

PROJECT FINAL REPORT

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Nanoporous Metal-Organic Frameworks for production
(nanoMOF)

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² The home page of the website should contain the generic European flag and the FP7 logo which are available in electronic format at the Europa website (logo of the European flag: http://europa.eu/abc/symbols/emblem/index_en.htm logo of the 7th FP: http://ec.europa.eu/research/fp7/index_en.cfm?pg=logos). The area of activity of the project should also be mentioned.

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1 Publishable summary

1.1 Executive summary

The nanoMOF-project focused on the development of novel metal-organic frameworks, the formulation and integration of these MOF materials into products and systems. Three high-potential application areas were chosen to demonstrate the applicability and performance of MOFs in industrial applications: 1) MOFs for gas purification, 2) MOFs for safe gas delivery systems, and 3) MOFs for catalysis. A consortium was formed by 17 beneficiaries from 10 European countries, from leading technology developers, through equipment suppliers and major end-users.

For each application area, specific MOFs were developed and evaluated, starting from simple networks leading to more complicated structures in the end (e.g. CPO-27, new MOFs based on isonicotinic acid, Zirconium MOFs, iron MOFs, nickel MOFs, copper MOFs, isoreticular series of Ni-MOFs, DUT-MOFs, HPW/Cu₃(BTC)₂, ZIF-8, CaBDC-MOF). Cu₃(BTC)₂ was identified as a valuable compound for gas purification and was selected for upscaling in the demonstrator and prepared as several kg batch. For gas storage well established materials (MIL-100, Cu₃(BTC)₂) were produced in a kg-scale. For catalytic applications, heteropolyacids in MOFs were established.

The processing of the synthesized MOFs essentially determines the applicability and performance of the MOF material in the final products. For skin and respiratory protection applications, three-dimensionally loaded MOF-functionalized nonwovens were produced and evaluated. The combination of MOF adsorbers with conventional carbon based adsorbents proved to be beneficial. Furthermore, alternative processing routes such as electrospinning, direct fixation by directed growth of MOF on the fibre surface, and simple entrapment of MOFs in the void spaces between the fibres have been performed. Evaluation tests focused on the capacity and the stability of the novel textile air filters and the fulfillment of the ABEK requirements. First large-scaled samples (few square meters) of MOF loaded textiles were produced in upscaling tests and show promising performance data.

For the use of MOFs as a bulk material, spherical granules with satisfactory adsorption properties in a wide variety of sizes are required. Shaping technologies like the oil drop process and the gelation process were developed to achieve required size of MOF granules (< 1 mm). For application in catalysis, encapsulated heteropolyacid MOF (HPW@Cu₃(BTC)₂) was coated on substrates.

To demonstrate the potential of the novel MOF materials, dedicated demonstrators were developed, equipped with a well-suited MOF-material, synthesized and processed within the nanoMOF frame. The following demonstrators were developed and tested:

- Protective gloves from textile filters with Cu₃(BTC)₂- impregnated adsorbents
- Filter canisters for respiratory protection by using a stack of nonwoven filters with Cu₃(BTC)₂ and flat filter media with impregnated carbon adsorbents
- Filter canisters for respiratory protection by using a stack of flat filter media with Cu₃(BTC)₂ and carbon adsorbents
- Gas purifier unit containing Cu₃(BTC)₂ coated spheres, equipped with a colorimetric loading sensor and a trace gas analyzer
- High pressure gas cylinder loaded with MOF granules
- A test platform, designed as batch- and continuous tubular reactors, for esterification of oleic acid with glycerol for the selective production of monoglyceride equipped with different MOF catalysts

All activities in the field of MOF synthesis, processing and demonstration were supported by the development and manufacturing of the required equipment for the experiment implementation, production and for test purposes. Dedicated analysis of the adsorption performance of the (processed) MOFs as well modeling and simulation activities, were essential for the nanoMOF progress.

The success of the nanoMOF project can be shown on hand of 24 peer-reviewed papers, the presentation of nanoMOF results at more than 30 conferences and the two well-attended workshops, organized by the nanoMOF consortium.

1.2 Summary description of project context and objectives

Metal-Organic Frameworks (MOFs) represent a novel class of nanoporous materials with extremely high specific surface areas surpassing that of traditional adsorbents such as zeolites and activated carbon. The overall objective of this Large-scale integrating collaborative project is to engineer MOFs for industrial applications in catalysis, gas storage, and gas purification using the modular construction principles of MOFs for pore size engineering and functionalization. The project substantially strengthens the position of Europe in the industrial use of Metal-Organic Frameworks, a research area so far dominated by US and Japanese companies and research organizations.

Focussing on environmental applications of MOFs, the integrating project has targeted to establish an internationally leading position for Europe, using the direct integration of MOFs into products. Major efforts in recent years were devoted to the exploration of building principles of MOFs and basic structural characterization demonstrating the outstanding properties of this new class of nanoporous solids. However, for the industrial utilization and commercialization, large-scale production, integration in products such as textile filters for air purification, performance evaluation in catalytic and separation processes under realistic conditions is necessary. The project has explored new MOF materials and their functionalization specifically designed for applications in separation (gas purification), gas storage, and heterogeneous catalysis.

NanoMOF-project has focused beyond discovery and has integrated MOFs into products with industrial impact within a strong cooperation of established MOF research institutions and industrial end users.

Three major impact areas have been selected:

Area 1 focuses on the one hand side on separation processes for downstream feed purification in chemical industry. Highly selective separation processes are crucial for the efficient production of industrial gases. The modular concept allows tailoring MOF materials in pore diameter and pore functionality by introducing functional groups and accessible metal centers in the pore interior. The latter allows adjusting the materials properties and tailor pore sizes for specific molecules to be removed, resulting in increased energy efficiency and lower degree of waste production.

For many industrial downstream applications, hydrocarbon feedstock has to be purified before further processing to prevent poisoning of catalysts. Sulphur in the form of H_2S or an organic compound is present in almost all hydrocarbon feed streams, ranging from naphtha to middle distillates. For some downstream applications, such as fuel cell reformer units sulphur reduction to less than 200 ppb wt. sulphur requires hydrogenation to H_2S followed by adsorption. Product purity to achieve can be below the limit of commercially available sensing techniques. Selective hydrogenation catalysts, installed downstream have to be perfectly protected to pursue their basic activity and selectivity. MOF materials can be tailor made in pore size, surface functionality, and binding affinity towards small molecules resulting in a unique selectivity and high capacity for separation processes. The concept of accessible metal sites in MOFs is a key technique to achieve a high adsorption selectivity and binding strength for compounds such as H_2S . Thus, they are ideally suited for downstream purification.

As a second target in area 1 the high selectivity and capacity for toxic volatile compounds was used for the integration into protective clothing and gas masks. Air permeable protective clothing and gas mask filters require a high adsorption rate and high binding strength for gases like ammonia, but also hydrophobic MOFs for organic toxic volatile compounds. At the same time integration into textiles and immobilization of porous particles is a key target. For a high adsorption rate, MOF nanoparticles are beneficial due to enhanced transport and reduced diffusion limitation. MOF/fibre composites must be

designed to guarantee air permeability for protective clothing and selective adsorption of toxic compounds at the same time.

Area 2 focuses on gas storage. In nanoporous solids such as MOFs, gases can be stored in the adsorbed state. Due to the higher density of the adsorbed molecules, the effective storage capacity can be significantly increased by a factor of 2.5-3 as compared to empty cylinders. Not only the capacity is increased but also the pressure needed to store the gases is reduced improving the safety of the storage system. For highly toxic gases used in semiconductor industry, adsorptive storage in MOFs should be used for the first time to reduce handling and contamination risks by reducing the storage pressure needed for operation. Selective removal of contaminants is a key issue in electronic grade gases and air purification. For electronic grade gases, the adsorbent can be designed to act as a getter system for the removal of contaminants in high purity gases. The modular concept of MOFs allows adjusting the chemical functionality to specifically remove the contaminants but release the stored gas. For such a "safe delivery system", MOFs need to be processed into compact bodies.

Area 3 focuses on catalysis. Catalysis is an ecologically responsible and economically attractive technology that can cope with consumer expectations of ever increasing quality of goods and services, with societal demands for increasing effectiveness to maintain global competitiveness and with the concern of environmental protection. Three extraordinary properties of MOFs are expected to lead to exceptional catalytic performances: (1) the high specific surface area; (2) the well-defined pore size, and (3) the unique coordination chemistry of transition metals and main group elements. These properties should be enabling the development of highly selective catalysts for atom and energy efficient processes. The proposal is focusing on novel MOF materials based on tin and titanium, metals for which only few MOF examples exist so far. The replacement of liquid Lewis acids based on titanium and tin by solid MOF catalysts for (trans)esterification processes in the oleochemical area is targeted. These generic model reactions with a practical scope are particularly relevant to the conversion of fatty acids and triglycerides into a variety of valuable products for cosmetics, foodstuff, detergents, etc. A multidisciplinary approach involving (1) synthesis and evaluation of catalyst materials; (2) characterization and kinetic evaluation; (3) modelling of the catalytic process and (4) pilot scale validation in a balanced industrial-academic partnership was aimed.

The general key targets for nanoMOF project were the development of novel metal-organic frameworks, the formulation and integration of these novel and known MOF materials into products and systems. The industrial research and generic engineering objectives were:

- Exploration of new materials and novel nanoporous structures with customized functionality for industrial processes or products
- Processing technology for MOFs and integration in textiles
- Development of air filter modules
- Protective clothing for personal protection
- Gas purification/adsorption system for removal of minority contaminants in clean industrial processes
- MOF compacts with high packing density
- Safe delivery gas storage system for toxic gases for semiconductor industry
- Lewis type MOF catalysts for monoglyceride production processes
- Simulation and modelling of the gas / MOF interactions
- Crosscutting engineering: equipment and dedicated software for process monitoring and quality assurance
- Evaluation of long term potential strategic value of MOF technology by "road mapping"

1.3 Description of the main S&T results/foregrounds

1.3.1 WP2: Synthesis of MOF

The synthesis strategy of the consortium was organized in a horizontal and vertical structure. For each of the tasks strategic synthesis partners were responsible to achieve the cluster targets. For each task, specific MOFs were developed starting from simple networks leading to more complicated structures in the end. The progress in MOF materials development was monitored via three MOF generations of materials where 1st gen. MOF represented early developments with satisfactory performance and 3rd gen. MOF more sophisticated structures developed at the end of the project. For the development of novel structures, on the one hand side, rational approaches were used but also some partners used high throughput screening very successfully to discover new MOF structures. 1st gen. MOF materials were selected for upscaling to the kg scale. Upscaling was performed by JM and TUD.

1.3.1.1 Task 2.1 Gas purification

For hydrogen purification and removal especially of sulfur containing compounds various MOF materials were synthesized. In the early phase, CuBTC was evaluated and established as a valuable compound for purification. Upscaling was realized at a later stage of the project. New MOFs based on isonicotinic acid were developed by SINTEF. Zirconium MOFs were investigated as a class of relatively stable MOF materials but price and performance were not promising and thus this route was not followed. The interaction of H₂S with open metal sites was studied by TUR in depth giving suggestions for rational MOF development with enhanced performance (Figure 1.3.1-1). In the end, one MOF was selected for upscaling in the demonstrator and prepared as several kg batch by JM.

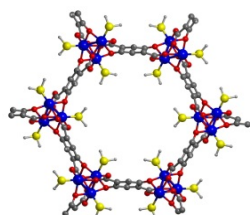


Figure 1.3.1-1: Modeling of H₂S Adsorption in CPO-27

1.3.1.2 Task 2.1 Protective Equipment

For respiratory and textile filter applications novel MOF materials were developed by TUD and UGR. Particle size adjustment was an important issue to fulfill the pressure drop and processing requirements. Syntheses for MOF nanoparticles were developed. Copper pyrazolato compounds were promising candidates in the beginning of the project. UGR studied the adsorption of several toxic gases and simulants using column experiments. Zn₄O(3,5-dimethyl-4-carboxypyrazolato)₃ (Figure 1.3.1-2) was discovered as a highly stable and hydrophobic MOF with excellent performance in the adsorption of toxic compounds.

