

# Enmix A.I.S.B.L.

# European Nanoporous Materials Institute of Excellence

Newsletter - No. 5, August 2014

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Editorial

4<sup>th</sup> ENMIX Workshop

# Partner Profiles:

- Leibniz University of Hanover, D
   Institute for Physical Chemistry and Electrochemistry
- Italian National Research Council (CNR)
   Institute of Structure of Matter

# Company Profile:

• Clariant Produkte (Deutschland) GmbH, D

Dear Partners and Friends of ENMIX,

Welcome to the fifth newsletter of the European Nanoporous Materials Institute of Excellence (ENMIX)!

As you certainly know Horizon 2020 is the biggest EU Research and Innovation programme ever with nearly 80 billion Euro of funding available over 7 years (2014 to 2020). ENMIX must take this opportunity to initiate and/or participate in as many as possible Calls which are directly or indirectly devoted to nanoporous materials. As a benefit from its membership in SPIRE, ENMIX is well prepared to get early access to forthcoming Calls and to bring up new topics for future Calls. Several project proposals and project ideas are currently on the way!

We are very much pleased to invite you to attend the 4<sup>th</sup> ENMIX workshop which will take place from September 17-19, 2014, at Hotel Golf, Bled, Slovenia. The workshop will be held under the general theme "Nanoporous Materials for Advanced Applications", and four sessions devoted to "Oil and Biomass based Chemistry", "CO<sub>2</sub> Capture and Valorization", "Fundamental Research on Nanoporous Materials", and "Water Treatment" are currently planned. You will find more detailed information on the workshop in this newsletter and on our website www.enmix.org.

To foster the cooperation between ENMIX labs, an ENMIX Young Scientist Forum will be founded. The kick-off meeting of the ENMIX Young Scientist Forum will take place in Ljubljana immediately after the 4<sup>th</sup> ENMIX workshop. We hope that the new forum will be a great success and a valuable tool for strengthening the ENMIX network also on the level of the PhD students and Postdocs. We hope to have an active participation from all the ENMIX laboratories!

As usually, the present newsletter also contains profiles of two of our academic ENMIX partners, viz. the University of Hanover / Germany and CNR / Italy, and one profile of a company, this time Clariant, which is strongly engaged in the field of nanoporous materials.

Enjoy reading the newsletter!

Elias Klemm

Slavko Kaučič

7 Yours

# The 4th ENMIX Workshop entitled

# **Nanoporous Materials for Advanced Applications**

will take place from September 17-19, 2014, at Hotel Golf, Bled, Slovenia, organized by V. Kaučič (local organizer) and E. Klemm (CEO of ENMIX).



The workshop will start on September 17, 2014, around noon and will end also around noon on September 19, 2014.

The program will include **4 keynote lectures**, about **14 oral** presentations, a poster session, the ENMIX Award ceremony, and a conference dinner.

On Friday afternoon (Sept. 19) and Saturday morning (Sept. 20) an

# **ENMIX Young Scientists Forum**

will be founded and organised.

"Registration is open! See: www.enmix.org"

# Leibniz University Hannover, Germany Institute of Physical Chemistry and Electrochemistry Group of J. Caro

Research in the group of J. Caro at the Institute of Physical Chemistry and Electrochemistry is focused on inorganic materials for energy effective separation and catalysis including the fundamental aspects of energy transformation, energy transport and energy storage. The detailed working fields are

- Catalysis reaching from inorganic preparations (catalyst. membranes) on one hand side and engineering aspects like catalytic membrane reactors on the other hand.
- Study of the catalytic processes of syngas by partial oxidation of methane, methane aromatization, oxidative coupling of methane, ammonia oxidation to NO, olefins by oxi-dehydrogenation in different reactors (fixed bed, membrane reactors)
- Membrane gas separation using different kinds of inorganic membranes like zeolites.
   MOFs, mixed matrix, carbon, perovskites.
- Membrane applications in dye sensitized solar cells (after Grätzel), and fuel cells (proton conducting membrane with modifiers)
- Preparation, stabilization and assembling of metal, oxide and semiconductor nanoparticles for applications in catalysis, photovoltaics

# Organigram of the Caro research group

Head: Prof. Dr. Jürgen Caro
Vice: Prof. Dr. Armin Feldhoff
Secretary: Yvonne Gabbey-Uebe
Technicians: Kerstin Janze, Frank Steinbach

