

***IN-Situ*** Study and **DE**velopment of  
Nano**POR**ous Materials (INSIDE-PORes)

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# Roadmap

for the

**E**uropean **N**anoporous **M**aterials

**I**nstitute of **EX**cellence (ENMIX)

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# Preface

This document presents the research mapping of the European Nanoporous Materials Institute of Excellence (ENMIX) arisen from the EU-FP6 Network of Excellence (NoE) *IN-Situ* Study and **DE**velopment of Nano**POR**ous Materials (INSIDE-POReS). The NoE INSIDE-POReS assembles top research groups in a coherent field of activities related to nanoporous materials. Establishing the ENMIX is an appropriate measure to secure the established contacts and networking in the field of porous materials into a sustainable body with the aims of promoting excellence and coordinating high-level research in the areas of preparation, characterization and industrial application of nanoporous materials. Furthermore, ENMIX will constitute an attractive platform for research organizations, governmental bodies and industry, and it will act as a unique and international competence and knowledge center for research and consultation.

The roadmap aims at implementing an ambitious industry-led integrated program of research, technology development and demonstration activities in the areas of synthesis, adsorption, membranes and catalysis using nanoporous materials. Intensive and detailed discussions, taking into account innovative research trends, growing industrial needs, literature data, etc., conducted by the four pillar leaders of the NoE, Prof. P. Cool, University of Antwerpen (Belgium), Prof. F. Rodríguez-Reinoso, University of Alicante (Spain), Prof. F. Kapteijn, Technical University of Delft (The Netherlands), and Prof. J. Weitkamp, University of Stuttgart (Germany), provided many insight perspectives and suggestions for defining a research roadmap for the ENMIX activities. From the discussions between these internationally recognized research experts in the fields of synthesis, adsorption, membranes and catalysis using nanoporous materials, it became obvious that there were numerous synergies not only between these four research pillars of the NoE, but also between this user-driven research roadmap and the priorities identified by several national and international programs. This document seeks, *inter alia*,

to encourage members of the ENMIX consortium and others to make proposals which will help to move practice forward by achieving some of the goals we have identified.

Defining a roadmap is an ongoing process, and the resulting roadmap needs to be considered as a "living document". Consequently, based on new ideas, the roadmap will need to be updated periodically to incorporate these new ideas and environments.

We hope that the ENMIX research roadmap will be of considerable interest for decision- and policy-makers and stakeholders at different levels in Europe within the frame of nanoporous materials.

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# 1 Introduction

## 1.1 Definition of nanoporous materials

Solid materials are usually classified into either dense or porous. In porous materials, holes, cavities or channels are running through the entire solid matter, illustrative examples from every-day life being a sponge or a Swiss cheese. It has long been recognized in materials science that the width of the pores, i.e. the free distance between opposite pore walls, is of prime importance for the properties and applicability of a porous material. Today, materials with very narrow pores in the nanoscale range, i.e. from ca. 0.1 to 100 nm, are commonly referred to as *nanoporous materials*. Note that the lower end of this range, viz. from ca. 0.1 to 1 nm, coincides with the dimensions of the vast majority of molecules. As will be shown in more detail below, it is this similarity of molecular dimensions and pore widths that forms the basis for some unique and most striking applications of nanoporous materials in modern separation processes and heterogeneous catalysis.

In 1985, the International Union of Pure and Applied Chemistry (IUPAC) introduced a classification of porous materials which is also based on the pore width  $d_p$ . In this terminology, pores with  $d_p < 2$  nm are referred to as *micropores*, those with  $2 \text{ nm} \leq d_p \leq 50$  nm as *mesopores* and those with  $d_p > 50$  nm as *macropores*. In the modern scientific and technical literature, both terminologies are customary, and it is to be noted that the pore diameter of nanoporous materials covers the entire range of micropores and mesopores plus the lower end of macropores in the IUPAC classification.

Funded by the European Commission within its Sixth Framework Programme, the European Network of Excellence (NoE) *IN-Situ* Study and DEvelopment of NanoPORous Materials (INSIDE-PORes) is an alliance of research institutions which have been performing cutting-edge research and accumulating know-how in various sub-fields of the science and application of nanoporous materials. Building on the combined experience and skills within the NoE, it is intended to further amplify the strengths of the partner institutions and to

make full use of the synergies, thereby strengthening Europe's position in the science and application of a most important family of high-tech materials.

## 1.2 Examples for nanoporous materials

To-date, a broad variety of nanoporous materials are known, some of these occur in nature and many others must be prepared synthetically. Their framework, i.e. the solid matter surrounding the nanopores, can be crystalline or amorphous, inorganic or organic or even an inorganic-organic hybrid. Chemically, the framework can be built from carbon or from polyhedra of metal oxides, typically tetrahedra or octahedra. A plethora of both main-group elements and transition metals from the periodic table have been incorporated into such frameworks. Here, silicon and aluminum play by far the most prominent role, but other typical framework-building elements include phosphorus, germanium, boron, gallium, titanium, zirconium, vanadium and numerous others. Following is a brief description of four selected families of nanoporous materials that have recently received particular attention in the scientific and/or technical literature.

*Activated carbon* is conveniently made from natural products, such as wood, fruit stones and others, by proper thermal and/or chemical treatment. The industrial domain of activated carbon is its use as an adsorbent in large-scale separation and purification processes. Activated carbon can be tailor-made with pore widths in the range of some tenths of a nanometer, and as such it is capable of separating substances with molecules of different size, hence the term *carbon molecular sieves*. Another fascinating variant of activated carbons are ordered mesoporous carbons which can be made by using a suitable template, e.g. a mesoporous silica: The mesopores are filled with a concentrated aqueous solution of an organic precursor, e.g. a sugar, followed by its thermal decomposition and dissolution of the inorganic template, e.g. in HF.

*Zeolites* are crystalline inorganic materials with strictly regular pore shapes and widths, typically in the range from 0.3 to 0.8 nm. They have long been known as minerals occurring

in nature, but it was only with the advent of their synthetic preparation in the late 1950s that they gained industrial importance. Today, zeolites are used on a large scale as ion exchangers (e.g. as water softeners in laundry detergents), adsorbents and catalysts. Obviously, due to their pore size in the range of molecular dimensions, zeolitic adsorbents may act as molecular sieves. Zeolite catalysts are unique in that they enable *shape-selective catalysis* which may be understood in terms of a combined molecular sieving and catalytic action. Zeolites are almost always made by hydrothermal synthesis, often in the presence of a structure-directing agent, e.g. an organic ammonium ion or an amine. As a rule, silicon and aluminum occur as framework metals, but more recently, purely siliceous zeolites and zeolitic titanosilicates, aluminophosphates and silicoaluminophosphates also gained industrial importance as catalysts. Today, more than 175 different zeolite framework types are known.

*Ordered Mesoporous Materials (OMMs)* typically consist of an amorphous framework from  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$  or any other oxide with regular pores of a diameter in the range of ca. 2 to 15 nm. They are prepared by precipitation of the oxide in the presence of a suitable structure-directing agent, e.g. of the cetyltrimethylammonium type. Since 1992, the science of OMMs received considerable attention, in part because they can be looked upon as resembling zeolites with a significantly increased pore width, but no industrial-scale application of these materials has so far been convincingly reported.

*Metal-Organic Frameworks (MOFs)* are hybrid materials the three-dimensional frameworks of which are composed of inorganic and organic moieties linked by strong bonds. A large variety of MOFs were synthesized and characterized in recent years. Some of these materials showed extremely large adsorption capacities for gases like hydrogen or methane. However, their full potential on an industrial scale remains to be explored in the near future.

### **1.3 Properties of nanoporous materials**

It must be borne in mind that in the focus of this NoE is the interaction of gases or liquids with nanoporous materials. This includes, in particular, the adsorption of components from



gases or liquids onto the surface of the materials, the flux of fluid components through membranes made from the nanoporous materials and the catalytic conversion of fluid components on the surface of the materials. Following is a brief discussion of the properties of nanoporous materials that are most relevant to the envisaged applications.

A high *specific surface area* is a direct consequence of the porosity. Zeolites typically exhibit 500 to 700  $\text{m}^2 \cdot \text{g}^{-1}$ , values around or even above 2 000  $\text{m}^2 \cdot \text{g}^{-1}$  can be reached for activated carbons and OMMs, and values as high as 3 000 to 4 000  $\text{m}^2 \cdot \text{g}^{-1}$  have been reported for certain MOFs. Such high surface areas bring about high adsorption capacities which are in turn beneficial for gas storage, the cycle length in adsorption processes and catalytic applications.

The *pore width* and the *pore width distribution* in nanoporous materials can, in many instances, be manipulated and tailored for a specific application by advanced synthesis methods and/or post-synthesis modification techniques. A completely uniform pore width can often be attained, especially with zeolites and OMMs. This is highly relevant, if molecular sieving of an adsorbent or a membrane is aimed at or if shape selectivity effects are to be exploited in heterogeneous catalysis.

Equally important are the *rates of diffusion* of guest molecules inside a nanoporous host. In their pores, at least four different types of diffusion may occur, viz. ordinary gas diffusion, Knudsen-type diffusion, configurational diffusion and single-file diffusion. The prevailing diffusion mechanism is largely determined by the size of the diffusing molecules and the pore width of the porous solid. It is evident that tailoring of the latter is of prime importance in all those cases where a separation of adsorptives is based on different rates of uptake by the adsorbent.

*Acidity and basicity* are among the most important chemical surface properties of porous materials. They determine to a large extent the selectivities of adsorption, transport rates through a membrane and the catalytic properties. For a reasonably complete picture of

surface acidity and basicity, it is vital to collect information on (i) the nature of acid or basic sites (Brønsted vs. Lewis sites), (ii) their concentrations and (iii) their strength distribution. This is feasible with modern characterization techniques that are available at various partners of the NoE.

*Hydrophobicity vs. hydrophilicity* of the solid surface is of similar importance, especially when it comes to the separation of polar from non-polar or less polar compounds. Moreover, the hydrophobicity of the surface can be a decisive factor for the selectivity of catalytic reactions. Several techniques have been advanced by the partners of the NoE for reliably measuring surface hydrophobicities or hydrophilicities.

Other *specific surface properties* may be required to meet the specific demands of an adsorptive or membrane separation or a catalytic reaction. A broad assortment of modification techniques is available for this task. Among these methods are ion exchange in an aqueous suspension or in the solid state, chemical vapor or liquid deposition, impregnation, grafting, dealumination or desilication of zeolites and OMMs, surface modification of carbons with acids or other chemicals etc.

Finally, the *stability* of a nanoporous material is of vital importance in any adsorptive, membrane or catalytic application. This includes chemical stability against all fluid components in the system, thermal stability in processes at elevated temperatures and mechanical stability in processes where the adsorbent or catalyst is in motion like, e.g. in a fluidized or entrained bed. The thermal stabilities of zeolites and OMMs are generally considered to be excellent, and so is that of carbons in a non-oxidative environment, while the thermal stability of MOFs requires careful attention.

## **1.4 Societal challenges**

Our highly developed societies are facing numerous challenges which call for significantly improved or completely new technologies in the forthcoming decades. A few examples for

such challenges are listed in Table 1 along with possible technologies that are expected to contribute to meeting the respective challenges. In all examples listed, new or improved nanoporous materials will play a pivotal role.

**Table 1:** Some societal challenges expected in the forthcoming decades and examples for novel or significantly improved technologies that will contribute to meeting these challenges. Nanoporous materials will play a pivotal role in all these technologies.

<b>Societal challenge</b>	<b>Examples for required technologies</b>
Cleaner transportation fuels from less valuable fossil raw materials (heavy oils, oil sands, coal)	(i) Deep desulfurization and denitrogenation (ii) Demetallization (iii) Removal of aromatics from diesel and jet fuel (iv) Improved Gas-To-Liquids (GTL), Biomass-To-Liquids (BTL) and Coal-To-Liquids (CTL) processes
Environmental protection	(i) Producing low-cost oxygen from air for burning coal in power stations (oxyfuel concept) (ii) Carbon dioxide capture (concentration and hydrogenation with hydrogen made from solar energy) (iii) Desulfurization of fuels by selective adsorption
Hydrogen supply	(i) Producing hydrogen reliably and at lower cost from conventional sources (ii) Producing hydrogen using solar energy <ul style="list-style-type: none"> <li>• photovoltaics and water electrolysis</li> <li>• photocatalytic water splitting</li> </ul>

**Table 1:** Continued

<b>Societal challenge</b>	<b>Examples for required technologies</b>
Saving energy	(i) Sorption systems in cooling and heating devices (ii) Controlled nanoporous ceramics for light emission (iii) Alkane/alkene separation by sorption or membranes
Bulk chemicals	(i) Developing solid acid catalysts with increased acid strength (ii) Replacing alkenes as chemical feedstocks by the much cheaper alkanes
Health and health care	(i) Removal of Volatile Organic Compounds (VOCs) from air (ii) Development of nanoporous materials for controlled drug release
Security and safety	(i) Removal of toxic compounds from air in emergency cases

## 1.5 Markets for nanoporous materials

A few figures may suffice to underline the economic importance of nanoporous materials. It is generally expected that these markets are steadily growing.