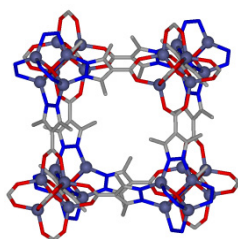


Figure 1.3.1-2: Structure of Zn₄O(3,5-dimethyl-4-carboxypyrazolato)₃

Several MOF materials were synthesized in larger scale for WP 3 (processing) for example for NRF for textile integration. An important task was also to measure properties of MOFs after processing to

achieve quality control. For demonstration, two materials were produced by TUD at a scale of 10 kg and integrated in respiratory filter demonstrators as well as protective clothing. These results were very promising and disseminated at trade shows.

1.3.1.3 Task 2.2 Gas Storage Electronic grade Gases

UGR and TUD delivered various materials for electronic grade gas storage. Among them iron MOFs, nickel MOFs and copper MOFs were the most promising. While in the early stages also several established materials (such as MIL-100) were synthesized in larger amounts, in the later stage of the project several novel MOF materials were developed. For example, an isoreticular series of Ni-MOFs was discovered by UGR.

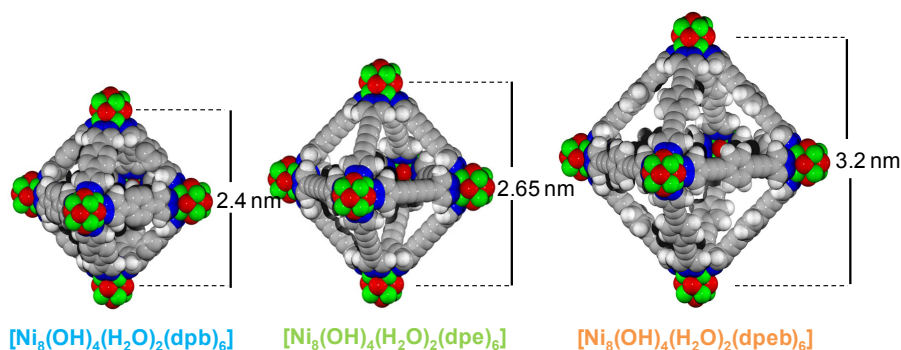


Figure 1.3.1-3:

But also TUD could establish a number of new MOFs of the DUT series (DUT = Dresden University of Technology). DUT-8 turned out to be an interesting material with gate pressure effect which may be promising for gas storage applications.

1.3.1.4 Task 2.3 Catalysis

Catalytic materials were developed by KUL and CNRS. In the early stage of the project heteropolyacids (Keggin-ions) in MOFs were established by KUL as a promising and new class for esterification reactions. The occlusion of the polyacid occurs within the synthesis as a self-assembly.

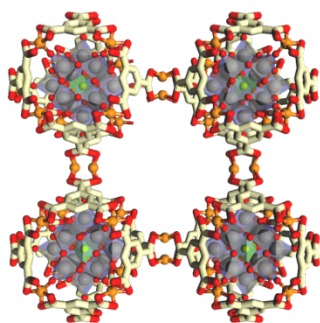


Figure 1.3.1-4: MOF loaded with Keggin-ions.

CNRS at the same time developed MOF materials with dedicated functionalization for the catalytic tests. Such post-synthetic functionalization can induce a higher activity and selectivity starting from available precursor materials. An example for such a post-synthetic modification strategy is shown in the following.

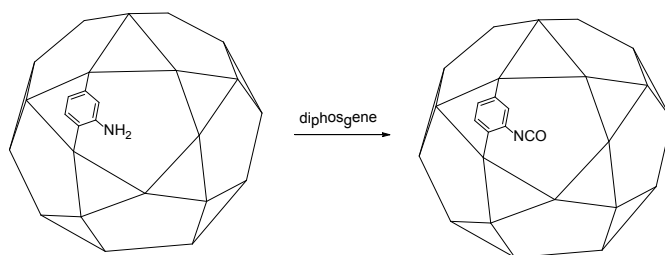


Figure 1.3.1-5:

In most of the cases, amino MOFs were used as the starting compounds in well-established structures (for example MIL series). However, cost and performance driven in the later stages of the project, group 2 element MOFs were established as highly active, cost-efficient and environmentally friendly catalysts and the focus was shifted. Due to the shift of resources in the consortium catalyst upscaling to the kg scale was canceled.

1.3.2 WP3: Processing of MOFs

1.3.2.1 Task 3.1: Textile integration for protective clothing (NRF, TUD, OUV, BLU, INN)

NORAFIN

The key aspects of Task 3.1 (NRF) are:

1. basic process researches with focus of the maximization of the particle loading,
2. the choice of an appropriate binder system for the permanent 3D-particle fixation,
3. tests of different binder systems for the MOF-particle binding,
4. tests of a new particle insertion technology at the basis of foam,
5. lamination and sewing tests with binder
6. works on the increase of wash permanence by variation the binder concentration and fibre titer

Norafin produced and optimized the basis nonwoven material from different fibres (e.g. PET, aramides, viscose, flax) for the MOF-functionalisation. Thereby an important role played the properties of the **nonwoven basis material** (mass area, elongation, tensile strength, pore size, thickness). After that, the nonwoven fibres are coated with a binder (system) to fix the **MOF-particles** at one point at the fibre surface. As **binder** self-cross-linked copolymer based on acrylate, latex, ethylene vinylacetate and aliphatic polyester-polyurethane are tested. In the next step, the adhesive nonwoven fibres are loaded by means of a **low pressure technology** with the MOF-particles. Besides a **new scattering-suction technique** to integrate and fix MOF-particles into different nonwovens depending on the application requirements is developed. The result was a three-dimensional loaded MOF-functionalized nonwoven material.

Norafin tested different MOF-loaded nonwovens with various parameters and determine their dependences

- Fibre properties: e.g. fibre material, fibre diameter, fibre length
- Nonwoven properties: e.g. mass area, thickness, elongation, tensile strength
- MOF-particle properties: e.g. particle size, particle contribution, hydrophilic/ -phobic
- Binder properties: e.g. adhesiveness, wash resistance, minimal particle loss

The developed MOF-particle loaded nonwoven for **protective clothing** fulfill the following criteria: low mass area, low thickness, high particle loading capacity, good wash resistance, high air permeability (breathability) and high mechanical stability. Thereby a textile air filter for protective clothings with 40 g/m² PET spunlace nonwoven is developed. This substrate showed very good

properties regarding air permeability (500-800 L/(m²*s), at p= 100 Pa), mass area (25-45 g/m²) and thickness (< 0,6 mm).

For **respiratory protection** the blend with 75% 17 dtex PET and 25% 1,7 dtex PET, loaded with CuBTC was the best version regarding thickness, pressure drop and loading capacity.

TU Dresden

Immobilization of MOF-particles via electrospinning

A lab scale test apparatus for electrospinning (ESP) was used to deposit MOF-particles (Cu₃(BTC)₂, MIL-100(Fe) and FeBTC-Gel) in a network of non-woven fibres. Polyvinylpyrrolidone (PVP) in ethanol and polyacrylnitrile (PAN) in dimethylformamide (DMF) were used as polymeric binders. With ESP the production of homogeneous functional covers with high ratios of MOF/Polymer of around 80 wt.% was achieved. First upscaling tests were made on the semi-industrial electrospinning device «Nanospider» at Norafin. Cu₃(BTC)₂ with PAN as binder was used as a model system to process several larger samples (few square meters) of textiles covered with MOF/PAN-fibre-layers. By adsorption measurements, it was shown that the inner surface area of the MOF is not blocked by the polymeric binder and therefore completely accessible. A maximum loading of 2.5 g MOF/m² textile could be achieved by one spinning step.

MOF-loaded textiles

For the direct fixation of MOF particles on textiles, trials for the directed growth of Cu₃(BTC)₂ on the surface of various aramide, viscose and natural flax fibres have been performed. A direct chemical fixation of MOF particles on the fibre could lead to a strong bonding and therefore high stability without negative effects on the porosity and adsorption behavior. Tests in this field have shown that particles can be synthesized on the fibre surface. In the case of flax fibres the presence of lignin and different pectines provides a variety of functional groups on the surface that can be utilized as anchoring points for the growth of MOF crystals directly. Therefore, no chemical modification was performed in these cases. Another way to immobilize MOF particles in a textile is the simple entrapment of MOF in the void spaces between the fibres of a nonwoven material. This was first tested utilizing the iron trimesate system (FeBTC) which is prepared in form of a gel. By comparing differently structured textiles it became obvious that needlepunch materials are capable of immobilizing much more MOF particles, compared to spunlace non-wovens, reaching loadings of around 60 wt.-%. Unfortunately the weak physical bonding of MOF-particles in the textiles lead to huge mass losses during washing tests, making the approach ineffective for real applications. Therefore so called BiCo nonwovens have been loaded with FeBTC-gel and Cu₃(BTC)₂ slurries. To test this approach BiCo-nonwovens have been loaded with MOFs and heated above the melting point of the shell polymer. Nitrogen physisorption measurements showed only minor differences for the textiles before and after thermal treatment. Thus, thermal stability of the MOFs and pore blocking effects seem to be no problem. Compared to FeBTC, the particle size of the infiltrated Cu₃(BTC)₂ was much smaller, leading to a smaller portion of particles with direct contact to the fibre surfaces. This explains the enormous mass loss during the first washing step, since there is no additional physical entrapment. Nevertheless, a residual loading of approximately three weight percent can be retained over all cycles. Although this value is rather low, the positive effect of the adhesion can be easily demonstrated when comparing the BiCo-nonwoven with a non-functional standard textile. From the tests, it can be seen that for the non-functional textile the MOF particles are completely washed out already during the first washing step, whereas the BiCo-substrate is able to bind a significant amount of copper trimesate as is demonstrated by the blue color. These results are promising for future experiments since no complicated chemical functionalizations of the substrates are necessary. The relatively low loadings in the case of Cu₃(BTC)₂ may easily be increased by simply using larger MOF particles for infiltration.

BLÜCHER

BLU developed several types of textile filters for the two applications skin protection and respiratory protection. The requirements and test systems are summarized in the Table 1.3.2-1.

Table 1.3.2-1: Requirements and test systems for textile filters

Requirement / Test System	Skin protection	Respiratory protection
Capacity Cyclohexane / GD / NH ₃ / H ₂ S	Channeling < 3 % - cumulated Breakthrough < 50 µg / cm ² /h	According to DIN EN 14387
Conditions for testing	70 -85 % RH @ 20 – 80 °C	10 – 80 % RH @ 20 – 23 °C
Mechanical stability	Scrub test	Stability in filter canister
Particle size (depending on processing method)	0,5 mm	50 µm – 2 mm
Filter medium height	< 1 mm	< 50 mm
Filter weight	< 300 g/m ²	Filter canister max. 500 g
Air permeability / Pressure drop filter medium	>100 l/m ² /s	< 40 Pa/cm for 0,064 m/s
Oeko Tex Standard	Extractable heavy metals: Cu < 50 mg/kg	Not applicable

Skin Protection

The choice of the MOF type for the skin protection had the following priorities:

1. High capacities for the test substances
2. Stability under humid conditions/ ÖkoTex standard
3. Suitable particle size
4. Sufficient mechanical stability of the MOF material

Some MOFs have no cyclohexane capacities under humid conditions. Therefore, the MOFs should be combined with carbon for the textile filters.

The following types of filter materials were developed

- combination of MOF in a nonwoven with a carbon filter
- filter with one layer of MOF-carbon composite

The filters for the skin protection consist of modified spherical adsorbents (diameter: 0,2 -0,6 mm) between two textile layers. The filter production is performed by the BLUECHER-screen printing technique on a flexible polyester carrier, which is afterwards laminated with a flexible, thermoplastic polyurethane meltblow (TPU-MB) cover. For the final product – the glove – this filter is combined with an external fabric. The stability after washing and scrubbing were good for the CuBTC-PBSAC filter. The Oeko-Tex limit of 50 mg/kg is exceeded by the laminated filters with a factor of 2 - 4. However, the values are still quite low compared to copper impregnated carbon, which gave values between 1.200 -26.000 mg/kg adsorbent. The impregnation of PBSAC with CuBTC has still to be optimized to lower the amount of extractable copper.

Respiratory Protection

The choice of the MOF type for the respiratory protection had the following priorities:

1. High capacities for the test substances
2. Suitable particle size
 - for a bulk bed (0,7-2 mm)
 - for a flat filter (about 100 µm)
3. Stability under humid conditions (70% rh)
4. Sufficient mechanical stability for the production

The filter for respiratory application needs a low respiratory resistance which can be achieved by using larger particles (0,7 - 2mm) in a bulk bed or by producing a filter medium with high air permeability from the smaller sized particles (50 – 100µm).