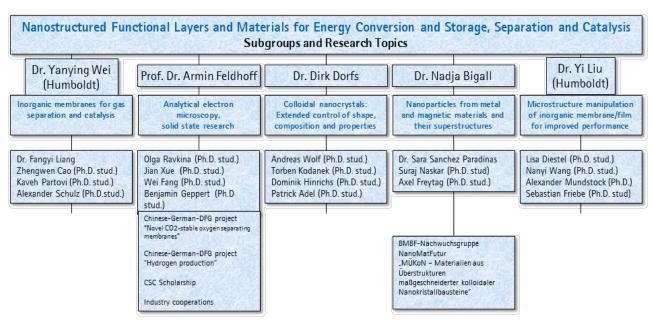


Figure 1: The organogram of the Caro group, state March 2014. Third party additional money of about 1.5 Mio € per year.

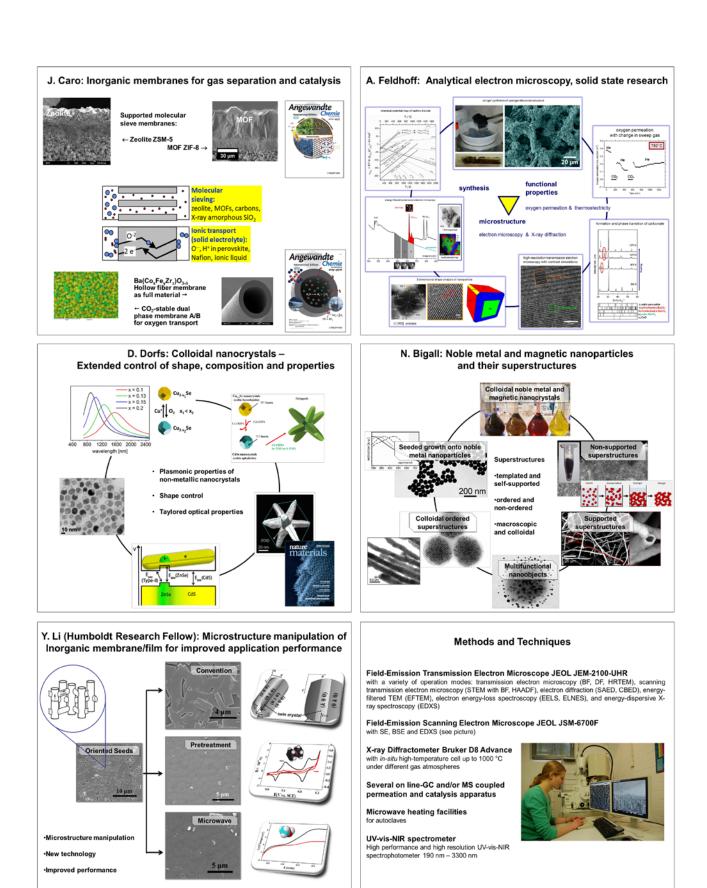
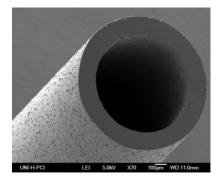


Figure 2: Main research activities of the Caro group, state March 2014. The research fields of 5 principal investigators are shown.

### Catalytic Membrane Reactor: Use of oxygen transporting perovskite membranes

Two recent examples shall demonstrate our concept of catalytic membrane reactor with oxygen-conducting perovskite membrane. Two types of membranes have been used: Tubular geometries as hollow fibers from a spinning process and planar geometries as discs.



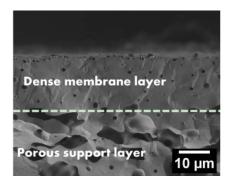


Figure 3: Hollow fiber perovskite membrane with 1 mm outer diameter and 150  $\mu$ m wall thickness of the chemical composition BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Zr<sub>0.2</sub>O<sub>3- $\delta$ </sub> prepared at the FhIGB Stuttgart by Dr. T. Schiestel (left), and a high-flux 20  $\mu$ m thin perovskite layer of the composition Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3- $\delta$ </sub> (BSCF) on a porous support of the same composition made by FZ Jülich by W. Meulenberg and S. Baumann. The same membrane structure was prepared with the chemical composition La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3- $\delta$ </sub> (LSCF).