The worldwide markets for *activated carbons*, as of 2004, have been estimated to be of the order of  $700\,000 \text{ t} \cdot \text{a}^{-1}$ . Assuming an average price of ca.  $2\,000 \text{ US } \$ \cdot \text{t}^{-1}$ , the total market value of these nanoporous materials reaches some  $1.5 \cdot 10^9 \text{ US } \$ \cdot \text{a}^{-1}$ .

Today's estimated market for synthetic zeolites amounts to some  $1.7 \cdot 10^6 \text{ t} \cdot \text{a}^{-1}$  worldwide. Of these, ca. 75 % are zeolites A and P for use as detergent builders, ca. 12 % zeolites A

and X for adsorbents and ca. 13 % zeolites for use as catalysts, mostly zeolite Y for Fluid Catalytic Cracking (FCC).

Finally, the worldwide market value for solid catalysts, the majority of which is believed to be based on nanoporous materials, amounts to roughly  $10 \cdot 10^9 \text{ €} \cdot \text{a}^{-1}$ , as of 2007, and is expected to reach  $13 \cdot 10^9 \text{ €} \cdot \text{a}^{-1}$  by 2012.

## 1.6 Abbreviations and acronyms relevant to INSIDE-POReS

AISBL	Association Internationale Sans Bût Lucratif (International Non-Profit Organization)
EMH	European Membrane House (the AISBL of NanoMemPro)
ENMIX	European Nanoporous Materials Institute of Excellence (the AISBL of INSIDE-POReS)
ERIC	European Research Institute of Catalysis (the AISBL of IDECAT)
IDECAT	Integrated Design of Catalytic Nanomaterials for a Sustainable Production
INSIDE-POReS	<i>IN-Situ</i> Study and DEvelopment of NanoPORouS Materials
NanoMemPro	Expanding Membrane Macroscale Applications by Exploring Nanoscale Materials Properties
NoE	Network of Excellence
SME(s)	Small and Medium Enterprise(s)

## 2 Objectives of the Network – ENMIX

The NoE INSIDE-POReS has been erected as a start-up vehicle assembling top research groups in a coherent field of activities related to nanoporous materials. Most of these partner groups had not collaborated before, as they were generally operating in different fields of research and/or applications. INSIDE-POReS has achieved establishing a true networking with an intensity that goes far beyond a mere continuation of already existing contacts. Installment of the NoE has thus been a very successful action in setting up collaborative research activities and the exchange of researchers, enabling access to the equipment available in the partner groups and liberating synergies that would otherwise not have been experienced.

It is one of the lessons learnt by the partners that setting up a new NoE is a demanding and time-consuming task which requires much energy of the participating groups. Only by now a true research collaboration and the contours of the resulting synergies are becoming visible. Serious efforts are required to further strengthen the network and to guarantee its viability beyond the duration of funding by the European Commission.

Establishing the **E**uropean **N**anoporous **M**aterials **I**nstitute of **E**Xcellence (INSIDE-POReS ENMIX) is an appropriate measure to secure the established contacts and networking in the field of porous materials into a sustainable body with the aims of promoting excellence and coordinating high-level research in the areas of preparation, characterization and industrial applications of nanoporous materials. ENMIX will constitute an attractive platform for research organizations, governmental bodies and industry, and it will act as a unique competence and knowledge center for research and consultation. Its attractiveness will originate from the broad range of technical and service facilities and the availability of a complementary and far-reaching expertise.

The main objective of ENMIX is to secure the consolidation of the existing NoE INSIDE-POReS into a sustainable network organization. This will be realized by several objectives on the scientific, technical and educational level, as specified below:

- Initiatives for research proposals in the field of nanoporous materials on the international level, e.g. within research programs and contracts administered and financed by the European Commission, other national and international agencies and industrial or commercial enterprises in cooperation of the participating institutions.
- Development of the SUPERTOOL, a system of complementary techniques available for studies in the field of porous materials, integrated at different levels, from a series of distributed stand-alone techniques to highly integrated and centrally controlled facilities operating simultaneously for *in-situ* studies.
- Offering consulting and technical service facilities.
- Development and maintenance of a data base related to porous materials.
- Improving the level of education of European researchers through initiatives in the areas of courses, workshops, Master and PhD programs and continuing education in the field of porous materials. The spreading of excellence between higher education, the pertinent industries and SMEs represents a key target.
- Enhancing the mobility of personnel, especially of young researchers, will be of particular importance and facilitate reaching several of the above-mentioned objectives.

The activities of ENMIX are complementary to those of two other NoEs funded by the European Commission, viz. IDECAT and NanoMemPro. Together with their AISBLs, i.e., ERIC and European Membrane House, respectively, ENMIX will explore the opportunities of founding completely novel institutions with the objective of fostering the European research

and technology in the field of porous solids. Among the most far-reaching visions, one can think of, is a virtual European Institute of Nanoporous Materials with an associated industrial park.



## 3 Short- and Long-Term Research within ENMIX

### 3.1 Synthesis

#### 3.1.1 Introduction

Nanoporous materials play an important role in chemical processing in which they can be successfully used as adsorbents, catalysts, catalyst supports and membranes and form the basis of new technologies mainly due to their unique structural or surface properties, which can be tailored to a certain extent to meet the process needs. The growing drive to obtain new materials with pores in the micro-, meso- or combined micro/mesoporous region reflects the importance of improving the performance of existing nanoporous materials with respect to their molecular sieving and molecular transport behavior. Furthermore, *in-situ* and *ex-situ* modification and/or activation techniques became key tools to tune, in a controlled way, the ultimate properties of the nanoporous materials. It is clear that the focus on atoms forming different structures of precise geometry with pores of uniform shape throughout the entire crystal, using various structure-directing templates, is not limited to carbon, silicon and/or aluminum, but also various d- and other p-block elements will be considered in order to obtain very specific interactions with the surface.

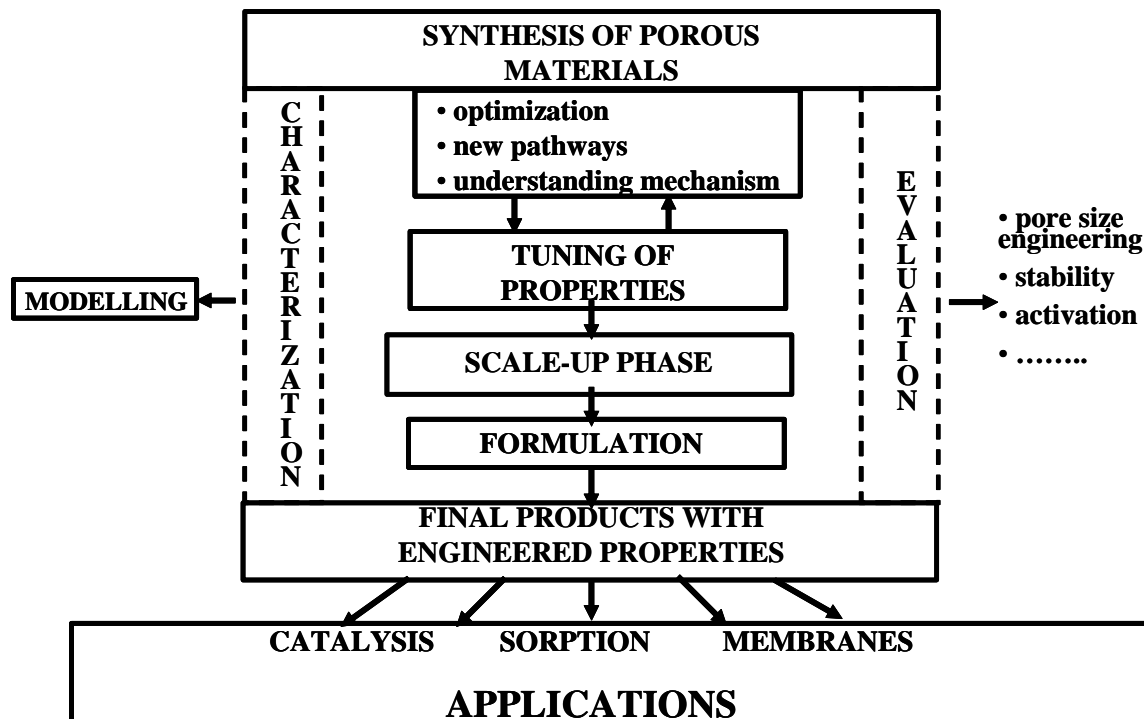
In the last decade, there has been an impressive progress in the development of new nanoporous structures. Not only activated carbons, carbon molecular sieves and the traditional zeolites are of interest, but also porous materials such as novel microporous zeolites, mesoporous molecular sieves, pillared clays, sol-gel derived metal oxides, mesoporous activated carbons, carbon nanotubes and inorganic/organic hybrid frameworks are gaining increasing attention. The synthesis and tuning of the properties of nanoporous materials remain largely unexplored and constitute one of the main objectives of the NoE INSIDE-POReS. To reach these objectives in the whole field of applications of porous materials, the synthesis pillar plays an important and vital role within the NoE since it

provides the porous materials with superior properties. Among the challenges, the synthesis pillar has to meet, is the preparation of new porous materials with a high adsorption capacity and selectivity, good kinetic (diffusion) and physical (bulk density, crush strength, erosion resistance) properties together with a good lifetime performance (chemical, thermal and mechanical stability).

Furthermore, the understanding of the synthesis process is essential for developing novel active porous materials with well-defined properties and for enabling cost-, energy- and environmentally efficient processes.

### **3.1.2 Roadmap for the synthesis pillar**

The roadmap for the synthesis pillar, which reflects the general research strategy to form nanoporous materials with a unique performance, is given in Figure 1. It shows the different steps going from the synthesis (A) to the tuning of properties (B), scale-up phase (C) and formulation (D) leading to a final porous product with engineered properties, applicable in adsorption, membrane and catalysis applications. Each step requires detailed characterization and evaluation efforts of the obtained products and will be carried out by the different partner laboratories. Furthermore, special attention will be paid to modelling activities based on the results obtained from the material characterization and evaluation.



**Figure 1:** Roadmap scheme for the synthesis pillar.

### 3.1.2.1 Synthesis of nanostructured materials

In the short-term (< 5 years), the activities in the synthesis pillar are concentrated on the synthesis of micro-, meso- and combined micro/mesoporous siliceous and non-siliceous materials. To obtain these nanoporous materials in a reproducible way, taking into account the cost, energy and environmental efficiencies, the synthesis procedures have to be optimized with respect to the synthesis conditions (temperature, solvent, pH, stirring time, aging etc.) and the role and type of the template/co-template. In this way, the synthesis procedure can be tuned to change in a controlled way the structural aspects (crystallinity, surface area, pore size distribution, stability, particle size etc.), morphology (tubes, fibers, spheres, layers etc.) and properties of the nanoporous materials.

The targeted nanoporous materials are:

- microporous zeolite materials (MFI, LTA, FAU etc.)
- mesoporous siliceous and non-siliceous materials (MCM, SBA, MSU, MCF, mesoporous carbons, metal oxides etc.)