The following techniques were developed

- Co-Agglomeration of CuBTC with spherical adsorbents (PBSAC)
- Agglomeration of CuBTC-PBSAC
- Production of flat filter with CuBTC
- Production of flat filter with CuBTC-PBSAC

Co-agglomerates of CuBTC and PBSAC

CuBTC by the TUD (particle size: 50 µm) was combined with small size spherical adsorbents by BLUECHER (particle size: 50-100 µm). The agglomeration was done by heating the components with hot melt adhesive in a rotary kiln. The resulting co-agglomerates were in the size range of 0,2-0,5mm and had good mechanical stability. The breakthrough measurements of the co-agglomerates show high NH₃ - and H₂S-capacities in correlation with the CuBTC content. The cyclohexane capacity corresponds to the carbon content. For the use of the co-agglomerates in respiratory canisters, the size of the agglomerates (0,2-0,5 mm) is still too small. Larger size CuBTC-PBSAC-co-agglomerates were produced with larger size spherical adsorbents (0,3 - 0,6 mm) in a second step. But the CuBTC content of the co-agglomerates correlates with the particle size and is rather low for the larger particles. Resulting from this the NH₃ - and H₂S -capacity of these Co-agglomerates is quite low.

Agglomerates of CuBTC-PBSAC

Agglomerates of CuBTC-PBSAC by the TUD were produced with hot melt adhesive in a rotary kiln. The size of the resulting samples was in the required range (0,7-2,5mm) and the mechanical stability was good. Breakthrough measurements of the agglomerates by the IWS showed high capacities for the test substances and only a small decrease (capacity in % weight) by the binder content of the agglomerates. The breakthrough criteria according to ABEK1 criteria are fulfilled for the small size agglomerates (0,71-1,25 mm), so a respiratory canister can be produced with them.

Flat filter media with CuBTC

Flat filter with CuBTC by JM (size range about 100 µm) were produced with the BLUECHER technique by spraying hot melt adhesive on a carrier and scattering the particles. The flat filter with three layers of CuBTC has an area weight of about 200 g/m² with a CuBTC content of 53 g CuBTC/m². The mechanical stability of the filters is good, the height is small with only 0,6mm/ layer. The filter height (12 mm for 20 layers) is small and therefore suitable for a respiratory filter, but the pressure drop is high (about 123 Pa for 20 layers). Because the capacity is quite low, the minimal number of layers for the ABEK requirements (>> 20 layers) exceeds the requirement for the respiratory resistance (maximum 100 Pa for 30 L/min). So this type of filter may only be used as a supplementary filter

Flat filter media with CuBTC-PBSAC

Flat filter with CuBTC-PBSAC by TUD (size range 0,45 - 0,63mm) were produced by the BLU technique with spraying hot melt adhesive on a carrier and scattering of the adsorbents. The CuBTC-PBSAC have capacities for inorganic and organic substances – so they may be used as a single material for a respiratory canister. The flat filter medium with three layers of CuBTC-PBSAC has an area weight of about 860 g/m², which is comparable to a filter with activated spherical adsorbents. The mechanical stability of the filters is very good. The flat filter with CuBTC-PBSAC show low pressure drop (22 Pa/ 6 layers) and height (12 mm/ 6 layers) and quite long breakthrough times for H₂S, NH₃ and Cyclohexane. This material is suitable for a respiratory canister by using a higher stack, which is still in line with the requirement for the respiratory resistance (maximum 100 Pa for 30 L/min).

For a respiratory filter, the requirements for

- high capacity
- low pressure drop
- sufficient mechanical stability

are fulfilled by the agglomerates and the flat filter media.

For a filter canister production, the following materials may be used:

1. Agglomerates of CuBTC-PBSAC
2. Flat filter with CuBTC (as additional layer)
3. Flat filter with CuBTC-PBSAC

1.3.2.2 Compact (for advanced gas delivery system)

The focus of work done in this task was set to define properties of the material and structures and to find a type of MOF suitable to perform sufficient, to obtain finally an appropriate adsorbing material. Another crucial step within this activities was to find a suitable processing method which one hand allows manufacturing compact granules with sufficient properties for the advanced gas delivery system and on the other hand allows a wide variety of batch sizes (from 5 g up to kg size) accordingly the availability of MOF powder.

In close accordance with the other cluster partners for the first feasibility trials, the following boundary conditions were determined. It was agreed that the compact material which should be used for the save gas delivery task should be shaped as **spherical granules** having a diameter above 1 mm. Further it was decided to utilise FeBTC powder as MOF type to find a suitable shaping process. This was done because FeBTC in powder form (FeBTC-Gel) can be scaled up at Johnson Matthey in a cheap and easy way and it is assumed that the results of these first trials can be transferred to other MOFs. The aim of the feasibility trials was to find out if an oil drop process is a feasible production method to manufacture small batches of FeBTC spheres. Therefore 250 g FeBTC synthesized by Johnson Matthey was used. As binder aqueous polymer dispersions were used. For the trials a lab unit for carrying out the oil-drop process was build up. Per trial from 50 g FeBTC a aqueous suspension was made containing FeBTC, polymer dispersion and a jellifying agent. This suspension was dropped into a bin containing a hydrophobic phase on the top and a hydrophilic phase on the bottom. As a FeBTC-suspension drop is passing through the hydrophobic phase it is formed into an almost spherical shape and when entering the hydrophilic phase these drops are jellified to stable granules. The granules then were taken out and dried. Using an oil drop process spherical shaped granules could be manufactured from FeBTC powder.



Figure 1.3.2-1: FeBTC-spheres

The granules made are shown in Figure 1.3.2-1. The granules showed sufficient mechanical stability, as well as diameter and sphericity. The material was delivered to the partner for further testing and usage in the demonstrator.

1.3.2.3 Granular bodies for demonstrator gas purifying system and catalysts in oleochemical production (TUD, BGU, KUL, JM, SH)

The activities focused on the development of concepts for shapes and bodies in adsorbent beds of plug flow reactors with appropriate dimensions and acceptable pressure drop. This involves the macroscopic modeling of adsorbent and catalyst reactor systems. The granulation of MOF pellets should performed without any significant loss of accessible surface area. The key tasks were the evaluation of the binder and the process optimization.

TU Dresden

By using the above mentioned FeBTC-gel precursor solution it was possible to generate compact monolithic MOF particles of several millimetres size. A method for the preparation of almost perfectly

spherical particles is the gelation of the MOF-gel precursor solution in single droplets. Due to the slow drying process the formation of cracks can be minimized during the shrinkage, leading to almost perfectly shaped spherical particles of around 1-3 mm in size.

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KUL has demonstrated coating of $\text{Cu}_3(\text{BTC})_2$ encapsulated heteropolyacid MOF -denoted as $\text{HPW}@\text{Cu}_3(\text{BTC})_2$ - on three different substrates; copper ball, silica and polystyrene bead. In term of stability, according the SEM analysis, $\text{HPW}@\text{Cu}_3(\text{BTC})_2$ was found detaching from the surface of the copper balls after ultrasound treatment for 5 minutes, indicating physical attachment. In order to enhance the stability of $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ coating, a chemical bonding method was implied. The silica crystals were modified with imidazole attaching the keggin polyanions on the N-terminal acting as 'template' for the growth of $\text{HPW}@\text{Cu}_3(\text{BTC})_2$ crystals. At room temperature, $\text{HPW}@\text{Cu}_3(\text{BTC})_2$ was found coated on the surface of the silica according to SEM attempt to coat $\text{HPW}@\text{Cu}_3(\text{BTC})_2$ on polystyrene bead was also demonstrated. The silica-coated $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ was used as a fixed catalyst bed for continuous catalytic reactor fixed with a static mixer. For the demonstration of continuous process of esterification reaction, KUL also contributed in preparation of ZIF-8 pellets and giant size CaBDC MOFs. Giant size CaBDC MOF was prepared through hydrothermal synthesis approach. CaBDC MOF is a highly crystalline non-porous MOF material as confirmed by XRD. SEM imaging showed giant size particles of approx. 0.5 mm in length and 100 microns in diameter for CaBDC MOF.

1.3.3 WP4: Analysis and modelling of MOF functionalities

Main objective of work package 4 was to give cluster-oriented support of during synthesis and processing of novel MOF materials for the target applications.

The special focus was on

- the analysis of the kinetics of the gas adsorption on MOFs for (a) air filters and the identification of MOF adsorbents for the removal of sulphur containing compounds from natural gas for fuel cell applications in Cluster1,
- the analysis of the capacity of the gas storage in MOF material in Cluster 2, as well
- the analysis of the catalytic selectivity of MOF materials (Cluster 3).

1.3.3.1 Task 4.1 Analysis of the kinetics of the gas adsorption on MOFs for filter applications and separation process

Work in Task 4.1 was strongly associated with the targets of Cluster 1: Identifying promising MOF materials and analyzing their adsorption performance at application related test conditions. In addition, evaluation of the influence of processing and shaping of MOFs powders into easy to handle spheres or textile filters on the adsorption characteristics was focus of this task. Due to a strong crosslink with WP2 and WP3, it was possible to identify three promising generations of MOFs materials for filter applications and to develop the required synthesis, processing and shaping technology without loss of the MOFs properties. The novel materials show an excellent adsorption behavior for selected toxic industrial chemicals and outperform the state of the art materials.

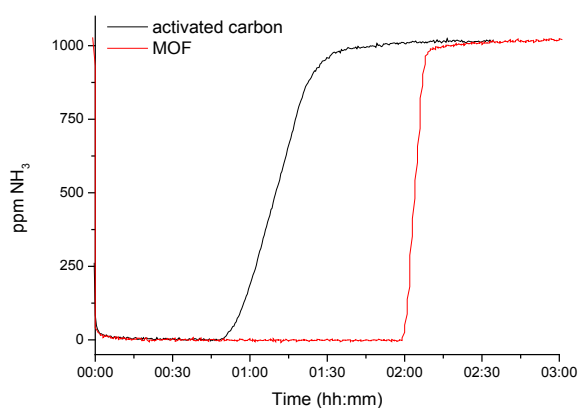


Figure 1.3.3-1: Comparison between breakthrough curves of activated carbon and a MOF using ammonia as test gas.

1.3.3.2 Task 4.2 Analysis of the capacity of the gas storage in MOF material

MOF materials are highly suitable for the efficient storage of gases, amongst others for storage and capturing of electronic gases at safe pressure and the posterior delivery of the stored gas with enhanced purity. It could be shown, that MOFs with small pores might be adequate for trapping of gas at low concentrations whereas MOFs with large pore size will be adequate for storage.

As representative example of electronic gases, which are hard to compress, krypton gas was chosen for investigations. Krypton is usually stored in steel cylinders at pressures between 80 and 140 bar. Due to the low compressibility of this gas, the compression up to higher pressure is not economical. Therefore, the storage in a porous medium can be an efficient alternative. In the frame of the project, the most suitable MOFs were evaluated, and it could be shown, that the effective storage capacity in MOF filled cylinder can be significantly increased by a factor of 2.5-3 as compared to the empty one.

1.3.3.3 Task 4.3 Analysis of the catalytic selectivity of MOF materials

Monoglycerides are attractive natural emulsifiers for application in food and beverages, personal care products and pharmaceuticals. The current industrial monoglyceride production is based on a

homogeneous catalytic process, which is performed at high temperature (250 °C). The monoglyceride selectivity is limited to 50% due to formation of di- and triglyceride side products and soap. The high reaction temperature also bears the risk of deterioration of taste, aroma and color of the final product. Within the Task 4.3, the target of this project was to develop a stable heterogeneous metal-organic framework (MOF) catalyst for selective synthesis of monoglycerides aiming at >90% yield. Direct esterification reaction of oleic acid with glycerol was selected as a model reaction.

Experimental data needed for kinetic simulation were obtained by running the esterification reaction of oleic acid with glycerol as in a batch reactor under vacuum to remove the produced water. The monoglyceride selectivity at high conversion was limited to 40-60%. A kinetic model was built based on partitioning of the molecules between the immiscible oleic acid and glycerol phases, thermodynamic equilibrium and estimated kinetic constants. The simulation revealed that the monoglyceride selectivity is limited by the low solubility of glycerol in fatty acid.