Studying the methane de-hydro-aromatization in a non-oxidative fixed bed reactor (6  $CH_4 \rightarrow C_6H_6 + 9$   $H_2$ ) and in a membrane reactor with oxygen transporting  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF) membrane (6  $CH_4 + 9/2$   $O_2 \rightarrow C_6H_6 + 9$   $H_2O$ ), the aromatics (benzene, toluene, naphthalene) yield in the membrane reactor after 1000 min time on stream was found to be three times higher than the yield in the classical fixed bed reactor. The improved performance of the membrane reactor is explained by the in situ combustion of the abstracted hydrogen which gives steam as an oxidant to avoid coke deposition. The use of a co-feed methane/oxygen feed in the classical fixed bed reactor is not possible since the relative high oxygen partial pressure destroys the active catalyst phase  $Mo_2C/HZSM-5$  which is only stable in reducing atmospheres or in the presence of low oxygen partial pressures as found in the membrane reactor. Table 1 shows that the aromatics yield in the membrane reactor is much higher in the BSCF membrane reactor than in the non-oxidative fixed bed reactor.

Table 1: De-hydro-aromatization of membrane in different reactors

Time / min	Aromatics yield / %		- CH <sub>4</sub>	Aromatics
	Membrane reactor	Fixed bed reactor		333333333 333333333
100	6.0	5.5	- 32000	State of the state
200	4.9	3.6	2e-	$\Omega^{2-}$
500	4.0	1.3	20	
580	3.3	1.1	Z.	Cao,
1000	3.0	0.4	Air	O2 depleted air

Jiang, H. Luo, S. Baumann, W.A. Meulenberg, J. Assmann, L. Mleczko, J. Caro: Natural gas to fuels and chemicals: Improved methane aromatization in an oxygen permeable membrane reactor, Angew. Chem. Int. Ed. 52 (2013) 1394-13797.

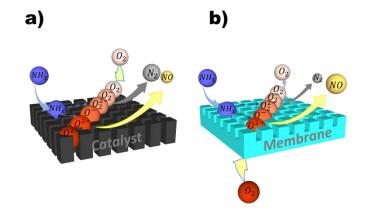
A perovskite-type catalytic membrane reactor with oxygen conducting perovskite membrane could be successfully evaluated in the <u>ammonia partial oxidation to NO</u>. Here the perovskite membrane has a double function: The La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-6</sub> (LSCF) perovskite membrane separates oxygen from air which is necessary in the Ostwald reaction for the ammonia partial oxidation according to  $4 \text{ NH}_{3} + 5O_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}$ , but no precious Pt/Rh metal was necessary since the LSCF perovskite surface itself was the catalyst. To enlarge the active surface, a porous LSCF layer was on top of the dense LSCF layer (Figure 3, right).

In the ammonia oxidation, 95 % NO selectivity and 81 % ammonia conversion could be achieved in a catalytic membrane reactor with asymmetric perovskite LSCF oxygen-permeable catalytically active membrane at  $850\,^{\circ}\mathrm{C}$ . The oxygen used in the selective ammonia oxidation is taken from the perovskite membrane, and the membrane is re-oxidized on the air side. In the classical Mars and van Krevelen mechanism, this re-oxidation takes place by gaseous oxygen present in the co-feed (Figure 4).

Z. Cao, H. Jiang, H. Luo, S. Baumann, W.A. Meulenberg, H. Voss, J. Caro: An efficient oxygen activation route for improved ammonia oxidation through an oxygen-permeable catalytic membrane, ChemCatChem 6 (2014) 000.

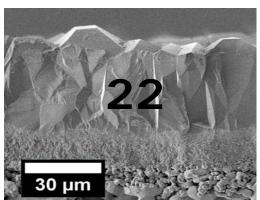
Figure 4: When using co-feed NH<sub>3</sub>/O<sub>2</sub> mixtures, high concentrations of adsorbed molecular oxygen spoil the selectivity in the case of the co-feed fixed bed (a). When the oxygen comes through the membrane, the LSCF membrane provides highly selective atomic oxygen species.

- a) In a partial oxidation on a perovskite catalyst in a classical co-feed fixed bed reactor, high concentrations of adsorbed molecular oxygen compete with oxidation by lattice oxygen and spoil selectivity.
- When sending the lattice oxygen through a membrane, only low concentrations of adsorbed molecular oxygen is found on the reaction side.



### Gas Separation by Membranes: Supported zeolite and MOF molecular sieve membranes

Membrane separation technology of gases and liquids is considered a key technology of a modern economy since membrane separation is an energy-efficient and environmentally friendly technology with low energy input and without waste. Increasingly powerful inorganic membranes like thin metal, ceramic or molecular sieve films are going to be developed since they open new applications like purification of natural gas, separation of air into oxygen and nitrogen, production of hydrogen for green technologies, processing of bio-fuels and chemicals in bio-refineries.