- combined micro/mesoporous siliceous and non-siliceous materials
  - mesoporous materials with microporous walls
  - mesoporous materials with an internal microporous phase
- layered and pillared layered materials
- activated carbons
- carbon molecular sieves

In the medium-term (5-10 years), special attention will also be given to the synthesis of silica-based mesoporous organic hybrid materials. Indeed, the symbiosis of organic and inorganic components can lead to unique materials the properties of which differ considerably from those of their individual, isolated components. Three pathways will be investigated for the synthesis of these hybrid materials: (1) subsequent modification of the pore surface of a purely inorganic silica material ("grafting"), (2) simultaneous condensation of the corresponding silica and organosilica precursors ("co-condensation") and (3) the incorporation of organic groups as bridging components directly and specifically into the pore walls by the use of bisilylated single-source organosilica precursors (resulting in Periodic Mesoporous Organosilica (PMO) materials). Furthermore, considerable research work will be carried out on other hybrid inorganic-organic framework materials in which both the inorganic (metal or metal clusters) and organic (linker/spacer) moieties are integral parts of a network with infinite bonding connectivity. Specifically, the synthesis chemistry of Metal-Organic Frameworks (MOFs), Covalent-Organic Frameworks (COFs) and Zeolitic Imidazolate Frameworks (ZIFs) will be studied to obtain an extensive class of crystalline materials with high stability, tuneable metrics, organic and inorganic functionality with permanent and dynamic porosities. The ultimate objective is the ability to design sophisticated molecular building blocks that would act as carriers of structural and functional information to be expressed in a specific target material having superior properties in adsorption, catalysis and membrane applications.

Another area of interest is the possibility of a re-use of the templates used during the synthesis of nanoporous materials or the development of synthesis routes without the use of templates to obtain materials with a specific micro-, meso- or combined micro/mesoporosity.

The long term (> 10 years) scenario will mainly be focused on the development of synthesis routes to form predictive structures obtained from theoretical models. The systematic enumeration of all possible networks of atoms in inorganic structures is of considerable interest. Of particular importance are the 4-connected networks which are relevant to a wide range of systems. Following a mathematical tiling theory, it was established that there are exactly 9, 117 and 926 topological types of 4-connected uninodal, binodal and trinodal networks. 126 hypothetical zeolite structures have been modelled in the composition  $\text{AlPO}_4$ . An effective filtering procedure is needed to identify the most plausible frameworks, which can be established via computational chemistry methods.

Characterization of materials is crucial for the quantification and prediction of their physical, chemical and mechanical properties. However, as the complexity of a system increases, so do the challenges involved in elucidating its structure. While molecular simulation and modelling have proved invaluable as complements to experiment, such simulations now face serious challenges: new materials are being synthesized with ever increasing structural complexity, and it may soon prove impossible to generate models that are sufficiently realistic to describe them adequately. Perhaps, ultimately, it will only be possible to generate such models by simulating the synthetic process itself. The strategy can be used to generate full atomistic models for mesoporous molecular sieves. Recently, a strategy was developed in which the synthetic process itself is simulated to generate full atomistic models for mesoporous molecular sieves.

Also, attention will be given to control the growth direction during the synthesis of nanoporous crystals using external force fields. Indeed, when the structure-directing templates can be oriented, a well-oriented pore structure can be obtained. The application of a magnetic and/or electric field during the synthesis can result in an alignment of the pores

in nanoporous materials. It is believed that the growth follows a catalyst-assisted growth mechanism.

Furthermore, technical possibilities will be investigated to transform the classical batch method to synthesize nanoporous materials into a semi-continuous or continuous process technology.

### *3.1.2.2 Tuning the properties of nanostructured materials*

The properties of the nanostructured materials can be changed, in a controlled way, using *in-situ* techniques and/or post-synthesis modification processes. The *in-situ* technique consists of the incorporation of specific elements into the framework of the nanoporous materials. On the other hand, the post-synthesis modification can be the result of an impregnation, ion-exchange process, molecularly designed deposition, functionalization techniques, molecular imprinting methods, modification by chemical reactions, deposition of nanoparticles with specific properties or controlled framework destruction. Special attention will be given to molecular imprinting methods, which generate nano-patterned materials containing very selective interaction sites, useful in applications such as separations, catalysis and sensors. In this way, the adsorption and catalytic behavior of these nanoporous materials can be tuned due to the introduction of specific sites at the surface and/or the engineered pore size distribution. Furthermore, changing the synthesis condition can lead to different morphologies (spheres, tubes, fibers, layers). Besides the tuning of the properties of micro-, meso- and combined micro/mesoporous siliceous and non-siliceous materials, attention will also be given to the stabilization of defect-hybrid structures, hydrogen-induced phase transformation in crystalline metals and alloys and hydrogen-induced lattice migration in metals and alloys.

Important at this stage of the synthesis and fine tuning of the nanoporous materials is the product evaluation, recipe validation and quality control carried out by all participating laboratories.

### 3.1.2.3 *Scale-up phase*

The validated processes for synthesizing nanostructured materials with tuned properties and superior performances in adsorption, membrane and catalysis applications have to be scaled-up from the laboratory (grams) to the pre-industrial (kilograms) scale. Important in these scaling-up efforts is the quality control of the obtained products. A possible process and equipment optimization can be necessary to obtain materials with superior performances.

Furthermore, a detailed investigation of the ultimate cost, energy and environmental efficiencies has to be made in order to manufacture nanoporous materials with specific properties in an economical way. Based on the obtained results, an industrial process scheme, including detailed synthesis and property tuning conditions, must be described.

### 3.1.2.4 *Forming*

In order to reach good kinetic and physical properties of the nanostructured materials with tailored properties, suitable for industrial use, a final tuning of the porous products is often needed. Indeed, these products have to fit into different application fields. Therefore, the role and optimal concentration of binder materials (alumina, bentonite etc.) in the ultimate porous products has to be evaluated so that suitable pellets, spheres, monoliths, honeycombs etc. can be formed for industrial processes. An attempt will be made to develop procedures for obtaining binderless nanoporous materials with good kinetic and physical properties.

During the different stages of the roadmap, in the development of nanoporous materials with tuned properties, continuous characterization and product evaluation efforts are essential. The *ex-situ* and *in-situ* characterization techniques provide the necessary information about the synthesized nanoporous materials and their properties. The *ex-situ* characterization techniques are important to obtain information about the chemical composition, structure, porosity, morphology, diffusion aspects, localization and nature of active sites, sorption selectivity/affinity, stability, catalytic activity etc. Techniques such as BET, SEM, TEM, XRD, ICP-AES, HRTEM, TGA/DSC, TPD, NMR, UV/VIS, FTIR, FT-Raman, ESR etc., have to be used.

The *in-situ* characterization techniques give rise to an effective monitoring of the dynamic evolution of the nanostructured materials and their properties and can lead to the development of predictive models and optimal control or smart engineering strategies. Techniques such as SAXS/WAXS, XRD/DLS, SAX/WAXS/DLS, neutron powder diffraction etc. can be used.

The evaluation of the obtained nanoporous materials is mainly based on their performance in various applications. Besides their performances also the advantages and limitations towards existing materials will be evaluated. The nanoporous products with tuned properties will be tested in view of four distinct processes, viz. separations and storage by adsorption, membranes, catalysis and long-term novel applications.

The described strategy for obtaining superior nanoporous materials with tuned properties implies an intensive exchange of synthesized materials and personnel between the partner laboratories. The prospect for such a close collaboration between the partner laboratories is excellent because of the complementary know-how and experience in the application fields of adsorption, membrane science and technology and catalysis.

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## 3.2 Adsorption

### 3.2.1 Introduction

It is clear that, since the first syntheses of zeolites in 1959, innovations in adsorbent development and desorption process cycles have made adsorption a key separation tool in the chemical, petrochemical and pharmaceutical industries. Further, in all future energy and environmental technologies adsorption will likely play either a key or a limiting role. From the point of view of the Network of Excellence INSIDE-POReS, these needs cannot be fulfilled by current commercial adsorbents, and a large effort has to be devoted to the development of new versatile and specific adsorbents.

Adsorption and separation technologies recover, isolate and purify products in virtually every industrial process. Pervasive throughout industrial operations, conventional separation

processes are energy-intensive and costly. Separation processes represent 40 to 70 % of both capital and operating costs in industry. They also account for 45 % of all the process energy used by the chemical and petroleum refining industries every year. Industrial efforts to increase cost-competitiveness, boost energy efficiency, increase productivity and prevent pollution demand more efficient separation processes. In response to these needs, we are seeking the development of high-risk, innovative separation technologies in processes for distillation, adsorption and dewatering. Also sought are innovative separation processes that are applicable to biomass slurries. Efforts must address the potential public benefits that the proposed technology would provide from reduced energy consumption and from the reduction of materials consumption, water consumption, and/or the dispersion of toxins and pollutants.

Adsorption uses adsorbents to remove substances from gaseous or liquid mixtures. Adsorption is effective for purifications, e.g. taking a contaminant ranging from 1 ppb to 1 000 ppm out of a stream of gas or liquid. In addition, adsorption is good for bulk separations, e.g. taking 1 to 50 % of a component out of a stream of gas, or maybe 1 to 10 % out of a liquid. Adsorption is also used for the recovery of certain constituents (e.g. solvents from air), preventing pollution, separating impurities from natural gas, petrochemical separations, hydrogen purification, recovery and reuse of sulfur dioxide for metal casting, and so on. Advances in and the expanded use of adsorption have resulted in substantial energy, environmental and economic benefits in a number of industrial settings. One prominent example is in refineries and petrochemical plants, where pressure swing adsorption (PSA) has replaced cryogenic distillation as the most economical method for separating hydrogen from various compounds. By replacing cryogenic distillation with PSA, refineries and petrochemical plants have been able to reduce costs by anywhere from 60 to 90 %.

Only five types of generic adsorbents have dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, activated alumina and clays. The estimated worldwide sales of these adsorbents are:

Activated carbon	$1\,000 \cdot 10^6$ US \$ · a <sup>-1</sup>
Zeolites	$100 \cdot 10^6$ US \$ · a <sup>-1</sup>
Silica gel	$27 \cdot 10^6$ US \$ · a <sup>-1</sup>
Activated alumina	$26 \cdot 10^6$ US \$ · a <sup>-1</sup>
Clays	$16 \cdot 10^6$ US \$ · a <sup>-1</sup>

The new adsorbents requested by industry must have high capacity, rapid adsorption-desorption kinetics, improved selectivity, and operational stability at elevated temperatures in the presence of steam and other reaction components. The new adsorption processes must then take advantage of these new materials. Areas of special interest are, among the many dozens one can find in specific applications:

(1) development of high-capacity CO<sub>2</sub>- and CO-selective adsorbents that can operate in the presence of hydrogen and steam at elevated temperatures (working capacities in the range of 3-4 mol/kg are of particular interest), along with the development of new Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA) cycle designs (possibly a PSA/TSA hybrid cycle design), at either ambient or elevated temperatures, that take advantage of these new adsorbents;

(2) development of advanced structured adsorbent materials for use in rapid-cycle PSA and further development of the design of rapid-cycle PSA; the main application will be air separation to produce pure nitrogen and oxygen;

(3) development of novel PSA hybrid separation systems, e.g. with a structurally integrated permeable membrane;

(4) CO<sub>2</sub> removal via TSA and development of TSA and/or PSA/TSA hybrid cycles with improved materials for use in H<sub>2</sub> separation technology and other applications;

(5) improved hydrogen separations with Sorption Enhanced Reaction Processes (SERPs), using a thermal swing regeneration and new materials – novel approaches, such as

incorporating a high-temperature reversible metal hydride as a H<sub>2</sub>-selective adsorbent in a SERP to drive the equilibrium, should be considered;

(6) CO-selective adsorbents;

(7) improved adsorbents for the separation of paraffin/olefin mixtures are needed in the polymer industry;

(8) new adsorbents for appropriate drug and some specific compounds (e.g. pesticides) delivery;

(9) new adsorbents for the specific retention of some nucleids that can be produced in nuclear fission reactor accidents;

(10) improvements in the capacity to remove VOCs, using adsorbents to concentrate the organics and then using a catalytic process to destroy them;

(11) new adsorbents for the storage of important gases such as natural gas and hydrogen with the aim of reducing the air pollution by combustion engines;

(12) new adsorbents for energy storage, ranging from batteries to supercapacitors.

(13) selective adsorbents designed for the fast removal of some specific compounds for which the contact time is very short and, consequently, the kinetics of adsorption must be very fast; a combination of microporosity and mesoporosity is needed for this application;

(14) application of the design principles of reticular chemistry to create three-dimensional covalent organic frameworks, which are entirely constructed from strong covalent bonds and have high thermal stability, high surface areas and extremely low densities.

There has been impressive progress in the development of adsorbents in the last two decades. Although from the practical point of view activated carbon, zeolites and clays constitute the largest part of adsorbents in use and they receive most of the advancements being developed, other adsorbents are attracting much interest. Examples are mesoporous molecular sieves, pillared clays, sol-gel derived metal oxides, carbon molecular sieves,

mesoporous activated carbon, carbon nanotubes, carbon nanofibers and metal-organic frameworks (MOFs). The adsorption properties of most of these new adsorbents remain largely unexplored, and this constitutes one of the objectives of this NoE.