The intrinsic phase problem was overcome by using tert-butanol solvent to obtain a homogeneous mixture of the fatty acid and glycerol. A series of potential MOF catalyst candidates: HPW@Cu₃(BTC)₂, HPW@MIL-101, Al-MIL-53-NH₂, In-MIL-68-NH₂, UiO-66, UiO-66-NH₂, SnEOF, ZIF-8, ZnF(TAZ-NH₂) and CaBDC were screened for direct esterification reaction of oleic acid with glycerol at 150°C in the presence of tert-butanol solvent. SnEOF (tin elemental-organic framework) catalyst showed moderate catalytic activity and achieved 100% monoglyceride selectivity. However, a severe leaching of Sn was noted from the ICP analysis. Due to the low chemical stability of SnEOF MOF, further work on discovering a stable and active MOF catalyst for heterogeneous catalysis of the targeted esterification reaction was performed. Another MOF catalyst known as ZIF-8 (zeolitic imidazolate framework-8) was found to be active, selective, and reusable without significant loss of catalytic performance. A minimum leaching of Zn (2wt%) is observed. The amount of leached Zn is however exceeding the initial target of 5ppm allowed for any transition metal in the final product.

The performance of MOF catalysts was demonstrated in a fixed bed continuous flow reactor. The testing of the ZIF-8 catalyst in packed-bed was problematic because of insufficient stability of ZIF-8 catalyst pellets resulting in excessive pressure drop. The problem could be overcome using another MOF catalyst composed of calcium terephthalate (CaBDC). Giant size CaBDC crystals measuring 0.5 mm were packed in the reactor. At a reaction temperature of 200 °C, 75-80% conversion in oleic acid was achieved with monoglyceride selectivity >95%. Under the investigated reaction conditions, the conversion was limited to around 80% by the thermodynamic equilibrium. The CaBDC MOF showed a weight loss of more than 10% of the catalyst was measured after about 200 h on stream. Development of more stable MOF catalyst material will be needed for this application.

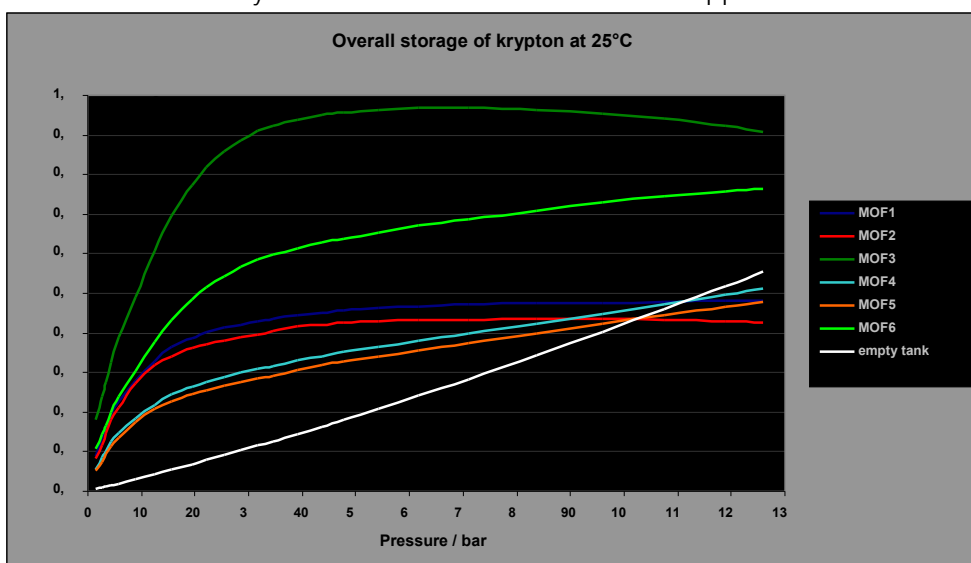


Figure 1.3.3-2: At low pressure, MOF filled cylinders enable higher storage capacities for Kr compared to the empty cylinder (white line).

1.3.3.4 Task 4.4 Safety of MOF materials

Metal ions or metal clusters are always present within the MOF structure. Although several metals do not bear a health risk, MOFs can contain toxic heavy metals which release into the environment needs to be avoided. Within the project, several MOF exposure scenarios like dust formation during processing of the usually very fine MOF powders, the leaching of MOF catalyst into oleo-chemical products or the skin compatibility of MOF containing textiles have been addressed. It could be shown, that the release of MOF nanoparticles while shaping can be avoided using state of the art powder processing technology. However, the leaching of metal ions from MOF catalyst into oleo-chemical products or the skin compatibility according to Oeko-Tex100 standard remains challenging and need to be further addressed.

1.3.4 WP 5: Equipment

Work Package 5 was divided into five tasks for equipment development with partners collaborating to achieve the objectives within each task. Outlined below are the details of the main results for each hardware development task.

1.3.4.1 Task 5.1: Development of novel, generic gas analysis equipment

TDL Sensors were primarily involved with Task 5.1, work consisted of designing, building and testing laser based instrumentation for measuring low level concentration H₂S in a carrier gas stream. Laser based instruments use the interaction of light and a target gas for concentration determination based on absorption spectroscopy. The instrument design was to be generic, flexible and suitable for integration with gas delivery systems for gas storage capacity testing of MOF materials.

An instrument based on photoacoustic spectroscopy was designed and built; it measured the interaction between modulated laser light and the target gas as a change in pressure with a very sensitive microphone, this photoacoustic setup allowed ppm level H₂S to be measured.

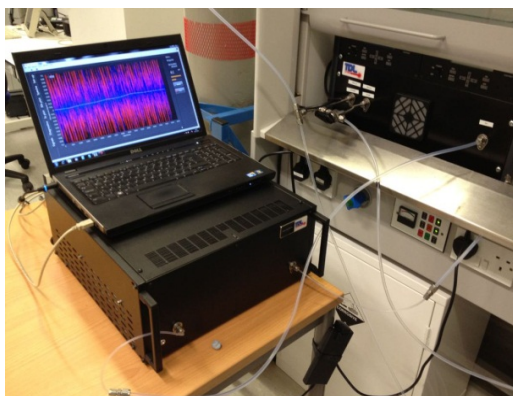


Figure 1.3.4-1: Laser based photoacoustic analyser developed within Task 5.1

Work was then undertaken to transform the laboratory based bench-top instrument to a robust, self-contained, portable instrument as all MOF testing was to take place at partner sites. This final version of the instrument was successfully used to establish the performance of the MOF Demonstrator Unit (Task 6.1b) in conjunction with the low cost colour sensor developed in Task 5.3.

1.3.4.2 Task 5.2: Development of dedicated test equipment

Over the NanoMOF project, Johnson Matthey (JM) rig facilities were used to evaluate the TDL gas analyser and to test MOF samples. The JM test equipment consists of a GC, a furnace and different gas lines connected to the inlet via a series of mass flow controllers. The inlet to the MOF sample tube

is connected through mass flow controllers to N_2 or CH_4 . There is also another group of gases, which can be optionally connected via a solenoid valve, this can switch to air, N_2 , H_2S or CO_2 . Fraunhofer IWS designed and constructed a similar gas delivery system.

For measuring the gas storage capacity within MOF filled cylinders, SIAD developed a small high pressure setup with 15 ml cylinder to be able to test adsorption properties of small amount of MOFs. The maximum pressure of gas inside the cylinder is 200 bar. A 200 ml high pressure setup was then built for storage and purification tests where larger amounts of gas are needed, Figure 1.3.4-2. The gases adsorbed in the devices at room temperature are krypton, methane, carbon monoxide and nitrous oxide.



Figure 1.3.4-2: High pressure cylinder (200 ml) for storage and purification tests (left) and gas cylinder (15 ml) for high pressure tests (centre) and filling station (right).

1.3.4.3 Task 5.3: Development of low cost sensor for monitoring of the MOF loading

Work was carried out by TUR to investigate the spectroscopy of selected MOF materials and the interaction with H_2S , this was to be the basis for a low cost colorimetric sensor for MOF loading studies. An example study is the interaction between CPO-27-Ni and H_2S .

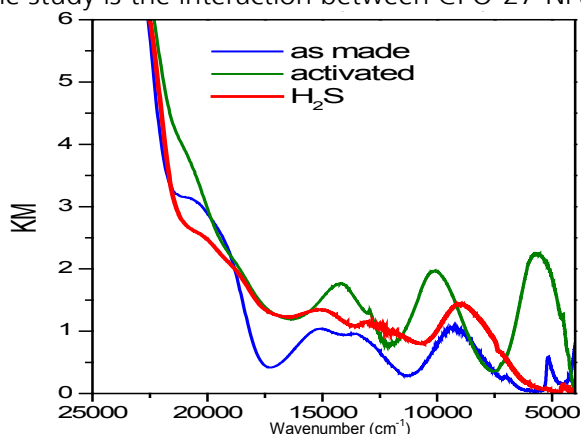


Figure 1.3.4-3: DR-UV-Vis spectra of CPO-27-Ni as synthesized (blue curve), activated at 200°C for 1 h (green curve) and with adsorbed H_2S (red curve).

Figure 1.3.4-3 shows the changes in the spectra of CPO-27-Ni upon H_2S adsorption. The changes observed (between blue and green) are assigned to the change in the Ni co-ordination upon the removal of water and the red curve illustrates the spectrum obtained upon the dosage of H_2S (40 Torr at RT) on this activated CPO-27-Ni. This results show the coordinative adsorption of H_2S to the open nickel site replacing H_2O . The small differences in the absorption maxima of the bands between the "as made" CPO-Ni and with dosed H_2S characterise these two forms with different colours - ochre and dark green. This visible colour change is very important for the colour sensor demonstrator.

IWS based the MOF loading sensor on the measurement of the color change of the MOF due to the adsorption of gases on open metal sites. The electronic scheme of the sensor module is shown in Figure 1.3.4-4.

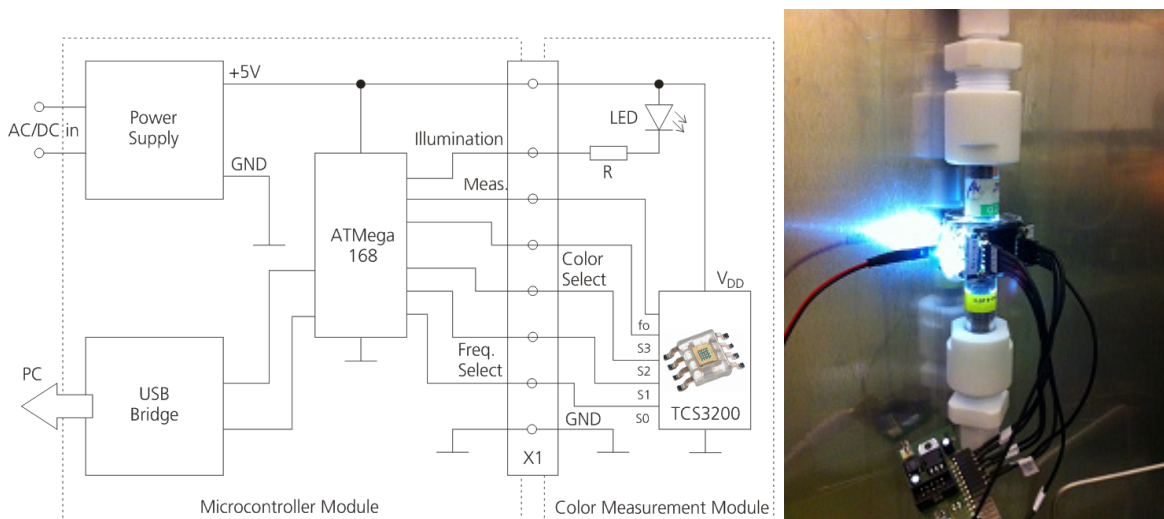


Figure 1.3.4-4: Electronic scheme of the loading sensor module and the sensor assembly mounted to the adsorption column.

A light emitting diode (LED) serves as light source and illuminates the adsorption column containing the MOF. The colorimetric sensor measures the back scattered light (i.e. light intensities of red, green and blue) from the MOF adsorbent inside the column. For sensor control and data acquisition, a microcontroller ATMega168 is used. It allows connecting the sensor to a PC for data visualization and if necessary calibration purposes. The complete setup mounted to the adsorption column is also shown in Figure 1.3.4-4.