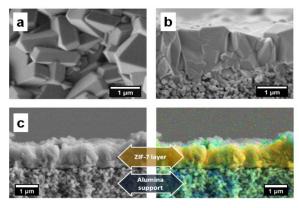
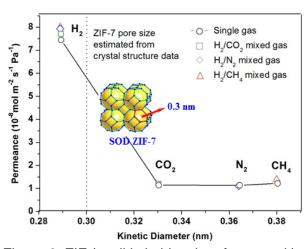


Figure 5: A relative thick supported ZIF-8 membrane is shown, grown on a graded asymmetric macroporous ceramic support (left). By using a seed technique and microwave heating, the MOF thickness could be reduced to about 1 µm.



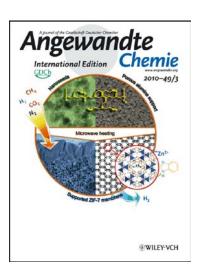


Figure 6: ZIF (zeolitic imidazolate framework) membranes as shown in Figure 5, have hydrogen selectivity.

Y. Li, F. Liang, H. Bux, A. Feldhoff, W. Yang, J. Caro, Molecular Sieve Membrane: Supported Metal-Organic Framework with High Hydrogen Selectivity, Angew. Chem. Int. Ed. 49 (2010) 548.

# Start of the Joint Laboratory on Inorganic Membrane Research Guangzhou (China) – Hannover (Germany) in November 2013

Chinese and German scientists play a worldwide pioneering role in this field, especially the groups of Haihui Wang at South China University of Technology and Juergen Caro at Leibniz University Hannover. Following the idea that one plus one can give more than two, Wang and Caro decided to start a Joint Lab on "Inorganic Membranes: Advanced Technology for Clean Energy and Clear Environment". This vision of a Joint Lab could be realized by the generous financing through the Sino-German Center for Research Promotion (SGC), Beijing. The SGC was founded jointly by the National Natural Science Foundation of China (NSFC) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) in 2000, and receives 50% of its funding from each of these organizations. SGC is unique in its status as a Chinese-German joint venture in research promotion.



On 26 November 2013, the Joint Lab was opened by a ceremony at the South China University of Technology (SCUT) in Guangzhou. By the end of the opening ceremony, the label of the Joint Lab at the main gate of the School of Chemistry and Chemical Engineering at the SCUT was unrevealed.

The photo shows the unveiling, from the left to right H.H. Wang, Z.G. Zhang, Q. Chang, M. Zhu (Chinese side), M.G. Zhao, J. Caro, J. Kuenzel (German side).

# Visiting Professorship for Juergen Caro from Leibniz University Hannover, Germany, at the Chinese Academy of Sciences

Chinese and German scientists play a worldwide pioneering role in this field of molecular sieve membranes, especially Prof. Aisheng Huang at the Ningbo Institute of Materials Technology & Engineering (NIMTE), Chinese Academy of Sciences (CAS) and Prof. Juergen Caro at Leibniz University Hannover. The two chemists Huang and Caro are also linked by a personal friendship dating back 6 years ago when A.S. Huang stayed together with J. Caro at Hannover University.

Huang and Caro decided to continue their cooperation, and to catalyze this cooperation, J. Caro has been appointed Visiting Professor at the CAS. A.S. Huang and Caro are also both principal investigators of the Joint Sino-German Lab on "Inorganic Membranes: Advanced Technology for Clean Energy and Clear Environment" which was founded in November 2013 and financed by the Sino-German Center for Research Promotion (SGC), Beijing. The SGC was founded jointly by the National Natural Science Foundation of China (NSFC) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) in 2000, and receives 50% of its funding from each of these organisations.



The picture shows Prof. Runwei Li, Vice Director at NIMTE, passing the document on the ceremony on Nov. 22, 2013.

#### **Breck Award of the International Zeolite Association**

J. Caro, professor of physical chemistry at Leibniz University Hannover has got together with Professor Michael Tsapatsis, University of Minnesota, USA, the Breck Award of the International Zeolite Association. The Breck Award is sponsored by UOP, a company belonging to Honeywell, and named after Donald W. Breck who was a former leading zeolite scientist of Union Carbide Corporation. The Breck Award is administered by the International Zeolite Association, and it is given every three years for the most significant contribution to Molecular Sieve Science and Technology made in the last 3 years. Caro and Tsapatsis have obtained the prize on the Moscow International Zeolite Conference in July 2013 in the presence of almost

thousand participants for their pioneering work on novel molecular sieve membranes.