### **3.2.2 Short-term (< 10 years) development of adsorbents and adsorption processes**

#### *3.2.2.1 Adsorbents*

##### ***Activated carbon***

As shown above activated carbon constitutes the most widely used adsorbent because it is considered the universal adsorbent. It generally exhibits a very large volume of micropores and mesopores and, as a result, a high surface area. Although it is mainly hydrophobic, the functionality (presence of heteroatoms) of the carbon surface can be adjusted by specific treatments, thus increasing its usefulness especially in liquid-phase adsorption processes. It is resistant to acidic and basic media, and the porosity can be adjusted to any particular need. Since, additionally, the cost is relatively low, it is easy to understand its wide use worldwide.

The major important developments needed in the area of activated carbon are related to their application in specific processes, since the area of general use of activated carbon is completely and satisfactorily fulfilled worldwide. Some of the areas of research are as follows:

*Carbon molecular sieves (CMSs)*. Carbon molecular sieves are mainly used in gas separation processes, such as (i) air separation for the production of nitrogen, (ii) the purification of natural gas by removing carbon dioxide and nitrogen and (iii) the production of olefins for the polymer industry, for instance the propane/propene separation. In most cases, the separation is achieved by kinetic effects by virtue of the differences in diffusion rates of different molecules. This is the case for air separation using CMSs since, if an oxygen-selective adsorbent is used, air separation can be accomplished with about one fourth of the

energy needed for the same separation by a zeolite, because oxygen diffuses 30 times faster than nitrogen. This kinetic separation is considered to be of great potential for the upgrading of natural gas by removal of carbon dioxide and nitrogen.

Mesoporous carbons. Their development has occurred more or less in parallel to that of mesoporous silicas and, because of their different surface chemistry, they can be complementary. The main approach for the synthesis of mesoporous carbons is the use of a template, in which the pores of mesoporous silicas are partially or totally filled with carbonizable precursors which, after carbonization, are separated from the silica by removing the latter (for instance by reaction with hydrogen fluoride). Although the porosity is rather regular because it is based on that of the silica precursor, the problem is the very high cost incurred by their synthesis. Consequently, new approaches are needed for the synthesis of much less expensive mesoporous carbons. The University of Alicante is attempting the synthesis from lignocellulosic precursors (for instance, fruit stones) subjected to a chemical activation in which the heat treatment and further gasification by steam or carbon dioxide are catalyzed, thus rendering the carbon mesoporous, with a small contribution of microporosity. If the microporosity is undesired, it can be removed by impregnation of the carbon with a pitch filling the micropores. After carbonization the remaining porosity will be that of the mesopores only.

Surface-modified activated carbon. In many applications the molecular weight or size of the species to be adsorbed may be too low for a physical adsorption process, and the molecules are not adsorbed or adsorbed to a too small extent. This is the case for many inorganic compounds such as hydrogen sulfide, arsine etc. In this case the adsorbent has to be surface-modified to increase the interaction of the carbon surface with the adsorbing species or to catalyze its conversion to other adsorbable species. Typical examples are the treatment with KI for the catalytic conversion of  $H_2S$ , or the treatment with sulfur species for the removal of mercury. Areas of research where this type of treatment is considered important in the next few years include the removal of sulfur from transportation fuels, the removal of carbon monoxide from hydrogen for fuel cell applications, etc.

Easy-regeneration adsorbents. The morphology may play an important role in aspects such as regeneration of spent adsorbents. For instance, the use of monoliths or activated carbon cloth or felt will make possible regeneration by application of an electrical potential, thus reducing the problem implied when using the conventional regeneration by passing a flow of superheated steam.

### ***Zeolites***

As described above, zeolites are also very important and versatile adsorbents, although their main use is as catalysts in the petroleum refining and petrochemical industries. Zeolites are crystalline aluminosilicate materials which possess a two- or three-dimensional network of porous channels and cavities of molecular dimensions (0.5-1.2 nm). Owing to this microporous structure, zeolites have the ability to act as molecular sieves. Additionally, due to the presence of a net negative charge in the anionic framework, zeolites exhibit surface acidity which makes them very attractive as solid catalysts, e.g. in Fluid Catalytic Cracking (FCC). The traditional zeolites, i.e. zeolites A, X and Y, remain the dominant adsorbents for commercial applications.

Despite their excellent properties, zeolite materials exhibit some important drawbacks in adsorption/separation processes when dealing with larger molecules and/or when faster adsorption kinetics are required. In order to overcome these disadvantages, the Network of Excellence INSIDE-POReS is working intensively in two different directions: On the one side, it is trying to develop mesoporosity in zeolites, and on the other side, it is trying to prepare zeolites with reduced crystal size. With respect to the first objective, success has been achieved by using both dealumination and desilication. The use of desilication in alkaline media appears to be more attractive because the acidic properties of the parent zeolite can be preserved. The second objective can be met by growing nano-sized zeolites inside the cavities of carbon materials which act as templates defining the final crystal size. The development of nanocrystals is vital for fastening the adsorption kinetics. Thus, among the main tasks of the NoE is the development of new zeolite-based materials in order to expand

their use in specific and/or new research areas dealing with adsorption and separation processes.

### ***Mesoporous silicas***

There will be an important effort in the synthesis of silica-based mesoporous hybrid materials since the symbiosis of organic and inorganic components can lead to unique materials. The prediction of structures and properties using molecular simulation will help to develop these new structures. Further developments are expected when introducing *in-situ* modifications of the structure to make the materials more selective towards the adsorption of specific compounds. This introduction can also use more traditional techniques such as ion exchange and functionalization or more advanced methods such as molecular imprinting. The possibility of manufacturing these new adsorbents with different forms (pellets, monoliths etc.) will also be very important for their application in new specific industrial needs.

### ***Hybrid adsorbents***

The synthesis of so-called hybrid adsorbents (organic-inorganic materials) has become very important in the last five years, and it will continue to be of prime importance in the future. A very good example for such materials in the class of Metal-Organic Frameworks (MOFs) which are crystalline solids that are assembled by connection of metal ions or clusters through molecular bridges. As such, they have the potential of exhibiting properties inherent to the building blocks, such as geometric rigidity, chemical functionality or chirality. Their preparation is often simple and scalable, and the yields are generally high. By careful use of the building blocks a certain degree of design can be wielded to produce targeted products. The materials are generally prepared in "one-pot" solvothermal syntheses under mild conditions. In their as-synthesized forms, the cavities within MOFs are filled with solvent molecules, and porosity has been accomplished in many cases upon removal of the guest species. Significant explorations will be required to satisfy the needs for new MOFs. To date, more than 5 000 two- and three-dimensional MOF structures have been reported in the literature, but only a fraction of these have been examined for their porosity, and far fewer of them have been tested in real adsorption processes. This is one of the jobs for the NoE,



and so is the search for important applications for these new adsorbents, mainly in the area of gas and energy storage.

### ***Miscellaneous adsorbents***

These will include traditional clays and pillared clays, the research on which is continuously growing due to the needs in specific adsorption- or catalysis-connected fields. In many cases the new materials developed are not properly pillared clays but artificially prepared pillared materials based on zirconium, silicon or other elements.

### ***Structured adsorbents***

An area of special interest is the development of activated carbons with morphologies adequate for the specific applications. Thus, more research is needed in the area of monolithic carbons in order to be able to prepare monoliths without the use of a binder because this will block an important part of the porosity of the activated carbon. In some cases the monolith will be dense, without channels, when the application implies the need for a large porosity per volume unit, as in gas (hydrogen, natural gas) storage. In other applications a high concentration of channels per unit of section area will be needed to facilitate the contact of the gas with the walls of channels and to decrease the pressure drop when using granular activated carbon. Furthermore, the same needs will increase the interest in the development of activated carbon cloth and felt with a highly developed porosity and an adequate mechanical strength, thereby overcoming today's weakness of these materials.

This approach must also be used for the synthesis of other adsorbents such as zeolites, which have to be prepared in different physical forms for practical applications. Although the pellet is the more common physical form, monoliths are also expected to be of importance.

### ***Compound-specific adsorbents***

The surface of some nanoporous adsorbents can be highly activated to obtain active sites which interact strongly and selectively with some compounds. Using special impregnation or molecular impregnation techniques, adsorbents with extremely high specific affinity can be obtained, which can be useful for gas sensors and/or personal protection.

#### *3.2.2.2 Adsorption processes*

##### ***Gas separation***

Because the adsorbent needs to be regenerated for most commercial applications, adsorption processes are necessarily cyclic. A number of cyclic adsorption processes are available, depending on the way the adsorbent is regenerated. When the process involves adsorption of a significant fraction (10 wt.-% or more from a gas stream) pressure swing adsorption is the more suitable system; if less than 10 wt.-% (usually 2 wt.-%) are adsorbed, temperature swing adsorption is generally the process of choice. Significant advances are still needed in these two and similar separation processes based on adsorption.

##### ***Personal protection and safety***

Protection against terrorism is one of the major issues nowadays. On the other hand, if an incident occurs, despite precautions taken to prevent incidents at all, it is important to reduce the consequences, i.e. to minimize the effects of Chemical, Biological, Radiological and Nuclear (CBRN) attacks. Minimizing the effect of CBRN threats means, in the first place, being able to provide an adequate respiratory protection for the first responders. Activated carbons and other nanoporous adsorbents can be used as protective barriers against toxic chemicals. Although impregnated carbons seem to be a good solution to this problem, there are still a number of unresolved issues such as the limited protection against certain chemicals, the fact that impregnating the adsorbent against certain threats diminishes its capacity against others, the high breathing resistance of filtering devices, the ageing of carbons due to the presence of water vapor, a large weight of the canister etc.

### ***Energy storage***

Direct storage of electricity in electrochemical supercapacitors is an important field of research for nanoporous solids. They intend to fill the gap between batteries and traditional condensers since they can exhibit simultaneously high values of energy density and power. They can store between 10 and 1 000 times more energy than conventional condensers, although providing lower power density. Since the mechanism of storing energy only implies the movement of ions from inside to the surface of the electrodes, without any degradation, the electrical double layer supercondensers are very reversible, being able to reach more than 500 000 cycles. The key for success lies in the two carbon electrodes, which should have an appropriate porosity and surface area. The development to these carbon electrodes is now the base of much research around the world.

### ***Gas storage***

The storage of natural gas has received the attention of many researchers along the last two decades, since it was considered a partial solution to the pollution caused by the combustion engine in transportation. The aim of the research was to prepare an adsorbent able to store a large amount of methane at an agreed relatively low pressure (3.4 MPa) and exhibiting an energy density of at least 150 V/V (providing 150 volumes of gas per volume of adsorbent), near the value reached when using compressed natural gas at 21 MPa. The main problem here is the need to develop adsorbents (mainly activated carbon) with a highly developed microporosity (around 0.8 nm pore size) and simultaneously a high bulk density. The best materials prepared to date are activated carbons, and research is directed towards the development of this porosity in consolidated dense monoliths with bulk densities as close to 1.0 g/cm<sup>3</sup> as possible. The situation for the storage of hydrogen is not as favorable since up to now the storage capacity found for the best carbon adsorbents is not above 2 wt.-%, far from the minimum value agreed as useful for industrial applications (6-7 wt.-%). Further work is needed in this field, especially for metal-doped carbons and some chemical modifications able to increase the adsorption capacity.

### ***VOCs removal***

This constitutes one of the NoE reference and case studies on adsorption, and several adsorbents are being used to concentrate the organic volatile compounds before catalytic destruction. This area of research is expected to grow substantially in the next few years, since the destruction of these volatile compounds is critical for a clean environment. The new developments will be in the synthesis of new adsorbents able to concentrate properly the volatile matter which will be destroyed by a catalyst supported on the same adsorbent. Of course, the number of compounds to be removed will continuously grow and, consequently, the need for new adsorbents will also grow.

### ***Biosorption***

Biosorption is potentially an attractive method for environmental decontamination from heavy metals and organic pollutants because biological materials and organisms could be selective; they do not require expensive and potentially hazardous chemicals and are not labor-intensive. The main disadvantages include a slow rate of the process and the need to dispose of the biomass containing concentrated contaminants. Living species are not able to survive if exposed to high levels of toxic chemicals and would not work in highly contaminated areas. Possible routes for improving efficiency of biosorption include creation of genetically modified organisms capable of higher accumulation rates and the combined use of biosorption and chemical/physical sorption, when both biomass and chemical sorbents are used. It is also possible to find and isolate new microorganism strains which are more resistant to high concentrations of pollutants.