1.3.4.4 Task 5.4: Development of high throughput synthesis and testing equipment

The high-throughput synthesis setup available at SINTEF has been adapted and used for rapid parallel preparation of MOF compounds to speed up the materials discovery process in the project. The parameters which govern the product obtained from the reaction include the type of metal salt and organic linkers, metal to organic ligand ratio and concentration, the solvent system and temperature. The HT-PXRD system available at SINTEF provided fast overview of material crystallinity and enabled efficient phase identification. A new Lynxeye silicon strip detector (Figure 1.3.4-5, left) provided significantly better resolution enabling many more applications, including powder pattern indexation, quantitative analysis and size-strain analysis.

In addition, a TG/DSC-MS system with automatic sample changer allowed further investigation of pre-selected samples on the basis of the diffraction analysis (Figure 1.3.4-5, right). It allowed rapid screening of these samples in respect to thermal stability and solvent content, temperatures of solvent loss and plateaus of stability of the desolvated compound.

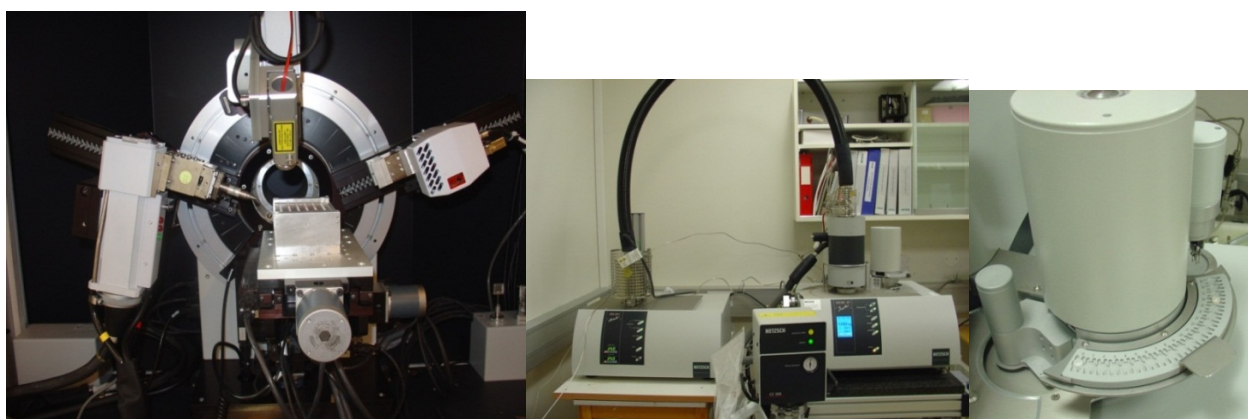


Figure 1.3.4-5: left: Image of Bruker AXS D8 instrument equipped with Lynxeye detector. middle, right: Image of TG/DSC-MS instrument (STA 449 F1 QMS 403C Aëolos) equipped with automatic sample changer.

Further on in the project the high-throughput equipment was used to synthesize new MOFs from inexpensive starting reagents. The used chemicals had to be relatively inexpensive since the newly produced materials with most promising properties needed to be scaled up to the kg scale for application in the envisioned areas. The high-throughput equipment was used to explore a relatively complicated system consisting of two metals and two ligands. The metals used were either Ni and Y, Co and Y or Zn and Y, and the ligands used were isonicotinic acid and terephthalic acid. Other synthesis parameters tested were various solvents, chemical ratios and temperatures.

1.3.4.5 Task 5.5: Processing equipment

During the project duration Norafin worked on the development of a continuous working machine for the three-dimensional functionalization of nonwoven substrates with different types of MOF-particles for the use as textile air filters in protective clothings and for respiratory protection. The functionalization process works without the use of any solvents and generates a punctual particle-fibre connection which gives the possibility to occupy nearly the total particle surface for the filtration process.

At the beginning of the project Norafin tested different types of nonwovens substrates with different types of functionalization techniques (presented in WP 3). The low pressure technique shows the best results regarding particles loading capacity which is crucial of the gas adsorption capacity and the break through time. At first Norafin used a lab unit for the loading of different substrate types and obtained very good results regarding the loading capacity (see Figure 1.3.4-6).

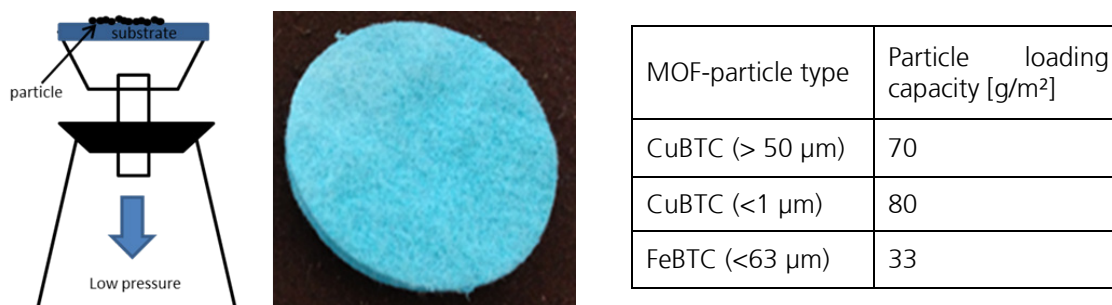


Figure 1.3.4-6: Scheme of the lab unit (left), a CuBTC loaded needlepunch nonwoven (middle) and the MOF-particle loading capacities (right)

With the gained experimental results in pre-tests in lab scale, Norafin transferred the results to a continuous, larger scale production process, Figure 1.3.4-7.

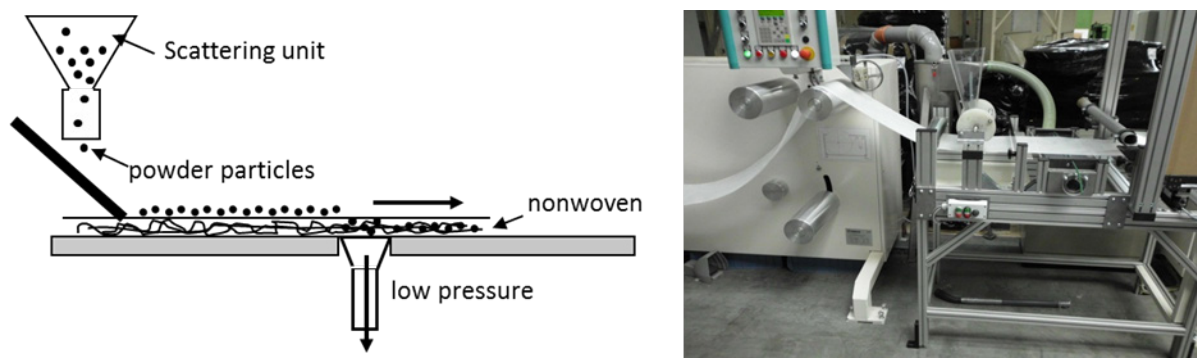


Figure 1.3.4-7: Principle of the dry loading process (left) and the scattering-suction unit (right)

With CuBTC-particles from the project partner JM, Norafin was able to produce a MOF-particle loaded 20 m roll (500 mm width) based on an open needlepunch nonwoven substrate for the demonstrator preparation (see Figure 1.3.4-8).



Figure 1.3.4-8: Continuously MOF-particle loaded PET-nonwovens for the demonstrator preparation (CuBTC <math><63 \mu\text{m}</math> from JM; loading capacity: 25 g/m²)

The development of the scattering-suction unit allows Norafin to load different types of substrates in a three-dimensional, dry way. Together with unique filtration properties of the nonwoven substrate Norafin is able to produce MOF-functionalized nonwovens with valuable filtration properties for a wide range of applications, not alone for protective clothing and respiratory protection.

In summary, a wide variety of different and complementary hardware development programs have been successfully undertaken and completed within the nanoMOF project.

1.3.5 WP 6: Demonstrator

1.3.5.1 Task 6.1 Air filter and gas purifier

6.1a: Air filters: Glove demonstrator for skin protection

Ouvry produced protective gloves from textile filters with CuBTC-impregnated adsorbents and organized tests carried out by Innovatext according to their specifications on the raw materials and demonstrators produced by Ouvry.

The demonstrator and materials were also tested in accordance with the standards specified in the PPE directives and according to Oeko-Tex[®] Standard 100 requirements. All results are reported in WP3 and WP4. Final results conclude that the demonstrator gloves meet the requirements, although in some cases only reach the lowest level (puncture and blade cut resistance). The properties of this research's main objectives perform above the requirements (thermal transfer properties, water vapour resistance, abrasion resistance, tear resistance, dexterity, burning behaviour, resistance against the penetration by liquids).

In certain aspects of Oeko-Tex[®] Standard 100 conformity the glove needs to be improved further, especially in fixation of heavy metal components. Leather accessories may also require attention to chromium content and short chain chlorinated paraffins.

Tests against TICs (Industrial chemicals)

The cumulated breakthrough for NH₃ is significantly lower (98 – 115 µg/cm²/h) than for untreated carbon (180 µg/cm²/h). Additional measurements with <math><5\%rh</math> showed no capacity for NH₃. In contrast to this there was an uptake of H₂S by the filter material even with <math><5\%rh</math>. The cumulated breakthrough for H₂S is significantly lower (262 - 243 µg/cm²/h) than for the control (353 µg/cm²/h).

6.1a: Air filters: Filter canister demonstrator for respiratory protection

Blücher produced two types of filter canisters for respiratory protection by using different types of material:

- Demonstrator type 1: A stack of nonwoven filters with CuBTC + flat filter media with impregnated adsorbents (PBSAC)

- Demonstrator type 2: A stack of flat filter media with CuBTC-PBSAC

Both types of demonstrator fulfill the DIN EN 14387 criteria for the breakthrough time of Cyclohexane, NH₃ and H₂S and the respiratory resistance.

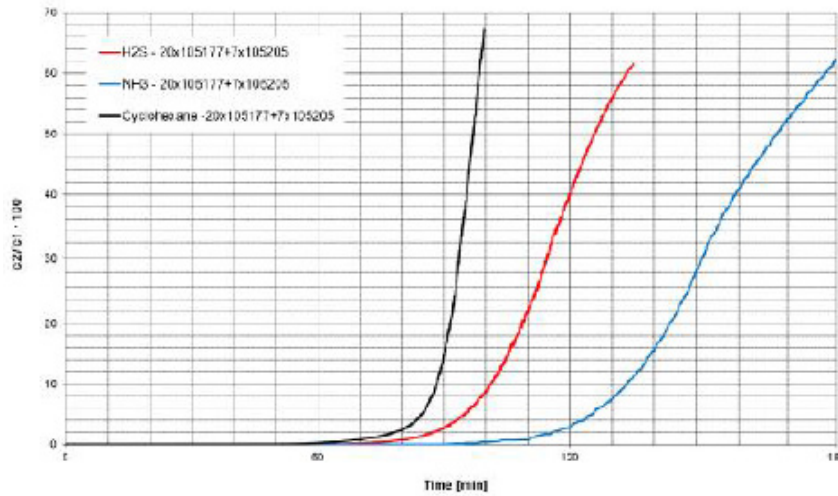


Figure 1.3.5-1: Break through curve of the filter canister type 1 (1000 ppm, 0,04 m/s, 20 °C, 70 % RH)

During the break through tests, a change in color of the CuBTC particles can be seen for every gas (mainly for Cyclohexane and H₂S). That is an indicator for the adsorption of the test gases (see figure below).

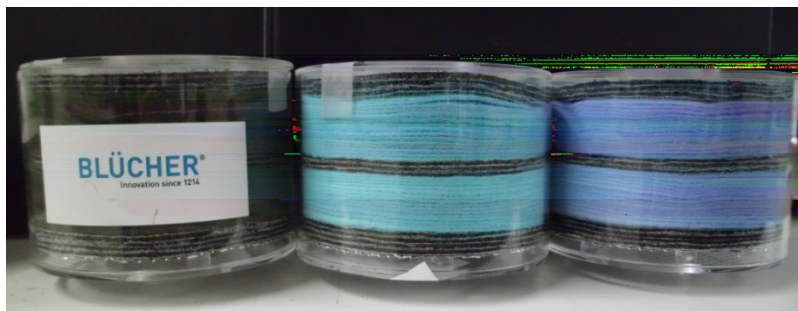


Figure 1.3.5-2: Filter canisters after the break through test with Cyclohexane; NH₃ and H₂S (from right to left)

6.1b: Gas purifier unit

Cu(II) 1,3,5-benzenedicarboxylate metal-organic framework coated onto clay beads was evaluated against sulphur species. The gas purifier unit consisted of a glass tube containing the CuBTC coated spheres (JM and SH), a colorimetric sensor (IWS) and an analyser (TDL).