The photo shows from the left: A. Corma, Chairman of the Breck Award Committee, University Valencia, Spain, J. Caro, Leibniz University Hannover, Germany, M. Tsapatsis, University of Minnesota, USA, and G. Bellussi, President of the International Zeolite Association, ENI Research, Italy.

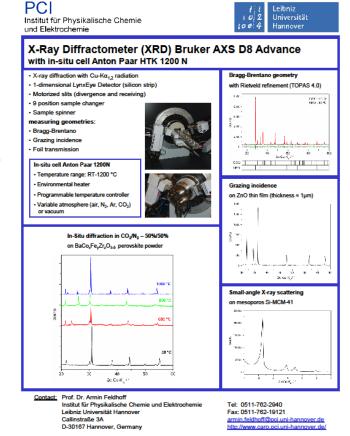
### Wilhelm-Ostwald-Medal 2013 for J. Caro

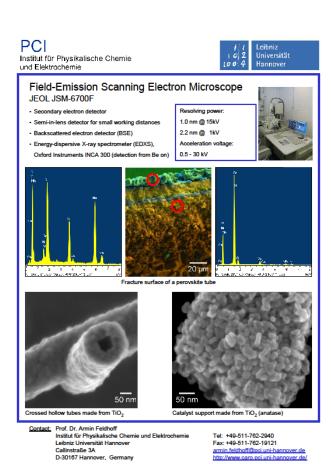


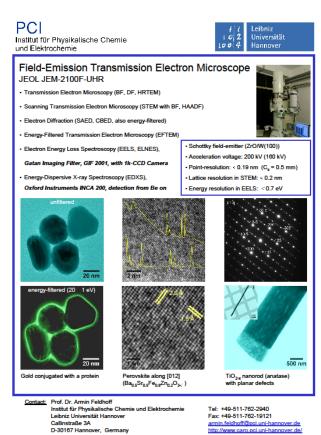
In April 2013, J. Caro ha sgot the Ostwald Medal of the Saxonian Academy of Sciences for his pioneering work on nanoporous materials in gas adsorption and membrane separation.

# **Equipment**

- 6 online-coupled HP gaschromatographs with permeation and catalysis apparatus
- Different microwave heating facilities with teflon autoclaves
- Different high-temperature ovens up to 1600 °C
- Zeta sizer
- Impedance spectroscopy
- UV-vis spectrometry
- · Confocal microscopy







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# Italian National Research Council Institute of Structure of Matter

The Italian National Research Council (CNR) is the largest governmental research body in Italy. It employs ca 4,400 researcher, with both permanent and temporary positions, some 600 graduated technical staff and ca 2000 technicians. It comprises 107 Institutes, grouped in 7 departments spanning from Biomedical Sciences to Cultural Heritage and Social Science and Humanities.

The Institute of Structure of Matter (ISM) belongs to the Department of Physical Sciences and Technologies of Matter (DSFTM) but it also has research interests connected with the Department of Chemical Science and Materials Technologies (DCSMT). The research activities in the Institute focus on synthesis and characterization of innovative materials, which are produced and studied with particular attention to their functionalities and their applications in the fields of advanced devices, magnetism and catalysis. The Institute Director pro tem is Dr. Claudio Quaresima. The Institute consists of 12 research groups, among these, the activities of 4 groups are described in more details in the following pages.



### Porous Materials and Heterogeneous catalysis group (Dr. Adriana de Stefanis)

The group was established over 25 years ago by the late Prof. Anthony A.G. Tomlinson and has experience in materials chemistry: colloids, clays, layered materials, zeolites, new porous materials including those designed not only from cheap raw materials, i.e. aluminas, silicas titanias and zirconias, but also new porous oxides and metals. Formulations include mainly powders but also membranes. The synthesised materials are investigated for sorption and catalytic properties, followed up by structural and spectroscopic characterisations, ranging from routine: UV/Vis (including reflectance and glancing angle), FT-IR including cells for following gas-solid interactions, e.p.r. + ENDOR, through to synchrotron radiation, XAS, and access to SAXS and SANS experiments for low-ordered materials. The group also has expertise in ion-exchange specialist chromatographic separations and small-scale catalytic reactions conducted by fast pyrolysis-based methods (gas/solid) adaptable also to multiphase catalysis. Modelling of sorption and catalysis processes and new porous structures is performed with the help of programs such as Cerius2 and Materials Studio.