A whole new family of suitably "formulated" biosorbents will be used in the process of metal removal and detoxification of industrial metal-bearing effluents. The sorption packed-column configuration is the most effective mode of application for this purpose. Recovery of the deposited metals from the saturated biosorbent can be accomplished because they can often be easily released from the biosorbent in a concentrated wash solution which also regenerates the biosorbent for subsequent multiple reuse. This and the extremely low cost of

biosorbents make the process highly economical and competitive, particularly for environmental applications in detoxifying effluents of, e.g.

- metal-plating and metal-finishing operations,
- mining and ore processing operations,
- metal processing, battery and accumulator manufacturing operations,
- thermal power generation (coal-fired plants in particular),
- nuclear power generation.

### **3.2.3 Long-term (> 10 years) development of adsorbents and adsorption processes**

The long-term scenario will be determined by the strong synergism between adsorption and catalysis since the former is always the first step in a catalytic process. Thus, there will be many new developments of adsorbents that, after appropriate treatments, will simultaneously act as a catalyst for the species previously concentrated on the surface of the adsorbent. The advancement in areas such as reduction of gas emissions, energy storage, selective adsorption etc. will dominate the scenario, and these advancements will also lead to advancements in the development of new more sophisticated adsorption processes.

#### *3.2.3.1 Adsorbents for reducing gas emissions*

In the push to develop methods for controlling greenhouse gas emissions, some of the biggest challenges have been finding ways to store hydrogen for use as a fuel, to use natural gas as an alternative fuel, and to capture and store carbon dioxide from power plant smokestacks before it reaches the atmosphere. Hybrid adsorbents such as MOFs are uniquely suited for all these applications because of their functional flexibility, their extremely light weight and their high porosity. Through reticular chemistry, it is possible to develop a process which allows utilizing the arsenal of organic building blocks to construct a large number of new structures, the components of which can be easily designed to suit a particular application. The pore size and pore functionality of these materials can be varied at

will. There will be a very large research effort in the development of these new adsorbents able to concentrate very large amounts of gases such as those mentioned above. Values of specific surface areas above 4 000 m<sup>2</sup>/g have already been published, but the application of the adsorbents to real processes has not yet led to large amounts of stored gas. Progress is expected in this area.

The progress in the field of these hybrid adsorbents will not stop the research on more conventional adsorbents, such as modified activated carbons and zeolites, since important advancements in these materials can also be expected in the next ten years or more, with special emphasis on the storage of hydrogen and carbon dioxide.

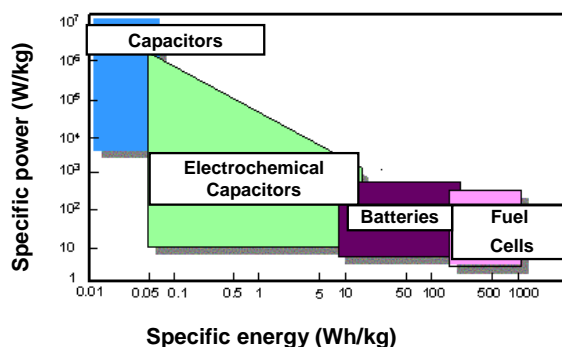
#### *3.2.3.2 Adsorbents for gas storage*

Since the storage of natural gas will be optimized in the next few years (see Section 3.2.2.2), at least from the point of view of applications such as gas transportation to remote areas and peak shaving, the long-term efforts will be centered on the storage of hydrogen. Many teams will continue their research on the use of special adsorbents, ranging from microporous carbons to MOFs, trying to use impregnation or imprinting techniques to increase the number and type of adsorption sites that are specific for the adsorption of hydrogen. This is a difficult task, but the joint efforts of many teams could lead to positive results.

#### *3.2.3.3 Adsorbents for energy storage*

Although Electrochemical Capacitors (ECs), also called supercapacitors, have been known for some years, it has not been until now that it is realized that they can be used as boost components supporting batteries or replacing batteries in electric vehicles and as energy sources for many other applications.

The reason why ECs are able to raise considerable attention is because they can fill the gap between batteries and conventional electrolytic capacitors (see Figure 2). In terms of specific energy as well as in terms of specific power this gap covers several orders of magnitude.



**Figure 2:** Plot for various energy storage and conversion devices.

The recent market introduction of low-cost ECs with large capacitance and the possibility to use them at high voltage allows a large number of new applications (present applications include back-up for videorecorders, car audiosystems, alarm clock radios, coffee machines, photo- and videocameras etc.) to be developed in the medium-term future, especially in electric, hybrid electric and fuel cell vehicles. In all cases the supercapacitor will serve as a short-time energy storage device with high power capability and allow to store the energy obtained from regenerating braking; it will help to reduce the size of the primary power source and keep it running in an optimized way.

#### 3.2.3.4 *Controlled compound delivery*

Drug delivery is one of the areas of future for adsorbents, and the research activity will grow tremendously as a consequence of a growing interest in medicine and pharmaceutical activities. Controlled drug delivery is becoming more and more important, not only for simple medicines such as pain-killers. Examples of introducing specific medicines in the right point of the brain to control endemic illnesses such as epilepsy will become common when the appropriate adsorbent is synthesized. Other areas of compound delivery not related to medicine will become also important in a near future. The controlled delivery of pesticides, fertilizers etc. will become a need to increase the production of agricultural products without increasing the environmental pollution. In this way, only the amount of chemical really needed will be delivered.

### *3.2.3.5 Compound-specific adsorbents*

The need for adsorbents in which active sites are specially developed to increase the interaction with adsorbing species will increase in the near future as a consequence of the increasing demand of this application in gas sensors and personal protection. In both cases the molecules have to be detected and adsorbed even though their proportion is very small. In this application the main advance will be in the development of new techniques to produce this special interaction, molecular imprinting being one of the favored candidates because it can be very selective; this should be paralleled by functionalization of the adsorbents to increase the degree of selectivity.

### *3.2.3.6 Biomolecular adsorption*

The adsorption of biomolecules (proteins, enzymes etc.) is going to become more and more important in the medium- to long-term future for biomedicine and related fields. For instance, when biomaterials are implanted into animals or humans, protein adsorption onto the foreign surface occurs within seconds of implantation. This rapid protein adsorption means that cells arriving at the biomaterial surface probably interact with the adsorbed protein layer rather than directly with the material itself. Thus, the initial protein adsorption onto a biomaterial surface plays a key role in how the body responds to an implanted biomaterial. Besides an in-depth future study of the kinetics and experimental methods to follow the adsorption process, a large effort will be devoted to the use of adsorption processes for purification of proteins, chemicals and biochemicals used in the manufacture of pharmaceutical and food products, for the purification of water and for other biochemical processes.

On the other hand, an important area for the future, related to water treatment in areas where water is not abundant, will be the bioregeneration process for renewing the adsorbent surface for further adsorption of organics during simultaneous adsorption and biodegradation processes. In this case the adsorbent will be "biologically" activated carbon, the use of which is becoming more generally accepted.



### *3.2.3.7 Bioseparation*

Bioseparation using novel and advanced porous adsorbents is a promising technology which has high potential for expansion in a number of biotechnological and biomedical applications. These include rapid cell separation from biological media such as blood; of particular interest is separation of stem cells which currently attract a lot of interest and are likely to be used in major innovative medical treatments such as regenerative medicine.

Extracorporeal (outside the body) medical adsorbents for blood and blood plasma purification are another major area for development. Here it is expected that novel materials will be more biocompatible than existing adsorbents for haemoperfusion. Thus it will be possible to use them uncoated for direct contact with blood; with an appropriate pore size such adsorbents will be able to adsorb large molecules such as proteins (antibodies), antigens and circulating immune complexes, thereby opening the door for treatment of autoimmune diseases which currently cannot be treated efficiently.

It is expected that the family of adsorbents for bioseparations will extend to natural biopolymers, activated carbons with controlled porosity and surface chemistry (by using polymeric precursors), and their composites. In addition to traditional granular adsorbent columns, porous monoliths will be developed. Monolithic columns will offer lower flow resistance, and provided they have a right combination of macro- and mesopores, they will offer an efficient device for fast bioseparations.

A separate and very important question is selectivity of separation. Although an obvious solution of this problem is to use principles of affinity chromatography by attaching covalently biospecific or bioselective ligands to the surface of an adsorbent, this is a very expensive solution and will be used in exceptional situations only when the target adsorptive is expensive and its recovery will cover the costs of the adsorbent. In most cases, however, a higher selectivity will be achieved by a combination of non-specific factors such as pore size, surface charge, hydrophobicity/hydrophilicity of the surface and other non-specific

approaches which, if applied in a combined manner, will provide the required selectivity without incurring very high costs.

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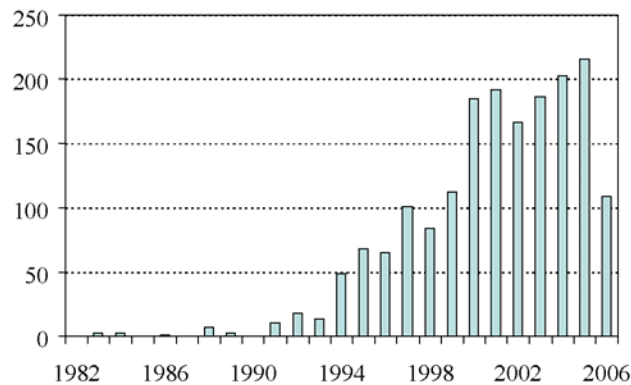
## 3.3 Membranes

### 3.3.1 Introduction

Intelligent membrane engineering can help to realize the process intensification strategy. Integrated membrane separations and new membrane operations, such as catalytic membrane reactors and membrane contactors, will play a crucial role in future technologies. However, so far no inorganic membrane is used in large-scale industrial gas separation. Membrane reactor technology has huge promise to deliver intensified processes that are more compact, less capital-intensive, giving higher conversions and selectivities in equilibrium- and kinetically controlled reactions, respectively. Membrane reactors are expected to save energy and costs of feed/product separation. So far, no chemical high-temperature membrane reactor is in industrial operation. The use of porous ceramic filter membranes in biotechnology is an exception.

Inorganic membranes, such as ceramics, metals and glass, show promising properties different from the organic ones. They can be backwashed frequently without damaging the separation layer. Inorganic membranes are highly resistant to cleaning chemicals, they can be sterilized and autoclaved repeatedly at 130 – 180 °C and can stand temperatures up to at least 500 °C. The latter properties recommend them especially for biotechnological processes. Inorganic membranes should have longer life spans than organic ones. The life span of a typical hydrophilic organic membrane is about 1 year, of a hydrophobic membrane 2 years, and that of fluoropolymers up to 4 years. Inorganic membranes are, however, much more expensive than polymeric ones, and they are brittle. Three types of inorganic membranes are close to a commercialization: Pd-based membranes in H<sub>2</sub> separation, perovskites in O<sub>2</sub> separation and zeolite membranes in shape-selective separations. Porous sol-gel derived X-ray amorphous metal oxides and carbon membranes are also potential candidates for an industrial use in a time scale between 5 and 10 years. The regular pore structure of a zeolite molecular sieve suggests that a thin supported zeolite membrane layer can discriminate between molecules of different size and shape. The pore diameter of the

separating zeolite layer is in the range of the kinetic diameter of the molecules to be separated in order to force molecular sieving as the determining diffusional regime. Further, besides the molecular exclusion effect, due to the interplay of mixture adsorption and mixture diffusion, reasonable separation effects on zeolite membranes can be expected according to specific adsorptive interactions and/or differences in the molecular mobilities.



**Figure 3:** Development of articles on zeolite/molecular sieve membranes/coatings/films in the open literature with (zeolit\* OR molecular sieve) AND (membrane\* OR coating OR film).

During the last 25 years, a high dynamics in the field of R&D on porous membranes can be observed (Figure 3). Hand in hand with progress in materials synthesis and molecular modelling based on adsorption and diffusion data of molecules in porous media, high-temperature stable pore membranes have been developed. This progress is reflected by the development of organic (Polymer of Intrinsic Microporosity, PIM, carbon by pyrolysis of polymers) and inorganic (zeolite, sol-gel derived metal-oxide) membranes as well as hybrid membranes as a combination of organic and inorganic materials.