The colorimetric sensor was placed around the cartridge to monitor the change in colour of the Cu-MOF material (see figure 1). The amount of hydrogen sulphide was analysed by a TDL sensor, which was connected to JM rig equipment.

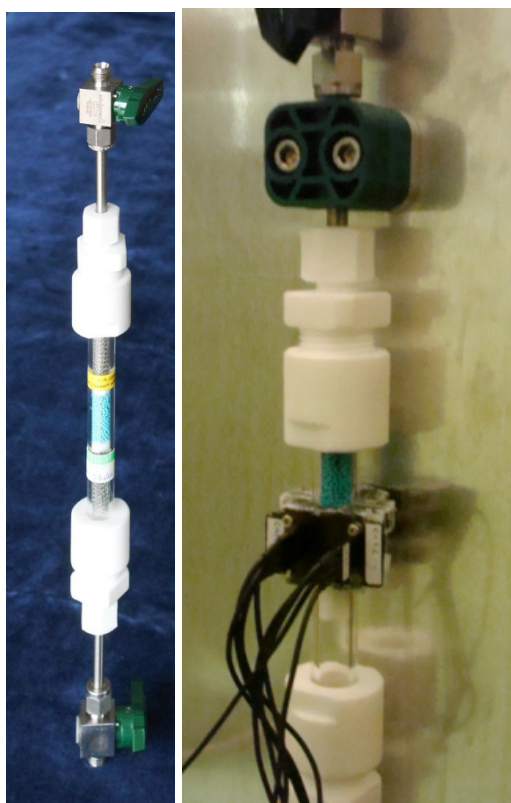


Figure 1.3.5-3: left: Assembled demonstrator unit for gas purification; right: IWS colorimetric sensor and Cu_3BTC_2 coated MOF

CuBTC was coated onto 1 mm spheres; the shell thickness of the coating was 200 microns approximately. The amount of CuBTC and binder coated onto the spheres was a 55% of the total weight. The test was performed with 1000 ppm of hydrogen sulphide (H_2S) and room temperature.

Three tests were carried out using different bed lengths. H_2S adsorption capacity was measured using the obtained breakthrough with 2 cm bed length, the CuBTC coated on clay beads showed 2wt% of H_2S . Data collected using 5 cm bed was used to compare the colorimetric data with the breakthrough time.

A longer bed (5 cm) was prepared in order to compare the data collected from the colorimetric sensor to the breakthrough time of the H_2S . Figure 2.2.1.1.2.2-2 shows that the colour change happened first (after 2 h of experiment). The H_2S breakthrough then follows after 5 h.

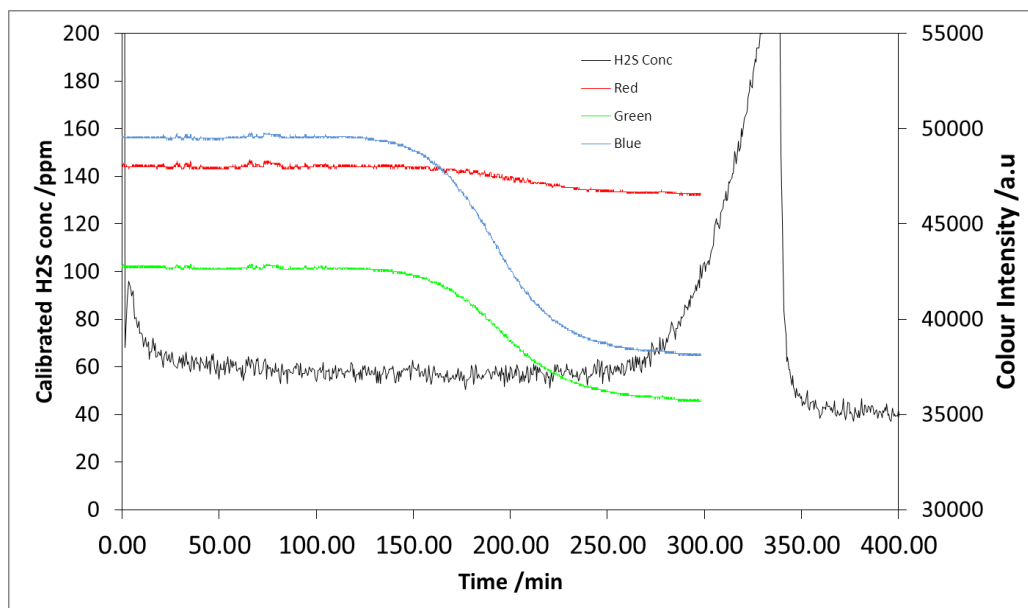


Figure 1.3.5-4: Colour intensity using 5 cm bed of Cu_3BTC_2 coated spheres

Cu_3BTC_2 material before testing showed a blue colour and after the testing was turned into a green-black material. This indicates the adsorption of H_2S on the surface of the spheres (see Figure 1.3.5-5).

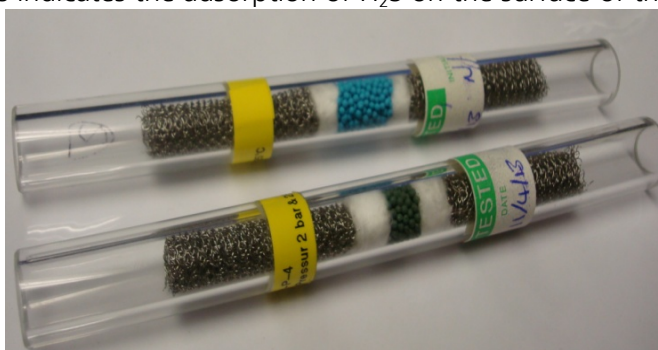


Figure 1.3.5-5: Cu_3BTC_2 coated spheres colour change from blue to green-black after the H_2S adsorption

1.3.5.2 Task 6.2 Safe gas delivery system

SIAD developed a dedicated high pressure gas cylinder for demonstration of the capability of the usage of MOFs for a safe storage of industrial gases. The demonstrator has been designed for a capacity of 200 ml granulated MOF.

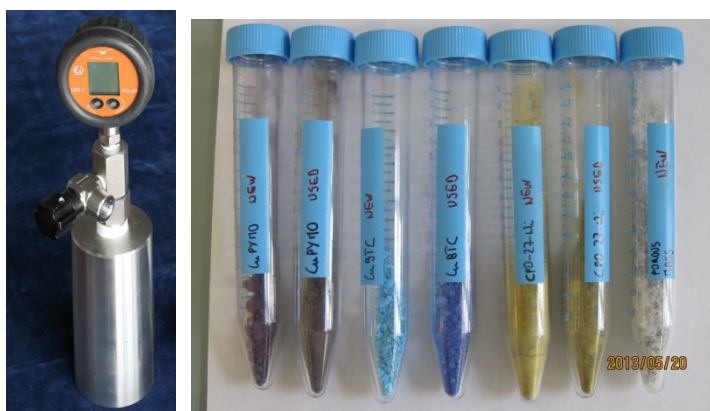


Figure 1.3.5-6: Assembled demonstrator unit for safety gas storage (left) filled with different MOFs (right)

The demonstrator unit has been equipped with five different MOFs ($\text{Cu}(\text{pymo})_2$, MIL-100(Fe), $\text{Cu}_3(\text{BTC})_2$, CPO-27-Ni, UiO-66). The storage capacity has been tested again CO, CH_4 and Kr. The usage of MOFs results in an increase of the storage capacity of the as cylinder up to a factor of 3.5, compared to an empty cylinder.

Furthermore, the effect of a significant purification of the gas during the gas release could be detected. The level of impurities in the released gas was reduced by a factor 5 compared of the raw gas.

In addition, the demonstrator setup has been successfully tested for the separation of a rare gas mixture.

1.3.5.3 Task 6.3 Pilot plant esterification process

In the present task dedicated to the esterification of oleic acid with glycerol for the selective production of monoglyceride, different generations of MOF catalysts were tested in batch and continuous tubular reactors.

A solvent was firstly chosen to allow the two immiscible phases, the organic phase containing fatty acid and the aqueous phase glycerol, to mix together.

In batch catalytic conditions performed at lab scale, the oleic acid concentration and reaction temperature were limited for the sake of the catalyst stability. The various experiments conducted yielded conversion of oleic acid saturating at about 60%. Therefore, given the constraints on operating conditions in batch due to the catalyst sensitivity, the experimental activity was shifted to tubular reactor experiments.

In continuous conditions performed at demo scale, either in homogeneous or heterogeneous flow reactor process, the oleic acid conversion varied from 40 to around 80%, depending on temperature and also residence time. This process is thermodynamically driven, as expected in esterification reactions, and limited here to around 80%. The lack of change in conversion when comparing homogeneous and heterogeneous operations is a result of the balance between the contribution of the catalytic process and the loss of volume taken by the solid catalyst in the reactor. After removal of t-butanol and water, the measured selectivity to monooleine was extremely high (>95%) in most experiments with dioleine as only by-product, thus well beyond the targeted value in the initial proposal (>80%). These results demonstrate the proof of concept of this new process. However, testing of the MOF catalysts so far has not indicated a significant contribution of catalyst to the oleic acid conversion.

Modeling work was also performed to support this continuous process and check its scale-up-ability on industrial level. Based on these simulations, the performances of the new NanoMOF process as compared to the existing one are summarized in the table here after. The negative points noted in the new process are principally due to the consumption of solvent as compared to Oleon process which is solvent free. As outlooks, the solvent content should be reduced by at least a factor of two.

Table 1.3.5-1: Pro and Cons of new process as compared to Oleon existing process.

Item	OLEON	NanoMOF at M48
Conversion	+	-
Selectivity	-	+
Glycerol separation yield	-	+
CAPEX	+	-
Waste	+	-
Raw material consumption	+	-

As a conclusion, the target of selectivity in monoglyceride is achieved. From NanoMOF testing results and process simulation, we expect that all of the NanoMOF targets can be achieved at demonstration scale. The reduction in waste production and energy consumption remains to be optimized to make it an economically viable process.

1.3.6 WP 7: Roadmap, conclusion, and outlook

For evaluation of future developments and focus in the research and application of MOFs a roadmap was developed. The roadmap identifies the gaps to fill for MOF to penetrate the markets and to give recommendations for further R&D programs. The topics, which are addressed in the roadmap, cover the domains of catalysis, protective clothes, respiratory filters, gas storage and gas purification. For the different topics, markets and technico-economical assessments have been performed when data are available. The main points which have been addressed are:

- Market analysis
- How MOF can contribute to sustainable growth in Europe and in the world
- What are the limiting factors, technology and scientific limitations, which prevent the penetration of MOF in the market. What are the gaps to be filled?
- Guidelines for future R&D programs

1.3.7 WP 8: Transversal activities: dissemination, Training

Dissemination and exploitation was an important topic of the nanoMOF project.

At the beginning of the project, a project website has been created with an internal and a public access (<http://www.nanomof-project.eu>). In total 9 GA meetings took place. Each meeting was used to learn more about the host organization, about its business and facilities. Beside the mandatory GA project meetings, Cluster meetings and WP-meetings were held as well as numerous phone conferences.

The scientific results obtained led to the publication of 24 papers in international recognized papers, and to the participation to 30 international conferences.

In addition, two dedicated events are particularly noteworthy. Two workshops were organized: The first workshop "MOF Synthesis and Structure" (25/11/2010, London/GB) focused on fundamental tasks in the synthesis of MOF, the second workshop "MOFs for industrial applications"(23/11/2011, Bergamo/I) focused on the potential applications of MOFs. In total 130 attendee from research and industry in the field of MOFs were brought together.

1.4 Potential impact

The discovery of porous hybrid materials constructed from inorganic nodes and organic multifunctional linkers has established a new area of inorganic-organic hybrids (Metal-Organic Frameworks, MOFs) with extraordinary performance as compared to traditional porous solids such as zeolites and activated carbon. The European joint project "nanoMOF" focused the activities to integrate nanostructured MOFs into products with industrial impact within a strong cooperation of established MOF research institutions and industrial end users. All parts of the development chain, respectively the future value chain, were addressed in the frame of the project: synthesis route of different MOF, up-scaling of MOF synthesis, processing of MOF material, integration of MOF into industrial relevant processes and products. The development of technologies and integration of MOFs are supported by advanced modelling, simulation and process monitoring techniques. The project aimed for a higher integration of MOFs into products with a high added value in order to propel Europe into an internationally leading position in the industrial use of MOFs.