# **Equipment**

X-Ray Diffraction (Seifert XRD 3003TT, Seifert XRD 3003P, Philips PW 1130/00); Thermogravimetry (Stanton Redcroft STA 1000); Physisorption/Chemisorption (Micromertics Gemini 2360); IR Spectrometers (PE 1760, PE Paragon 1000); UV-vis-NIR spectrophotometer (PE Lambda 9); Gas Chromatography; Mass Spectrometry; AAS (Varian 903), Sorption tests apparatus (non-commercial); Catalytic lab scale reactors; static autoclave (50 bar; 100 ml).

# Femto-Laser for Nanomaterials and Fast Spectroscopy (FemtoLas4NanoSpec) Laboratory (Dr. Antonio Santagata)

Ultrashort pulsed laser beams are employed for the production of nanostructured materials as well as time resolved spectroscopic methods for material characterization. The laser ablation technique is used in vacuum or gas environment for thin film depositions, on suitable substrates, of a wide variety of different materials which can be of technological interest (e.g. metals, oxides, carbides, nitrides, etc.). The peculiarity of the process induced by the use of ultrashort laser pulses, that is in the order of 100 fs, is related to the negligible electron lattice coupling effect following the excitation of the material's electrons caused by the incident laser pulse. This leads to the formation of plasma together with a non equilibrium fragmentation process generating a relevant amount (up to 80%) of ejected nanoparticles. The ablation process itself minimizes thermal mechanisms so that the nanoparticles produced retain the composition of the starting target. For the same reason ultra-short laser pulses are successfully used for high lateral resolution texturing of material surfaces (e.g. surface micromachining of Hf based ceramic material for CSP thermionic modules high efficient absorber, patent pending WO2014033690 A2 - appl. n. PCT/IB2013/058225). In liquid, the ultrashort laser ablation process straightforward generates nanoparticles, which can be even in a metastable phase (e.g. by ablation in water of: graphite, Ti or Ag, nanodiamonds -DLC, TiO<sub>2</sub> rutile microtubes or silver nanoparticles, have been produced, respectively). With the aim of characterising materials electronic structures and their adaptability for specific applications, such as donor-acceptor processes occurring in  $\pi$ -conjugated systems for optoelectronic applications, ultrashort laser pulses are employed for providing time resolved spectroscopic data (i.e. Pump and Probe or Up Conversion techniques). The FemtoLas4NanoSpec Lab capabilities have been exploited for carrying out the Combined Laser Nanotechnology -CLaN project founded by the Basilicata Region (http://www.pz.imip.cnr.it/clan/index.php/en/) within its Int. Cooperation Programme Framework.

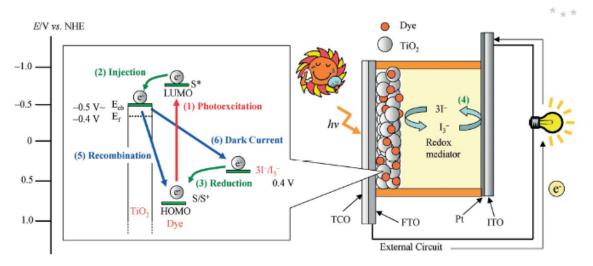


#### **Equipment**

The **FemtoLas4NanoSpec** lab is equipped with: 1) Ti:Sa ultrashort pulsed laser source (100fs, 800nm, 1 kHz, 4 mJ/pulse); 2) parametric amplifier (TOPAS C, 290-2500 nm, 50-300  $\mu$ J/pulse); 3) laser beam lines delay stage allowing time resolution of 1 fs; 4) two spectra detection systems equipped in turn with fast Intensified CCD or CCD detectors; 5) fast photodiode coupled with a Lock-in Amplifier and customized software for high resolution phenomena detection; 6) Time Correlated Single Photon Counting Module (TCSPC) with 10 ps time resolution working in the spectral range 300-900 nm; 7) ablation chamber facility. The ablation chamber which can work up to  $10^{-5}$  Pa, is equipped with an heating substrate holder ( $\leq 1500^{\circ}$ C) and remote controlled high precision translation stages (resolution 1  $\mu$ m) allowing well defined microtexturing of materials surfaces.