There is an impressive progress in the development of zeolite membranes during the last decade. Now the technologies are available to prepare zeolite membranes of sufficient quality and reliability. In the near future, in a hard competition with other separation techniques, the exploitation of hydrophilic zeolite membranes for the dewatering will go on, and there will be first attempts to use narrow-pore membranes zeolite for the separation of small molecules such as hydrogen. The main application field of zeolite membranes is believed to be the shape-selective separation of  $C_4$  to  $C_8$  hydrocarbon isomers, since there

exists no other proper separation technique for this problem. On a medium time scale, therefore, zeolite membranes will be developed which can do a unique job that no other membrane can do: Molecular sieving of molecules of almost identical or similar mass by size and shape.

Gas separation is highly competitive both within the membrane field itself and with other gas separation technologies. The key properties of a membrane process are flux, selectivity, operationability, stability and cost. The current rise in energy costs makes membrane separations – which can be generally low in energy consumption – more attractive. A huge impact on inorganic membrane R&D would be a successful application of inorganic membranes in important environmental and energy-related processes, such as the cost-effective purification of hydrogen and methane.

After the successful realization of an industrial separation process using zeolite membranes, the development of a (catalytic) membrane reactor becomes possible in the long term. Most probably, again the shape-selective separation behavior of zeolite membranes will be exploited here which recommends the extractor type membrane reactor.

The European Network of Excellence INSIDE-POReS can play a key role in this field. The synergy existing between its pillars (porous material synthesis, adsorption, membranes and catalysis) is an important feature and strength of the network. Membrane research can give important contributions to areas of clean fuels (e.g. bioethanol in sunfuels, H<sub>2</sub>O removal in the Fischer-Tropsch process and separation of isomers), health (e.g. membrane coatings – dosing control), environment (e.g. CO<sub>2</sub> separation and sequestration and H<sub>2</sub> separation), bulk chemicals (e.g. O<sub>2</sub>-membranes like perovskite membranes and H<sub>2</sub> removal from dehydrogenation reactions), hydrogen production (e.g. H<sub>2</sub> removal and CO<sub>2</sub> removal) and energy saving (e.g. light emitting diodes incorporating fluorescent ceramic materials).

### 3.3.2 Short-term (< 10 years) development of porous membranes

A remarkable progress was achieved by the synergistic co-operation of materials synthesis, molecular modelling based on adsorption and diffusion data and the development and testing of novel membranes.

#### 3.3.2.1 Zeolite membranes

Today, LTA membranes in the dewatering of ethanol by vapor permeation or by pervaporation have reached the commercial state. For shape-selective separations other zeolite membranes like types MFI and DDR are in technical scale. Further molecular sieve structures are tested as membranes. Most progress in the development of molecular sieve membranes was achieved for MFI type membranes (silicalite-1 and ZSM-5) since their preparation is relatively easy. They can be synthesized in a highly siliceous form which provides chemical stability and allows oxidative regeneration. Recent interesting developments comprise DDR and CHA membranes for CO<sub>2</sub> separations.

The major important developments needed for all systems is to further improve the flux levels in combination with demonstration of their longer-term stability for the envisaged application. New ways of synthesis, improved permeation tests and proper applications shall improve the zeolite membranes for their technical use. Increasing R&D activities are reflected by increasing publication activities. The application of a porous membrane offers huge promises, but it is still a challenge in itself. A few important cases are outlined below.

The most widely claimed structures of zeolite membranes are: MFI – silicalite-1/ZSM-5, LTA – A-type, FAU – Y-type/X-type, DDR and CHA – SAPO-34.

#### 3.3.2.2 Hydrogen separation

Gas separation membranes are widely used for H<sub>2</sub> recovery. This can be achieved in different ways, viz. by employing porous or dense membranes. Porous membranes are based on microporous amorphous oxides, zeolitic materials or carbon that rely on molecular sieving or

selective adsorption and diffusion. Dense membranes are on the one hand the Pd-based alloys and on the other hand the proton conduction membranes. These materials would in principle yield infinite selectivity for hydrogen due to their transport mechanisms.

Since the kinetic diameter of H<sub>2</sub> is around 0.29 nm, the pore diameter should be larger than this but smaller than the kinetic diameter of the molecules from which H<sub>2</sub> is to be separated. In general, microporous membranes based on amorphous metal oxides (SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>) are most often prepared by a sol-gel technique using spin coating or dip coating. SiO<sub>2</sub> sol-gel layers show excellent separation and fluxes but have a very limited hydrothermal stability which excludes their use for H<sub>2</sub> removal from atmospheres containing steam at high temperature. TiO<sub>2</sub> and ZrO<sub>2</sub> sol-gel layers are much more stable, but one does not succeed in preparing highly selective narrow-pore membrane layers.

Crystalline zeolite membranes offer much better thermal and hydrothermal stability. Gas permeation results for silicalite-1 (MFI) membranes have been reported in many studies in the literature.

The selectivity depends on the transport mechanism and molecular sizes. Adsorption-diffusion and size-exclusion phenomena strongly interplay, and their temperature behavior may completely reverse selectivities. For n-butane/hydrogen mixtures the butane adsorbs well and blocks the permeation of the much faster diffusing hydrogen. This yields n-butane selectivities ranging from >100 at room temperature to values below one, approaching the Knudsen selectivity above 400 °C. For isobutane the reverse is observed. Literature data suggest that this MFI membrane is a candidate for the use in an extractor membrane reactor for selective H<sub>2</sub> removal.

Carbon Molecular Sieve (CMS) membranes are less frequently used because of the poor mechanical strength of carbon, their instability in O<sub>2</sub>-containing atmospheres at elevated temperature and their susceptibility to strongly adsorbing components (solvent vapors,

moisture). However, in the absence of O<sub>2</sub>, CMS membranes offer excellent thermal and chemical stability as well as high separation factors.

Dense metal membranes selectively absorbing atomic H<sub>2</sub> are well-suited for high-temperature H<sub>2</sub> separation offering an infinite selectivity for H<sub>2</sub> and are mainly based on Pd and its alloys with Ag, Cu or Ru. Dense ceramic high-temperature inorganic mixed proton- and electron-conducting membranes consist of a ceramic solid oxide proton conductor and an electron-conducting second phase which could be a ceramic or a high-temperature resistant metal, e.g. Pd, Ni or an alloy. First studies are based on the perovskite-type materials SrCeO<sub>3</sub> and BaCeO<sub>3</sub> doped with Y, Yb or Gd.

Evaluating the current status, one can state that porous membranes successfully compete with dense membranes. On a short term, first technical membranes for H<sub>2</sub>-separation will be metal-based, whereas on a long term porous membranes will dominate the scene because of the higher fluxes, robustness and cheaper fabrication.

### *3.3.2.3 Carbon dioxide separation*

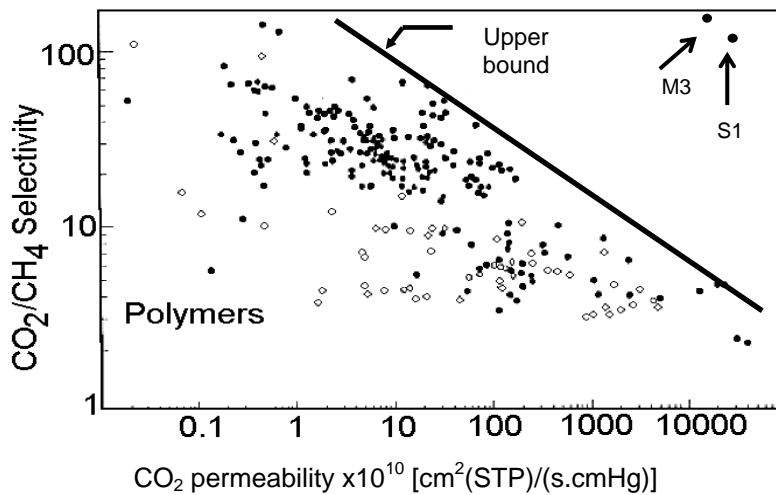
The development of proper separation technologies for the removal of CO<sub>2</sub> from exhaust gases and from natural gas is still a challenging problem. In natural gas treatment applications the feed gas usually stems directly from gas wells in a wide pressure range from 20 to 70 bar with 5 to 50 % CO<sub>2</sub>. The product gas must contain < 2 % CO<sub>2</sub>. At the moment it is not economic to produce natural gas from fields with CO<sub>2</sub> contents above 10 %. Glassy polymer membranes are used for natural gas purification (removal of CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S) but they suffer from swelling-induced plasticization by CO<sub>2</sub> and hydrocarbons incorporation. This kind of membrane failure would not happen with zeolite membranes since they are chemically stable towards organic solvents and plasticization due to gas absorption.

Although polymer membranes with a high performance for CO<sub>2</sub>/CH<sub>4</sub> exist, these membranes have only a rather low separation performance in the CO<sub>2</sub>/N<sub>2</sub> separation because of low diffusivity and solubility selectivities due to the similar size of CO<sub>2</sub> and N<sub>2</sub>. Both CO<sub>2</sub> (0.33 nm



kinetic diameter) and CH<sub>4</sub> (0.38 nm kinetic diameter) are relatively small molecules, that is to say much smaller than the pores of large- and medium-pore zeolites. Since the separation of zeolite membranes is based on competitive adsorption, the selectivities were found to be low. Nevertheless, most often MFI-type membranes were studied. The best results for the separation of CO<sub>2</sub>/N<sub>2</sub> mixtures on large-pore zeolite membranes were reported for FAU-type membranes. In contrast, small-pore zeolites like zeolites T (0.41 nm pore size), DDR (0.36 nm x 0.44 nm), and SAPO-34 (0.38 nm) have pores that are similar in size to CH<sub>4</sub> but larger than CO<sub>2</sub>. Recent reports show that these membranes show high CO<sub>2</sub>/CH<sub>4</sub> selectivities (> 100) due to a combination of differences in diffusion and adsorption.

For SAPO-34 and DDR membranes CO<sub>2</sub> selectivities above 100 were obtained for conditions near industrial requirements (Figure 4). The CO<sub>2</sub> flux and selectivity decrease in the presence of water, since water has a strong affinity to the hydrophilic SAPO-34 membrane. Therefore, the hydrophobic DDR membranes are more appropriate to separate CO<sub>2</sub> from humid gases.



**Figure 4:** Comparison of CO<sub>2</sub>/CH<sub>4</sub> separation selectivity versus CO<sub>2</sub> permeability for polymeric membranes and SAPO-34 membranes at room temperature and feed and permeate pressures of 222 and 84 kPa. M3 and S1 denote two SAPO-34 membranes.

Another separation problem of practical relevance is the CO<sub>2</sub> removal from N<sub>2</sub> in exhaust gases for CO<sub>2</sub> sequestration. Most studies have concentrated on MFI- and FAU-type

membranes with moderate success up to now. Their performance is mainly based on selective adsorption. Selectivities for CO<sub>2</sub> range widely from 2 to 50. Also here the narrower-pore SAPO-34 and DDR membranes seem to be viable alternatives.

#### *3.3.2.4 Dewatering of (bio)ethanol*

There is no doubt that there will be a worldwide increase in the production of ethanol, either as bioethanol or by ethylene hydration. The most common technology to produce ethanol is the hydration of ethylene in the gas phase at high temperatures and pressures, but increasingly bioethanol is being produced. As a blend for gasoline the water content must be reduced to 2 000 ppm, for the Ethyl-*Tert*-Butyl Ether (ETBE) production from isobutene and ethanol the water content must be < 500 ppm.

By distillation of an ethanol/water fermentation broth an azeotrope with an ethanol content of about 93 vol.-% bioethanol is obtained. The conventional dewatering of alcohols by azeotropic, extractive or two-pressure distillations is typically more energy-intensive and requires a complex process layout. Especially for ethanol/water and other systems possessing azeotropes, two alternative processes are available: Pressure swing adsorption employing 3A or 4A molecular sieves (LTA zeolite) and steam permeation using hydrophilic organic or inorganic (4A zeolite) membranes. The application of membrane processes is especially beneficial for systems of low relative volatility. The hydrophilic LTA zeolite membrane layer is extremely selective in the separation of water from organic solutions by vapor permeation and pervaporation and can be used, therefore, for the production of water-free ethanol. Some demonstrations are currently ongoing.

