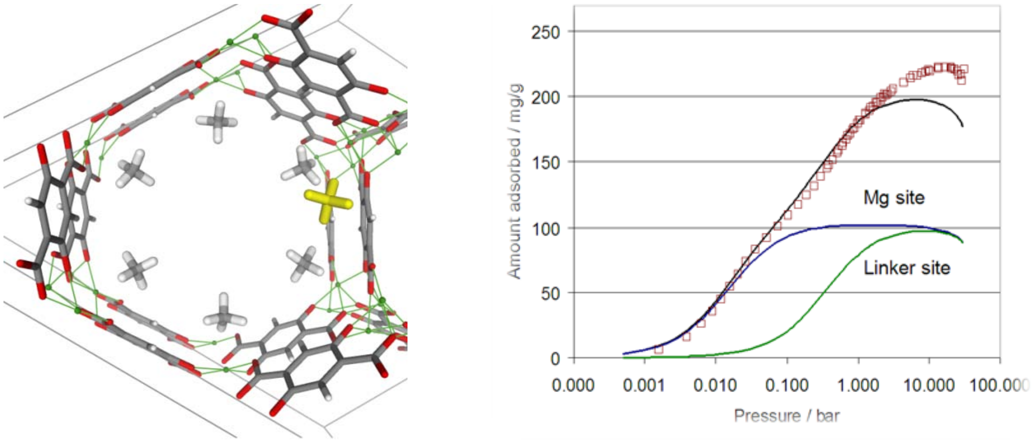

Figure 7: CH_4 adsorption in CPO27-Mg. The lines in the isotherm plot show the contribution that Mg and linker sites make to the adsorption isotherm.

Novel catalysts

Novel, highly dispersed hydrodesurfurisation (HDS) catalysts made from bimetallic MOF precursors. One typical example is shown in Figure 8 below where the catalyst precursor is formed by entering molybdenum hexacarbonyl into the CPO-27-Ni structure.

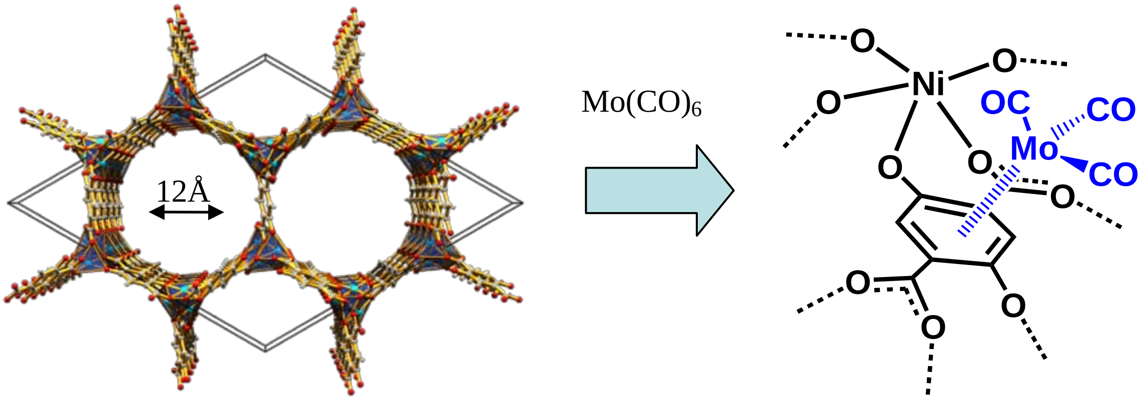

Figure 8: Bimetallic precursor hydrodesulphurisation catalyst formed in the reaction of CPO-27-Ni with $Mo(CO)_6$.

Some of the new MOF based highly dispersed HDS catalysts have shown activities close to twice that of a commercial high-surface area alumina-supported CoMo catalyst.

Also the development of Pt-based MOFs for C-H activation has further continued through the MOFCAT project.[6] Still the materials need to exhibit higher porosity and the right configuration of the platinum sited to be active for C-H activation, but stepwise more open structures are

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[6] Szeto, Kai C.; Kongshaug, Kjell Ove; Jakobsen, Soren; Tilset, Mats; Lillerud, Karl Petter. "Design, synthesis and characterization of a Pt-Gd metal-organic framework containing potentially catalytically active sites. " *Dalton Transactions* (**2008**), (15), 2054-2060

obtained, and we are certain that continuous long term targeted research on this some time in the future will lead to a successful result. A result that also may help to find successful synthetic routes for the other targeted single site catalysts aimed at in MOFCAT.

The way forward

We have throughout the MOFCAT project obtained a number of scientific results that have been published in peer review scientific journals and on a large variety of scientific conferences, workshops and meetings. But still, there are many loos ends after the project – half finished work and leads that certainly will be followed up in various follow up projects involving one or more on the groups that have been involved in MOFCAT. In addition, even if some of the target single site catalysts of MOFCAT were not successfully prepared during the 42 months project, we still believe this would be possible through long term stepwise research. Some examples of MOF based single site catalysts have recently appeared in the literature,[7] however not for the target reactions in MOFCAT.

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[7] L. Ma, C. Abney, W. Lin, "Enantioselective catalysis with homochiral metal-organic frameworks", *Chem. Soc. Rev.*, 2009, 38, 1203.