### Hybrid materials for molecular photovoltaic (Dr. Giovanna Pennesi)

Organic photovoltaic has an industrial interest particularly due to the need of enhancing conversion efficiency and lowering dissipated energy and production costs. Organic materials give the advantage of avoiding the conventional p-n junction (Si) giving much attention on charge separation at the interface donor/acceptor. All types of solid-state organic cells and dye-sensitized (Graetzel) cells are included together with all the hybrid technologies based on inorganic quantum dots incorporated in semiconductor polymeric matrices. In cells with planar or bulk hetero-junctions (PHJ o BHJ), the addition of phthalocyanines (Pcs) to polymers, fullerenes or carbon nanotubes is a possible strategy to reach high conversion coefficients. The optimization of all the various optical and electronic processes concurring at the solar light transformation into electricity is the main objective of the group studies, together with:



- 1) synthesis of phthalocyanine and porphyrin derivatives asymmetrically substituted with push-pull substituents;
- 2) synthesis of mixed phthalocyanine/porphyrin derivatives;
- 3) chemical-physical characterization of the products and anchoring tests to TiO<sub>2</sub>;
- 4) optical characterization (steady state and time-resolved absorption and emission);
- 5) electrochemical characterization;
- 6) photovoltaic cells preparation and testing (in collaboration).

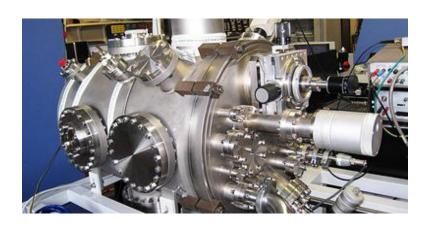
# **Equipment**

Controlled-environment facilities for air sensitive compounds syntheses.

Elemental analysis, UV-vis-NIR spectrophotometers for analysis both in solution (transmission) and solid state (reflectance); Steady state spectrofluorometer; FTIR spectrophotometers; powder x-ray diffractometer.

# Diamond & Carbon Compounds (DiaC<sup>2</sup>) Lab (Dr. Daniele M. Trucchi)

DiaC² has an experienced know-how in nucleation, deposition and study of properties of chemical vapor deposition (CVD) diamond. The group developed high performance diamond-based devices with an original design, by an appropriate tailoring of the building-block material properties: UV and X-ray detectors, dosimeters for radiotherapy, electron multipliers, nuclear-to-electrical energy converters. Room-temperature charged particles spectrometers based on proprietary metal-to-diamond technology, were successfully employed for monitoring of pulsed fast neutron sources at ISIS in UK. In the past few years, DiaC² also developed AIN thin films by pulsed laser deposition (PLD) and RF sputter techniques for electronic applications. Currently, DiaC² is involved in the development of high-temperature conversion modules for solar concentrating systems (www.ephestus.eu). The group is coordinating the EU project ProME³THE²US² (www.prometheus-energy.eu) for the development of photon enhanced thermionic emission devices for concentrated solar converters, in which a defect engineering strategy is applied on CVD diamond and III-V semiconductors.



### **Equipment**

DiaC<sup>2</sup> facilities include systems for the complete fabrication of devices: 1) Microwave CVD (2 kW, 2.45 GHz) and Hot-filament systems for mono- and poly-crystalline diamond film deposition; 2) Pulsed Laser Deposition (excimer laser, femtosecond laser) and RF sputtering systems for thin film deposition; 3) Optical photolithography (based on mask aligner Karl Suss MJB3) and Reactive Ion Etching (RF, 1 kW) systems for the definition of patterned structures; DiaC<sup>2</sup> also have a significant experience on material and device characterization. Microanalysis techniques that can be performed on materials include: SEM, AFM, Raman spectroscopy, XRD, XPS, UPS, spectral photometry. Fabricated devices can be electrically (resistivity, capacitance, DC and RF measurements) and optically (spectral photoconductivity, photoemission) fully characterized: all the characterization techniques can be integrated in a VTEC (Vacuum & Temperature Electronic Characterization) module, operating in the range 77-1300 K at pressures down to 10<sup>-9</sup> Torr.

# Contact:



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# Clariant

# **Overview and History**

Clariant AG is a global specialty chemicals company, headquartered in Muttenz, Switzerland. Today, Clariant is active in 4 Business Areas: Care Chemicals, Natural Resources, Catalysis & Energy and Plastics & Coatings. The Clariant organizational structure comprises 7 Business Units which are Additives, Catalysts, Functional Minerals, Industrial & Consumer Specialties, Masterbatches, Oil & Mining Services and Pigments.