The nanoMOF project was designed in such a way, that different application areas were addressed. All activities starting from the MOF synthesis, processing and up to the integration of MOFs were derived decidedly from the target applications.

Impact area "Gas purification": The purity of gases has an important economic and environmental relevance. Specific porous materials for selective gas adsorption require an application in advanced filter systems. Industrial feed gases and exhaust gases require a high purity to ensure durable processes and avoid pollution. The integration of MOFs into textile products enables the development of novel filter materials with high air permeability and a high capacity of the elimination of toxic compounds from air and industrial feed gases. For industrial and house-hold applications novel MOF-based gas purification systems can be developed.

Impact area "Safe gas storage and delivery": Safe and high capacity storage of high purity gases is crucial for tool operation in semiconductor and solar industry. With the aid of porous hybrid materials, the storage capacity of tank systems will be enhanced. Adsorptive gas storage is achieved under reduced pressure will improve handling safety. Furthermore, the adsorption of gaseous impurities results in a purification of the released gases.

Impact area "Catalysis": Catalysis is an ecologically relevant and economically attractive technology. The replacement of liquid acids by solid state catalysts avoids the production of toxic liquid waste. Decidedly designed MOF catalysts have the potential to support the conversion of natural resources into valuable products for the oleochemical industry.

The nanoMOF project produced significant contributions for all addressed application fields, in the whole MOF process chain. In the frame of the nanoMOF project, 16 exploitable results have been identified. This exploitable foreground has been clustered in different sectors of applications. The potential impact sectors are chemical industry, gas purification, personal protection, gas storage, oleochemical industry, material testing, training.

The exploitable results in the area of chemical industry have been especially focused on the ability to supply industrial quantities of MOF, because the limited availability of MOFs has being addressed as a major obstacle. The synthesis formulation and technologies for up scaling the MOF production, and the delivery of MOF in the kg scale are remarkable. Furthermore, the attention has turned to reduced solvent processes and solvent-free processes to scale up metal organic frameworks. This provides an opportunity to decrease solvent use drastically during the scale up. The nanoMOF project has demonstrated scale up of MOFs up to 20 kg by a reduced solvent method route for the different applications in the consortium. More sustainable processes have been identified as the way forward to scale up this type of material. The impact of this result on potential growth in Europe has been rated as been substantial and the impact will be immediate.

The exploitable results in the sector of gas purification has shown that the development of a MOF material for this application which may be regenerated (in contrast to current products) is possible and could create a niche application in this substantial market.

The application of H₂S removal acts as a demonstrator process. The knowledge gained from the work allows estimating the application of MOFs in related field as (ultra)purification, in a moderate volume, high value regime due to their advanced technology. Potential applications are seen in the field of nanotechnology, aerospace, automotive, biotechnology and medical applications.

The exploitable result in the field of personal protection has created foreground in the areas of skin and respiratory protection. The synthesis of porous material with high capacity for removal of toxic gas was demonstrated. A significant higher capacity for the target gases was shown compared to state of the art materials such as activated carbon. Afterwards the application of new gas filter structure with MOFs for respiratory protection was demonstrated in respiratory canisters. Novel air permeable textile material with MOFs for skin protection was demonstrated in special protective clothing. The developments are strongly linked with the dedicated technology developed for MOF-loading to nonwoven materials. A 3D-adsorption system with a very high active surface was created.

The technologies developed show in an exemplary manner the MOF formulation and processing up to a dedicated gas filter. Based on developed technology chain, further target gases are addressable. The technologies developed impact directly the equipment of first responders with an inherent need for skin and respiratory protection from chemicals (fire brigade, technical rescue, and police).

Beyond the personal protection, the activities spread to conventional fields of application of industrial gas filter.

In the area of gas storage the exploitable results are concentrated on the area of expensive gases for electronic industry. The work did show that gas storage in MOF-loaded cylinders is possible and also that loading cycles are possible. The total storage capacity for electronic grade gas increase, resp. the same storage capacity of gases is possible at lower pressure. Furthermore, the predicted effect of gas purification during the gas release was detected. For a successful application of the created foreground, that means for the industrial implementation, the availability of MOFs on a multi ton scale is required. Then, a product with reduce life cycle cost and environmental impact (especially the transportation of more gas per cylinder) may be achieved. In addition, the reduced gas pressure in the cylinder results in a higher safety during cylinder handling procedures. Lower pressure in the gas cylinder also results in lower requirements in gas infrastructure.

Furthermore, the selective gas adsorption on porous materials opens new concepts for gas separation, esp. in the production of rare gases.

The MOFs used in the cylinder has to be tailored processed to granulates, which match the requirements for being applied in gas storage as adsorbents. Developed technology for MOF shaping is essential for any MOF usage as bulk material as in gas separation and filtration processes.

The foreground in the sector of oleochemical industry was created in the area of esterification of fatty acids. The esterification of fatty acids for the food industry is a rather small market, but with high added value which may open perspectives for MOFs. The use of non-toxic metal in MOF catalyst enables the same or better performance of esterification processes at lower cost (regarding energy and by products). Furthermore, it causes a reduced carbon footprint. The improved reactor unit using a MOF catalyst created did work. The applied MOFs show process catalytic properties, which are not found in the classical acid/base catalysts. Regarding the contribution to a sustainable growth, this finding is interesting for the market of catalysts in chemical processing which is much segmented and MOF catalyst will have to find their way through to the special applications.

Although the area of testing is not an area exclusive to MOFs, exploitable results have been created which are especially in the area of laser gas analysers and infrared sensors for toxic gas monitoring. The foreground created in this area will have an impact of growth as devises will be sold also to other industrial areas and will stimulate growth also there. Besides this, a test equipment for analyzing

adsorptive and absorptive capacities of MOFs on a very small scale has been created which is applicable very general for porous materials, for any other adsorptive materials or for filter structures.

The last exploitable foreground has been created in the area of training. Within the nanoMOF project two workshops have been held. The workshops brought together experts from the scientific MOF community with potential user of the developed MOF technology from industry.

The material and knowledge created in the frame of project has been used for input into other MOF related conferences. The results of the nanoMOF-project were published in a series of scientific publications in international journals (24 papers). The nanoMOF-researchers participated in 33 conferences and reported on the nanoMOF-results.

But, the nanoMOF project identified the current hurdles for a further spreading of MOF technologies, as well. For all applications and impact areas, a tailored MOF production for suitable sized and physically stable MOF particles is mandatory necessary. The scaling up synthesis of the MOF material is still the limiting step in the progress of the technology. Production of MOF at semi-industrial and industrial scale will definitively open market opportunities. Directly linked to this issue are the cost of the MOF material, which have to be decrease significantly. It seems that there are no technological or scientific limitations but there are still some development steps to take.

The foreground created in the nanoMOF project will stimulate sustainable growth in Europe as the transportation of knowledge will help to find applications and exploitation of the results of the project as well as transfer of this knowledge to other areas of application.

All of the partners in the consortium follow up their exploitable results also after the project and expect, depending on MOF availability and price, to be able to market products in the near and midterm future.

2 Use and dissemination of foreground

2.1 Section A (public)

2.1.1 A1: Project Publications (Peer reviewed publication)

Copy from the participant portal (www.ec.europa.eu)

N°	D.O.I.	Title	Author(s)	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Date of publication	Relevant pages	Open access is/will be provided to this publication
5	10.1016/j.cattod.2011.03.017	Heteropolyacid encapsulated in Cu ₃ (BTC) ₂ nanocrystals: An effective esterification catalyst	Lik H. Wee	Catalysis Today	1 / 171	Elsevier		01/08/2011	00275-00280	No
6	10.1021/cm902899t	Adsorption of Harmful Organic Vapors by Flexible Hydrophobic Bis-pyrazolate Based MOFs	S. Galli	Chemistry of Materials	5 / 22	American Chemical Society		09/03/2010	1664-1672	No
7	10.1002/anie.201003314	Cation-Exchange Porosity Tuning in Anionic Metal-Organic Frameworks for the Selective Separation of Gases and Vapors and for Catalysis	Elsa Quartapelle Procopio, Fátima Linares, Carmen Montoro, Valentina Colombo, Angelo Maspero, Elisa Barea, and Jorge A. R. Navarro	Angewandte Chemie - International Edition	49	John Wiley and Sons Ltd		24/09/2010	7308-7311	No
8	10.1021/ja2042113	Capture of Nerve Agents and Mustard Gas Analogues by Hydrophobic Robust MOF-5 Type Metal-Organic Frameworks	Carmen Montoro	Journal of the American Chemical Society	31 / 133	American Chemical Society		10/08/2011	11888-11891	No
10	10.1002/anie.201303484	Highly Hydrophobic Isoreticular Porous Metal-Organic Frameworks for the Capture of Harmful Volatile Organic Compounds	Natalia M. Padial	Angewandte Chemie - International Edition	/	John Wiley and Sons Ltd		26/06/2013	0	No
11	10.1016/j.micromeso.2012.02.021	Adsorptive capturing and storing greenhouse gases such as sulfur hexafluoride and carbon tetrafluoride using metal-organic frameworks	Irena Senkowska	Microporous and Mesoporous Materials	/ 156	Elsevier		01/07/2012	115-120	No
11	10.1002/ade	MOF Processing by Electrospinning for	Marcus Rose	Advanced	4 / 13	Wiley-		01/04/2011	356-360	No

N°	D.O.I.	Title	Author(s)	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Date of publication	Relevant pages	Open access is/will be provided to this publication
	m.201000246	Functional Textiles		Engineering Materials		VCH Verlag				
12	10.1039/c2cc34840c	A highly porous metal–organic framework, constructed from a cuboctahedral supermolecular building block, with exceptionally high methane uptake	Ulrich Stoeck	Chemical Communications	88 / 48	Royal Society of Chemistry		03/10/2012	10841-180843	No
13	10.1002/cctc.201000055	Investigation of Acid Centers in MIL-53(Al, Ga) for Brønsted-Type Catalysis: In Situ FTIR and Ab Initio Molecular Modeling	Ugo Ravon	ChemCatChem	10 / 2	Wiley - VCH Verlag GmbH & CO. KGaA		11/10/2010	1235-1238	No
14	10.1039/c0cs00082e	X-ray absorption spectroscopies: useful tools to understand metallorganic frameworks structure and reactivity	Silvia Bordiga	Chemical Society Reviews	12 / 39	Royal Society of Chemistry		29/10/2010	4885-4927	No
15	10.1002/cssc.201000458	Tailoring Metal-Organic Frameworks for CO ₂ Capture: The Amino Effect	Jenny G. Vitillo	ChemSusChem	9 / 4	Wiley-VCH Verlag		19/09/2011	1281-1290	No
16	10.1039/c2dt31977b	Soft synthesis of isocyanate-functionalised metal–organic frameworks	Jenny G. Vitillo	Dalton Transactions	47 / 41	Royal Society of Chemistry		10/10/2012	14236-14238	No
17	10.1021/jp2117856	Quantitative Characterization of Breathing upon Adsorption for a Series of Amino-Functionalized MIL-53	M. Pera-Titus	Journal of Physical Chemistry C	17 / 116	American Chemical Society		03/05/2012	9507-9516	No
18	10.1021/jp210174h	Guest-Induced Gate Opening and Breathing Phenomena in Soft Porous Crystals: Building Thermodynamically Consistent Isotherms	Marc Pera-Titus	Journal of Physical Chemistry C	2 / 116	American Chemical Society		19/01/2012	1638-1649	No
19	10.1039/C1DT11700A	Engineering MIL-53(Al) flexibility by controlling amino tags	Tristan Lescouet	Dalton Transactions	43 / 40	Royal Society of Chemistry		06/10/2011	11359-11361	No
20	10.1039/c2jm15966j	Homogeneity of flexible metal–organic frameworks containing mixed linkers	Tristan Lescouet	Journal of Materials Chemistry	20 / 22	Royal Society of Chemistry		07/03/2012	10287-10293	No
21	10.1039/C0C01447H	Convenient synthesis of Cu ₃ (BTC) ₂ encapsulated Keggin heteropolyacid nanomaterial for application in catalysis	Lik H. Wee, Sneha R. Bajpe, Nikki Janssens, Ive Hermans, Kristof Houthoofd, Christine E. A. Kirschhock and Johan A. Martens	Chemical Communications	n/a	Royal Society of Chemistry		07/10/2013	8186-8188	No