For dewatering of the crude ethanol stream using membrane technology, Mitsui-BNRI played a pioneering role in the cost reduction of the membrane separation by integrating distillation and membrane separation in the so-called "Membrane Separation and Distillation" (MDI) process. From April to September 2003, Mitsui-BNRI successfully tested the dewatering of bioethanol in the pilot scale by using LTA membranes for vapor permeation in Piracicaba (São Paulo State, Brazil). The capacity was 100 l/h of a feed with 93 vol.-% ethanol, and the

product was a 99.65 vol.-% ethanol. As the next step, Mitsui-BNRI installed a larger capacity at Daurala Sugar Works (Uttar Pradesh State, India). The capacity of 30 000 l/d can be achieved with an LTA membrane area of 30 m<sup>2</sup>. Each membrane is inserted into a sheath tube (internal diameter 19 mm). The feed is evaporated by heating with steam. The feed is 93 vol.-% bioethanol, the product purity is 99.8 vol.-% ethanol for blending with automobile gasoline, the ethanol content in the permeate is < 0.1 vol.-%.

In recent installations in Europe, the adsorptive drying of ethanol was applied instead of the membrane technology. Ethanol produced by ethylene hydration is purified by distillation which is coupled with a zeolite adsorption section. By the so-called DELTA-T technology, the ethanol is purified to less than 100 ppm water. The preference of the molecular sieve adsorption process with zeolites for the dewatering of ethanol may be due to the fact that the azeotrope ethanol/water contains only a relatively low amount of water (4.4 %) so that the heat management of the cyclic adsorption processes is feasible. Since the azeotrope isopropanol/water contains more water (12.6 %), here steam permeation using hydrophilic organic or inorganic membranes has a higher realization chance in comparison with ethanol/water.

In Europe, Inocermic GmbH, which is a 100 % subsidiary of HITK, Hermsdorf, Germany, produces NaA membranes for dewatering processes, especially of bioethanol, by pervaporation and vapor permeation. The advantage is that feeds with 90 wt.-% ethanol can be used, so distillation has not be pushed to such a high water removal, thereby reducing the energy consumption. Four plants for bioethanol dewatering are currently under construction for mixing with gasoline.

The latest developments are the application of SOD and DDR membranes for water removal from mixtures with alcohol. The six-ring openings of SOD require operation temperatures above 100 °C to overcome the activation barrier. Pure water is obtained with fluxes up to 3 kg m<sup>-2</sup> h<sup>-1</sup> at 200 °C. DDR membranes operate at lower temperatures yielding selectivities up to 1 500 and fluxes of 2 kg m<sup>-2</sup> h<sup>-1</sup> at 100 °C.

### *3.3.2.5 (Bio)ethanol removal from fermentation batches*

Hydrophilic membranes like LTA and FAU can be used for water extraction. The alcohol is concentrated by distillation, and the starting feed of the hydrophilic permeation contains about 93 wt.-% ethanol. An opposite target can be the continuous removal of ethanol from the fermentation broth since the fermentation process stops at ethanol concentrations near 15 %. Hydrophobic membranes such as the MFI-type are in development to tackle this problem. Typically, a flux of about  $1 \text{ kg m}^{-2} \text{ h}^{-1}$  of 85 wt.-% ethanol is obtained from a feed with 8 wt.-% ethanol, corresponding to a separation factor of 57. The relatively low ethanol fluxes are due to the test conditions with real fermentation broths. There seems to be ample room for improving the membrane performance by optimizing the support structure, reducing the membrane thickness and increasing the Si/Al-ratio of the MFI membrane.

### **3.3.3 Long-term (> 10 years) development of porous membranes**

The long-term scenario will be determined by the strong synergistic co-operation of catalysis and membrane science in the development of catalytic membrane reactors. These concepts require progress in the synthesis of the corresponding materials as well as modelling of the interaction of reaction and mass transport in porous media. Novel porous membranes like hybrid materials-based ones will become available.

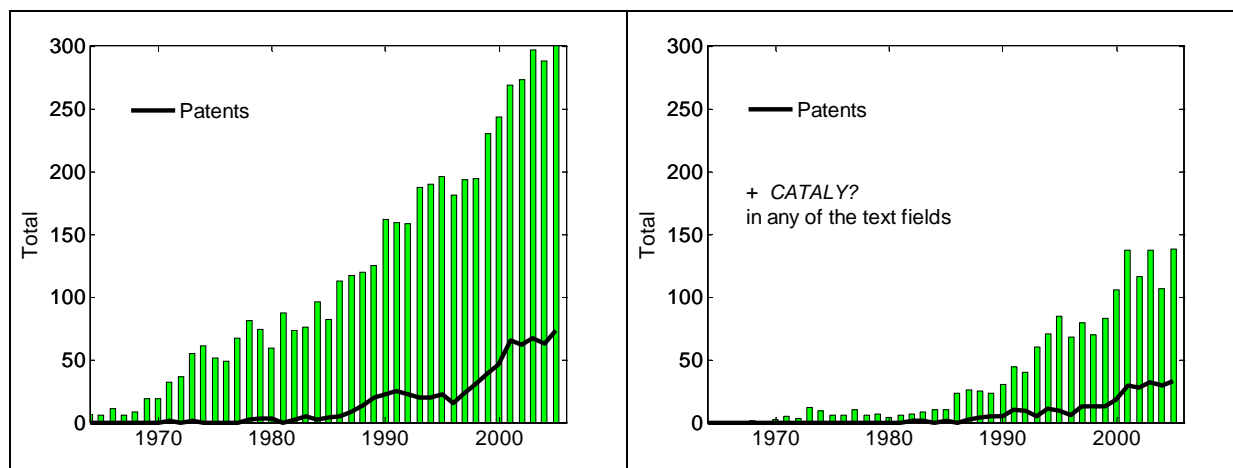
#### *3.3.3.1 Catalytic membrane reactors*

Catalytic membrane reactors have been receiving increased attention over the last two decades, in particular due to the progress made in the field of inorganic membranes. This is because conventional polymeric membranes, although they have reached some commercial success in membrane reactors mainly in biotechnology and in other low-temperature applications, have a limited thermal, chemical and also mechanical stability. Inorganic membranes, on the other hand, can withstand high temperature; they are chemically much more stable under the often harsh environment of industrial reactors, and they are mechanically more robust. Advanced inorganic membranes have become increasingly available which hold promise for selective separations under reaction conditions, e.g. based

on the molecular dimensions of the reactants or on component-specific chemical interactions with the membrane material. Examples include polycrystalline zeolite films, amorphous microporous oxide membranes and mixed ion- and electron-conducting solid oxides. These materials have reached impressive separation factors for different systems, not always as high as that of palladium alloy membranes for hydrogen first proposed in the late 1960s by Gryaznov and others, but high enough to let catalysis scientists and reaction engineers dream of advanced engineered catalysts with built-in shape selectivity effects. And from the process engineering side, the vision of process intensification through multifunctional reactors in the early 1990s has also breathed new life into research on catalytic membrane reactors, as they could allow for the elimination of process steps and so lead to more compact and cost-efficient plants than a conventional design with separate units.

A look at the requirements for successful integration of the different functions into one unit shows that the field of catalytic membrane reactors is a highly interdisciplinary research area connecting first of all membrane material science with catalysis research and chemical engineering. Catalytic membrane reactors have been addressed in numerous publications (Figure 5) and in many review articles and book chapters, including the one by Dittmeyer and Caro in the second edition of the Handbook of Heterogeneous Catalysis, and, so far the most comprehensive treatment, in the books by Hsieh and by Sanchez-Marcano and Tsotsis.

According to the IUPAC definition a membrane reactor is a device combining a membrane-based separation and a chemical reaction in one unit. Separation here normally implies that the membrane shows a preferred permeation for one or several of the constituents of the reaction mixture. For this functional integration various possibilities exist. Generally one can distinguish extractor and diffusor type systems where components are removed or added, respectively, to the reaction zone. This may occur selectively or non-selectively.



**Figure 5:** Left: Number of publications found by a search in the CAS database for the keywords *Membran?* and *React?* in the title. Right: Number of publications and patents with the additional keyword *Cataly?* in any of the text fields (for 2005 only up to November 3).

Besides the promise of functional integration enabling more compact and simple process schemes (process level) and the utilization of synergetic effects from the integration of reaction and mass transport into one unit (unit level), a third level exists where membranes may offer advantages for catalyzed reactions. This is on the level of the reaction, i.e. at the active sites; it requires that the catalyst is an *integral part* of the membrane. With dense membranes employed in a distributor membrane reactor, it would be possible that the membrane, due to its chemical nature, supplies one of the reactants in a special form which is more active or selective in the reaction that one wishes to catalyze than in its usual form. One example is a ceramic oxygen ion-conducting membrane which can pass oxygen ions to a solid catalyst attached to it instead of using molecular oxygen from the reactant gas phase. Other examples include silver membranes, which selectively permeate atomic oxygen, or membranes made from palladium or palladium alloys that are permeable exclusively to hydrogen in atomic form.

### 3.3.3.2 Novel porous membranes

Different concepts are followed to develop new porous membranes that may find application in separations and in catalytic membrane reactors:

1. New zeolite membranes
  - a. small pores of 8- or 6-ring windows
  - b. surface or pore modifications to alter adsorption, diffusion or catalytic performance
2. Multi-layer zeolite membranes
  - a. Improved selectivity by repeated crystallization of the same zeolite type
  - b. Novel properties by combination of layers of different zeolites
  - c. New application fields by combination of zeolite membranes with other inorganic ones
3. Novel porous materials
  - a. Metal Organic Frameworks (MOFs)
  - b. Covalent Organic Frameworks (COFs)

### ***Novel porous membranes for separations***

LTA (Linde type A) with a pore size of 0.42 nm in the Na<sup>+</sup> form is the first zeolite membrane that has reached a commercial status in the dewatering of (bio)ethanol and isopropanol by vapor permeation or pervaporation. However, the successful application of LTA membranes in dehydration is rather based on the hydrophilic character of zeolite LTA resulting in a preferential adsorption of water from mixtures than on real size-exclusion molecular sieving; when tested for hydrogen separation from gas mixtures, the LTA membranes showed only Knudsen separation. Recently, NGK announced the commercialization of another type of zeolite membrane, DDR (deca-dodecasil 3R), with narrow pores of 0.36 × 0.44 nm for CO<sub>2</sub> separation from CH<sub>4</sub>. Another promising development are H-SOD (sodalite) membranes with narrow pores of 0.28 nm. They have shown a reasonable water flux of 4 kg m<sup>-2</sup> h<sup>-1</sup> and an ideal separation factor  $PS$  (H<sub>2</sub>O/other components)  $\approx 10^6$ . Such narrow-pore zeolite membranes are interesting candidates also for hydrogen separation.

However, the most often used shape-selective zeolite membrane is MFI (silicalite-1) with a pore size of 0.55 nm; it is close to commercialization for isomer separation, for example of xylenes or normal from branched hydrocarbons. The advanced state of development of

silicalite-1 membranes was reached because its preparation is relatively easy, and also because this highly siliceous zeolite type provides excellent chemical stability and allows oxidative regeneration.

MOFs represent an interface between organic and inorganic compounds since they consist of metal ions linked by organic molecules (ligands). MOFs comprise ionic inorganic-organic hybrid materials, especially coordination polymers based on bi- to tetravalent carboxylic acids. This novel approach in preparing porous materials exhibits a rational and even more flexible design of the network compared to the already known inorganic materials. The first reports on MOFs in prospective industrial processes have already been published. Possible applications for MOFs are catalysis, gas purification and gas storage, which needs information on the molecular transport in MOFs. In spite of the considerable attention to MOFs, only a handful MOFs with permanent porosity have been reported so far, in part because framework stability after template removal in those materials has emerged as a serious problem. Studies on functional aspects, especially the application in membranes, accumulate rather slowly, and thus only two examples using MOFs in a gas separating membrane are known. Won et al. embedded a Cu(II) complex in a polymer matrix yielding membranes with high H<sub>2</sub>-selectivities and remarkable permeabilities. In another paper by Car et al., by incorporating different MOFs into the rubbery polydimethyl siloxane (PDMS) and the glassy polysulfone (PSf), the permselectivities and permeances could be slightly improved. It has been shown that the synthesis of supported MOF composite membranes based on manganese(II) formate (Mn(HCO<sub>2</sub>)<sub>2</sub>) and on Cu-BTC (Benzene-Tricarboxylic acid) is possible.