Clariant was formed in 1995 as a spin off from the chemical company Sandoz, which was established in Basel in 1886. Clariant expanded through the incorporation of the specialty chemicals business of Hoechst (Germany) in 1997, and the acquisitions of BTP plc (UK) in 2000 and Ciba's Masterbatches division in 2006. In 2008, the leading U.S. colorant suppliers Rite Systems and Ricon Colors were acquired. The latest acquisition, the highly-innovative specialty chemicals company Süd-Chemie (Germany), was completed in 2011. Today, around 18.000 people are working for Clariant. The net sales in 2013 were around 6 billion CHF.



Sandoz (est. 1886)	Hoechst	BTP Plc.	Ciba Masterbatches	Rite System Ricon Colors	Süd-Chemie
Clariant/IPO* from Sandoz	Acquired Hoechst Specialty Chemicals Business	Acquired BTP Plc.	Acquired Ciba Masterbatches	Acquired Rite System & Ricon Colors	Acquired Süd-Chemie
1995	1997	2000	2006	2008	2011

<sup>\*</sup> IPO: Initial Public Offering

### **Porous Materials in Clariant – Catalysts and Adsorbents**

Porous materials are especially important for the Business Units Functional Minerals and Catalysts which came into Clariant by the acquisition of Süd-Chemie. In Functional Minerals, predominantly a natural clay mineral called Bentonite is utilized for products offering solutions to different industries like consumer industry, e.g. purification of vegetable oils, detergent additives, animal feed additives as well as foundry and construction industry, e.g. additives for stabilizing moulding sands for iron castings and additives for supporting fluids in civil engineering works, tunneling, pipe jacking and drilling.

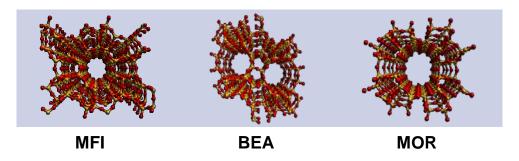
Porous materials play a major role for heterogeneous catalysis. For many catalyst systems not only the catalytically active material but also diffusion through the catalyst pores is crucial for the catalytic performance. Feed molecules need to arrive at the active sites as well as product molecules have to find their way out of the catalyst. By designing the pore system properly, mass transport limitations can be diminished leading to higher activity and/or better selectivity to the desired product(s).

The Business Unit Catalysts offers a wide portfolio of different catalytic solutions for chemical, petrochemical and refinery applications, e.g. for the production of hydrogen, methanol and ammonia as well for various selective hydrogenation and oxidation reactions. Another important area is (off-)gas purification. Clariant offers catalysts to reduce detrimental substances like  $NO_x$ ,  $N_2O$ , CO or VOCs as well as traps for sulfur, chlorine or mercury. The following picture shows different catalyst shapes which are optimized for the respective application.



## **Zeolites in Clariant – An important Class of porous Materials**

For petrochemical and refinery applications as well as for industrial gas purification, often zeolites are used as material basis of the respective catalysts. These are crystalline alumosilicates with a defined pore structure. Clariant is a leading global zeolite supplier and has a lot of experience in research and production of specialty zeolite catalysts like ZSM-5 (MFI), Beta (BEA) and Mordenite (MOR) for which you can see the structures in the following figure.



Besides of these standard types, many more zeolite types are available. We are also capable of scaling up customer recipes in dedicated pilot scale facilities. Production sites in different regions of the world guarantee a global supply network for our customers.

Zeolites are either sold as powders designed for customers who use them for their own catalyst production or they are further processed to final catalysts by forming them into shapes (e.g. cylindrical extrusions) with the help of binders (e.g. alumina and silica) followed by post-synthetic modifications with metals where required. For tailoring a zeolite catalyst for a specific application, the most important parameters are the choice of the right zeolite type (micropore structure), the Si/Al ratio, the crystal size but also the type of binder and the resulting meso-/macroporous pore system which is needed to adjust the mass transport of molecules in the catalyst shape.

Clariant offers specialty zeolite catalysts and adsorbents for many applications. The following list gives some examples which show the versatility and industrial importance of these materials.

- Methanol to gasoline
- Methanol to olefins
- Isomerization of light gasoline
- Dewaxing of gas-/lubeoil
- Oligomerization of olefins

- Aromatization
- Isomerization and separation of xylenes
- Toluene disproportionation / C9+ aromatics transalkylation
- Aromatic alkylation (e.g. benzene/toluene methylation)
- Abatement of NO<sub>x</sub>
- FCC additives

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