N°	D.O.I.	Title	Author(s)	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Date of publication	Relevant pages	Open access is/will be provided to this publication
21	10.1002/cctc.201200288	The Origin of the Activity of Amine-Functionalized Metal-Organic Frameworks in the Catalytic Synthesis of Cyclic Carbonates from Epoxide and CO ₂	Tristan Lescouet	ChemCatChem	11 / 4	Wiley - VCH Verlag GmbH & CO. KGaA		01/11/2012	1725-1728	No
22	10.1002/9783527635856.ch9	Metal-organic frameworks as catalyst for organic reactions	Lik H Wee, Luc Alaerts, Johan A Martens, Dirk Devos	Wiley Interdisciplinary Reviews: Cognitive Science	n/a	John Wiley and Sons Inc.		19/07/2011	191-212	No
22	10.1039/c3dt32714k	An alternative pathway for the synthesis of isocyanato- and urea-functionalised metal-organic frameworks	Tristan Lescouet	Dalton Transactions	23 / 42	Royal Society of Chemistry		27/03/2013	8249-8258	No
23	10.1002/cctc.201300581	Hierarchical Zeolitic Imidazolate Framework-8 Catalyst for Monoglyceride Synthesis	Dr. Lik H. Wee, Tristan Lescouet, Jayashree Ethiraj, Dr. Francesca Bonino, Dr. Roxana Vidruk, Dr. Eva Garrier, Dr. Dirk Packet, Prof. Silvia Bordiga, Dr. David Farrusseng, Prof. Moti Herskowitz and Prof. Johan A. Martens	ChemCatChem	1	Wiley - VCH Verlag GmbH & CO. KGaA		24/08/2013	0	No
23	10.1039/C2JM31536J	Fine tuning of the metal-organic framework Cu ₃ (BTC) ₂ HKUST-1 crystal size in the 100 nm to 5 micron range	Lik H. Wee, Martin R. Lohe, Nikki Janssens, Stefan Kaskel and Johan A. Martens	Journal of Materials Chemistry	n/a	Royal Society of Chemistry		02/05/2012	13742-13746	No
24	10.1007/s10562-013-0970-1	Synthesis of Monoglycerides by Esterification of Oleic Acid with Glycerol in Heterogeneous Catalytic Process Using Tin-Organic Framework Catalyst	Lik H. Wee	Catalysis Letters	4 / 143	Springer Netherlands		01/04/2013	356-363	No

2.1.2 A2: Project Dissemination Activities

Copy from the participant portal (www.ec.europa.eu)

N°	Type of activities	Main leader	Title	Date	Place	Type of audience	Size of audience	Countries addressed
1	Organisation of Workshops	TECHNISCHE UNIVERSITAET DRESDEN	"MOF Synthesis and Structure"	25/11/2010	London, UK	Scientific community (higher education, Research) - Industry	60	international
2	Organisation of Workshops	TECHNISCHE UNIVERSITAET DRESDEN	„MOFs for industrial applications “	23/11/2011	Bergamo, Italy	Scientific community (higher education, Research) - Industry		international
3	Posters	FRAUNHOFER-GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V	nanoMOF: nanoporous metal-organic frameworks for production	05/09/2010	Marseilles, France	Scientific community (higher education, Research) - Industry		international
4	Posters	FRAUNHOFER-GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V	Assessment of MOF performance for gas separation: FTIR based breakthrough testing	05/09/2010	Marseilles, France	Scientific community (higher education, Research) - Industry		international
5	Articles published in the popular press	INNOVATEX TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	Nanoporózus fém-organikus vegyületek gyártása (Nanoporous Metal-Organic Frameworks for production)	15/11/2010	Hungary	Industry		Hungary
6	Flyers	INNOVATEX TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	Nanoporózus fém-organikus vegyületek gyártása (Nanoporous Metal-Organic Frameworks for production)	06/07/2011	Hungary	Scientific community (higher education, Research) - Industry		Hungary
7	Articles published in the popular press	INNOVATEX TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	Félidős a textiles NanoMOF projekt (Textile NanoMOF Project at Halfway Point)	20/10/2011	Hungary	Scientific community (higher education, Research) - Industry		Hungary
8	Posters	INNOVATEX TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	NanoMOF – NANOPOROUS METAL-ORGANIC-FRAMEWORKS FOR PRODUCTION	08/05/2013	Hungary	Scientific community (higher education, Research) - Industry		international
9	Posters	TDL SENSORS LTD	The application of TDLS to evaluate Metal Organic Frameworks (MOFs) in new industrial products	11/07/2011	Zermatt, Switzerland	Scientific community (higher education, Research) - Industry		international
10	Posters	TDL SENSORS LTD	The application of TDLS to evaluate Metal Organic Frameworks (MOFs) in new industrial products	13/09/2011	Murnau, Germany	Scientific community (higher education, Research) - Industry		international
11	Exhibitions	Blücher GmbH	Application of Metal Organic Frameworks in Personal Protection	03/06/2013	Stockholm, Sweden	Scientific community (higher education, Research) - Industry	300	international
12	Flyers	NORAFIN INDUSTRIES (GERMANY) GMBH	MOF-particle loaded nonwovens	01/06/2013	Germany	Scientific community (higher education, Research) - Industry	150	international
13	Posters	NORAFIN INDUSTRIES (GERMANY) GMBH	Nanoporous Metal-Organic Framework (MOF)	24/05/2011	Germany	Scientific community (higher education, Research) - Industry		international

N°	Type of activities	Main leader	Title	Date	Place	Type of audience	Size of audience	Countries addressed
14	Posters	NORAFIN INDUSTRIES (GERMANY) GMBH	Nanoporous Metal-Organic Framework (MOF)	11/06/2013	Germany	Scientific community (higher education, Research) - Industry		international
15	Articles published in the popular press	NORAFIN INDUSTRIES (GERMANY) GMBH	MOF Shaping & Immobilisation IN: Metal-Organic Frameworks: Applications from catalysis to gas storage	01/12/2011	Germany	Scientific community (higher education, Research) - Industry		international
16	Oral presentation to a scientific event	INNOVATEXT TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	News from INNOVATEXT Institute	10/09/2012	Madeira, Portugal	Scientific community (higher education, Research)	32	international
17	Posters	INNOVATEXT TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	NanoMOF project – Nanoporous metal organic frameworks for production	30/05/2013	Budapest, Hungary	Industry	50	Hungary
18	Articles published in the popular press	INNOVATEXT TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	Nanokémia a védőruházatban – a NanoMOF projekt	20/05/2013	Hungary	Industry		Hungary
19	Oral presentation to a wider public	INNOVATEXT TEXTILIPARI MUSZAKI FEJLESZTO ES VIZSGALO INTEZET RT	News in the field of PPE raw materials	28/05/2013	Budapest, Hungary	Industry	50	Hungary
20	Posters	UNIVERSITA DEGLI STUDI DI TORINO	Tailoring MOFs for CO2 capture: the amino-effect	05/09/2010	Marseille (France)	Scientific community (higher education, Research)		international
21	Posters	UNIVERSITA DEGLI STUDI DI TORINO	Tailoring MOFs for CO2 capture: the amino-effect	27/09/2010	Lyon (France)	Scientific community (higher education, Research)		international
22	Oral presentation to a scientific event	UNIVERSITA DEGLI STUDI DI TORINO	Tailoring MOFs for CO2 storage: the amino-effect	26/07/2010	Lausanne (Switzerland)	Scientific community (higher education, Research)		international
23	Oral presentation to a scientific event	UNIVERSITA DEGLI STUDI DI TORINO	Amino-functionalised MOFs for CO2 storage: the role of the -NH2 groups	17/05/2010	Lausanne (Switzerland)	Scientific community (higher education, Research)		international
24	Posters	UNIVERSITA DEGLI STUDI DI TORINO	Response of CPO-27-Ni towards gas molecules	09/06/2011	Paris (France)	Scientific community (higher education, Research)		international
25	Oral presentation to a scientific event	UNIVERSITA DEGLI STUDI DI TORINO	Insight to the formation mechanism of the cluster based Zr-MOF, UiO-66: a Raman study	17/06/2012	Bari (Italy)	Scientific community (higher education, Research)		international
26	Posters	UNIVERSITA DEGLI STUDI DI TORINO	Green route to make reactive MOFs: diphosgene-free grafting of isocyanate groups	16/09/2012	Edinburgh (UK)	Scientific community (higher education, Research)		international
27	Posters	UNIVERSITA DEGLI STUDI DI TORINO	Element selective d-d transitions detected by Resonant Valence to Core XES: understanding molecular	16/09/2012	Edinburgh (UK)	Scientific community (higher education, Research)		international
28	Oral presentation to a scientific event	UNIVERSITA DEGLI STUDI DI TORINO	Green route to make reactive MOFs: diphosgene-free grafting of isocyanate groups	11/06/2013	Brussels (Belgium)	Scientific community (higher education, Research)		international
29	Oral presentation to	UNIVERSITA DEGLI STUDI DI	Design of hydrogen storage materials: A	04/04/2013	Pravets	Scientific community (higher		international

N°	Type of activities	Main leader	Title	Date	Place	Type of audience	Size of audience	Countries addressed
	a scientific event	TORINO	multitechnical approach		(Bulgaria)	education, Research)		
30	Oral presentation to a scientific event	UNIVERSITA DEGLI STUDI DI TORINO	Insights into adsorption of NH ₃ on HKUST-1 metal-organic framework: a multitechnique approach	23/06/2013	Alessandria (Italy)	Scientific community (higher education, Research)		national
31	Posters	UNIVERSITA DEGLI STUDI DI TORINO	Insights into adsorption of NH ₃ and H ₂ S on HKUST-1 metal-organic framework: a multitechnique approach	16/07/2013	Dresden (Germany)	Scientific community (higher education, Research)		international
32	Posters	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive capturing and storing greenhouse gases such as sulfur hexafluoride and carbon tetrafluori	17/09/2012	Edinburgh, UK	Scientific community (higher education, Research) - Industry	400	international
33	Posters	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive capturing and storing greenhouse gases such as sulfur hexafluoride and carbon tetrafluori	20/05/2012	Taipei / Taiwan	Scientific community (higher education, Research)		international
34	Posters	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive capturing and storing greenhouse gases such as SF ₆ and CF ₄	28/07/2012	Hiroshima, Japan	Scientific community (higher education, Research)		international
35	Posters	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive capturing and storing greenhouse gases such as sulfur hexafluoride and carbon tetrafluori	07/03/2012	Magdeburg/Germany	Scientific community (higher education, Research)		Germany
36	Posters	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive capturing and storing greenhouse gases such as SF ₆ and CF ₄	30/04/2012	Delray Beach, Florida,	Scientific community (higher education, Research)		international
37	Oral presentation to a scientific event	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive krypton storage	15/03/2013	Bad Wildungen, Germany	Scientific community (higher education, Research)		Germany
38	Posters	TECHNISCHE UNIVERSITAET DRESDEN	Adsorptive krypton storage using metal-organic frameworks	07/03/2013	Hamburg, Germany	Scientific community (higher education, Research) - Industry		Germany

2.2 Section B (confidential)

2.2.1 B1: Project Patents

Type of IP Rights	Application reference(s) (e.g. EP123456)	Intellectual Property Organisation	Subject or title of application	Confidential	Foreseen embargo date	Applicant(s) (as on the application)	URL of application
Patents	WO2012EP59094 20120516	-	PROCESS FOR PRODUCING PARTICLES COMPRISING METAL-ORGANIC FRAMEWORK COMPOUNDS	Yes		UNIV DRESDEN TECH [DE]; LOHE MARTIN R [DE]; ROSE MARKUS [DE]; KASKEL STEFAN [DE]; SENKOVSKA IRENA [DE]	http://worldwide.espacenet.com/publicationDetails/biblio?CC=WO&NR=2012156436&KC=&FT=E&locale=en_EP

2.2.2 Project Exploitable Foregrounds

See participant portal (www.ec.europa.eu)

3 Report on societal implications

See participant portal (www.ec.europa.eu)