Future work on MOF membranes should focus on a detailed examination of surface charges during synthesis, and the obtained results can be applied in a direct modification of *in-situ* synthesis and/or surface treatment in order to increase the amount of crystals on the supports. Finally, *in-situ* crystallization of other promising MOFs for new composite molecular sieving membranes is challenging. Pan et al. published the synthesis of a porous lanthanum-containing MOF with stability up to 450 °C, with high and selective H<sub>2</sub> adsorption rates.



### ***Novel porous membranes for membrane reactors***

Chemical modifications have been made in particular for MFI zeolite type membranes, e.g. by isomorphous substitution to give Al-, Fe-, B- and Ge-ZSM-5 membranes, by variation of the Si/Al-ratio and ion exchange. These numerous possibilities allow a fine adjustment of the membrane characteristics to tackle many different liquid and gas separation problems.

Multi-layered zeolite membranes with gradients of chemical composition or structure in the zeolite layers have the potential to expand the applications of zeolite membranes even further. Such membranes allow the intimate combination of different functions or characteristics in a single membrane, e.g. catalytic activity/inertness, hydrophobic/hydrophilic character and different pore sizes. Membranes which combine a catalytically active zeolite layer with an inert one are interesting for membrane reactors because they possess, in close proximity, reactive and passive environments for staged reaction and non-reactive separation and/or for the passivation of non-shape-selective external catalytic sites. The synthesis of multilayered membranes is a challenge, and further research is necessary.

There are ambitious attempts to combine zeolite layers with other inorganic membrane layers. As an example, for shape-selective oxidations a thin silicalite-1 layer was crystallized onto an oxygen-transporting perovskite membrane. Assuming that a mixture of the xylene isomers would be in contact with this bi-layer membrane facing the Ti-modified silicalite-1 layer, mainly the *p*-xylene would enter the silicalite-1 layer and could become oxidized to terephthalic acid with the oxygen released from the perovskite membrane.

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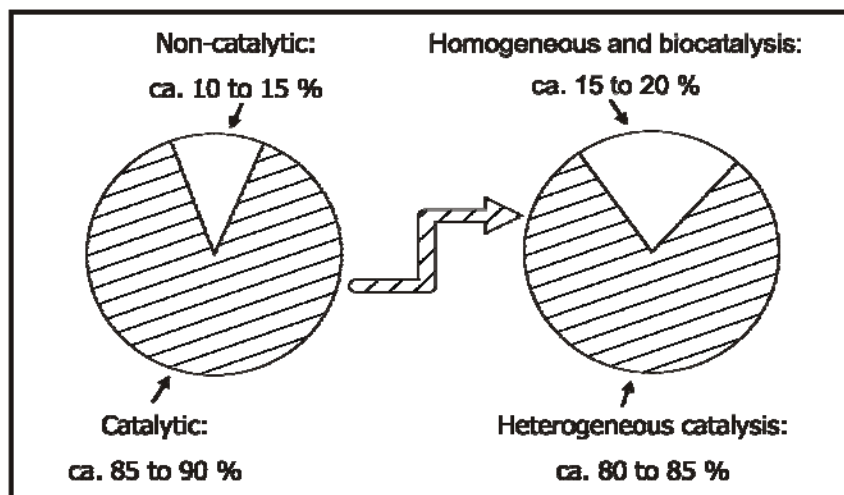
## 3.4 Catalysis

### 3.4.1 Introduction

Catalysis is an indispensable tool, whenever chemical substances are to be converted into more valuable or environmentally more benign products. Catalysis enables one to make chemical processes more selective for the desired products, more energy-efficient and/or environmentally more friendly. This is why today a catalyst is being employed in ca. 85 to 90 % of all chemical processes (see Figure 6, left).

Catalysis is usually classified into three main categories, viz. heterogeneous, homogeneous and biocatalysis. Of these, heterogeneous catalysis is playing by far the most important role covering some 80 to 85 % of all catalytic processes (see Figure 6, right). It is a salient feature of heterogeneous catalysis that the catalyst is a solid phase under process conditions, while the reactants and products occur in one or more fluid phases, i.e., gaseous, liquid or supercritical phases. In many instances, the solid catalyst is porous which brings about large specific surface areas, typically in the range of 100 to 1000 m<sup>2</sup> · g<sup>-1</sup>. Heterogeneous catalysis

is among the most important applications of such porous materials, besides adsorption and membrane technology. The estimated worldwide market volume for solid catalysts, as of 2007, falls between  $10$  and  $15 \cdot 10^9 \text{ €} \cdot \text{a}^{-1}$ . This is a steadily increasing market, and the prospects for significant innovations in this field are considered to be favorable.



**Figure 6:** Importance of catalysis in commercial-scale chemical processes.

INSIDE-POReS is a Network of Excellence (NoE) devoted to *nanoporous* solids, i.e., materials with comparatively narrow pores in a range from several tenths of a nanometer ( $10^{-9}$  m) up to about several hundred nanometers. In terms of the nomenclature approved by the International Union of Pure and Applied Chemistry (IUPAC), this includes materials with micropores ( $< 2.0$  nm), mesopores (2 to 50 nm) and the lower end of macropores ( $> 50$  nm). Nanoporous materials that have gained industrial importance as catalysts or catalyst supports include zeolites, activated carbons, metal oxides like alumina, silica or titania, and mixed metal oxides such as silica-alumina. Of these, zeolites are particularly worth mentioning, since they revolutionized a number of large-scale catalytic processes, especially in petroleum refining and basic petrochemistry. One figure may suffice to illustrate the economic benefit created by modern zeolite catalysts: Today, the estimated cost of worldwide petroleum refining would be higher by some  $20$  to  $40 \cdot 10^9 \text{ €} \cdot \text{a}^{-1}$ , if zeolite catalysts were not available.

In spite of the remarkable success achieved with nanoporous materials in the field of heterogeneous catalysis, much remains to be done in the decades to come. In the European NoE INSIDE-POReS with its four pillars (synthesis, adsorption, membranes and catalysis), the EU's research expertise in the pertinent fields of natural sciences has been bundled along with the necessary awareness of unresolved technical problems. A close cooperation and targeted interaction between the four pillars will create invaluable synergies which, in turn, will form an unprecedented basis for cutting-edge research in the field of heterogeneous catalysis. Significant progress can be expected to emerge from three sources.

(1) Together, the participating groups dispose of a unique arsenal of characterization techniques, both for *ex-situ* and *in-situ* investigations of nanoporous catalysts. The systematic use of these combined characterization techniques will enable a gradual move towards a true and deeper understanding of the mechanisms of heterogeneous catalysis and knowledge-based search for improved nanoporous catalysts.

(2) Modern materials science furnishes new and improved nanoporous solids at an unprecedented pace. Examples are mesoporous activated carbons, carbon nanotubes, carbon nanofibers, sol-gel-derived metal oxides and metal-organic frameworks (MOFs), to enumerate only a few. This plethora of emerging nanoporous solids can be looked upon as a unique source of catalytic materials, and exploring their potential as catalysts is among the objectives of this NoE.

(3) There are countless unresolved problems and open questions in applied heterogeneous catalysis. These pertain, *inter alia*, to (i) the manufacture of clean fuels (e.g. efficient removal of polycyclic aromatics from diesel fuel, jet fuel, light cycle oils from fluid catalytic cracking or coal-derived liquids, isobutane/olefin alkylation on solid catalysts etc.), (ii) the replacement of expensive raw materials for the chemical industry by cheaper ones, e.g. of alkenes by alkanes, (iii) the direct oxyfunctionalization of alkanes, desirably with dioxygen or air, (iv) a further replacement of liquid acid or base catalysts by modern, environmentally benign solid catalysts, (v) identification of enhanced catalysts for

applications in environmental protection, e.g. the combustion of traces of volatile organic compounds (VOCs) in air. Development of a comprehensive awareness of such open problems and of strategies for potential catalytic solutions is another objective of this NoE.

### **3.4.2 Short-term (< 10 years) development of nanoporous catalysts and techniques for their *in-situ* characterization**

Heterogeneous catalysis is a broad field of science and technology. In the definition of its main activities, which are briefly described below, the catalysis pillar had to be selective rather than exhaustive. In the identification of the NoE's short-term (< 10 years) activities, the following criteria were of prime importance:

- (1) Meeting challenges, the European society and markets are faced with: environmental protection and health care; clean fuels; cheaper and readily available raw materials for the production of bulk chemicals; novel or improved routes to chemicals with a rising demand.
- (2) Undertaking significant steps forward in modern catalysis research.
- (3) Interacting as closely as possible with the NoE's synthesis, adsorption and membrane pillars, thereby achieving the maximum possible synergy effects. In view of the highly interdisciplinary nature of heterogeneous catalysis, this appears to be a particularly important strategic issue.
- (4) Wherever possible, at least two partner groups from within the NoE should be involved in each activity.

#### *3.4.2.1 Stabilization of small metal clusters as guests inside nanoporous solids as hosts*

Very small (< 5 nm) metal clusters have recently been found to possess interesting catalytic properties which may significantly deviate from those of the same metal as a bulk material. Perhaps the best known example is gold which did not play a major role in heterogeneous catalysis for decades. It was only after the discovery of the exciting catalytic properties of gold nanoclusters (e.g. a strongly enhanced activity in the oxidation of carbon monoxide or the capability to produce propylene oxide by direct epoxidation of propene with *in-situ*

generated hydrogen peroxide) that the catalysis community developed a strong interest in this metal. Very small metal clusters, however, possess a high surface energy, and this brings inevitably about a strong driving force for their agglomeration and growth into much larger clusters with a concomitant loss of their unique catalytic properties.

Nanoporous solids, especially zeolites, offer, at least in principle, the fascinating opportunity to synthesize nano-sized clusters of catalytically active metals inside their pores and cavities. The rigid pore architecture will behave as a template which prevents the metal clusters from growing to a size beyond the pore size. If a zeolite with the appropriate pore architecture is employed, the metal nanoclusters will be entrapped inside the cavities which, conceptually, hinders them from migrating through the pores and agglomerating into large particles with the properties of the bulk metal.

In a combined effort involving several partner groups of the NoE, the preparation and stabilization of small metal clusters inside nanoporous solids will be systematically studied. In addition to gold, other catalytically relevant metals will be introduced as guests into appropriate nanoporous hosts. Examples for such metals are platinum, palladium, ruthenium, iridium, rhodium and silver, or their alloys. Nanoporous materials to be employed as hosts will be mostly selected from the family of zeolites, *inter alia* zeolites Y, ZSM-5 and MCM-22. Various techniques will be studied for incorporating the metal guests into the zeolitic hosts. Among these techniques are ion exchange in aqueous suspension, solid-state ion exchange, chemical vapor deposition and hydrothermal synthesis of the zeolites in the presence of metal compounds. The resulting host/guest materials must be characterized by a carefully selected assortment of physico-chemical techniques including transmission electron microscopy (TEM), determination of the metal dispersion, EXAFS and catalytic tests. Within the NoE, the necessary physico-chemical techniques are available.

### *3.4.2.2 Oxyfunctionalization of alkanes with dioxygen or air on small metal clusters stabilized inside nanoporous hosts*

The direct catalytic oxyfunctionalization of alkanes with the cheap, ubiquitously available and environmentally friendly oxidants air or oxygen is still at its infancy. Developing solid catalysts which are capable to convert alkanes aerobically with reasonable yields into alcohols, aldehydes and/or ketones with the same carbon number continues to be one of the main challenges of fundamental catalysis research.

Members of the family of novel nanoporous catalysts to be prepared as described in Section 3.4.2.1 of this roadmap will be screened for a potential activity in the aerobic oxyfunctionalization of an n-alkane with medium chain length, e.g. n-octane. These screening tests will be conducted both in the gas and liquid phase. Should a nano-sized metal or metal alloy with the desired catalytic properties be discovered, one might conceptually even think of a shape-selective oxyfunctionalization, that is a preferential formation of products that are oxygenated in a terminal position.

Obviously, the above-described search for novel oxyfunctionalization catalysts is highly ambitious and associated with a correspondingly high risk of failure. On the other hand, even a modest success (i.e., discovery of a new catalyst that gives relatively low yields of the desired oxyfunctionalized products) would mean a real breakthrough in heterogeneous oxidation catalysis.

### *3.4.2.3 Catalytic combustion of volatile organic compounds (VOCs) in air streams*

Cleaning air streams from VOCs is of ever increasing importance from the viewpoint of environmental protection and health care. Examples of VOCs to be removed from air streams include ethanol, ethyl acetate and toluene, i.e., low-molecular weight compounds that are typically used as organic solvents in countless applications. As already pointed out in Section 3.2.2.2, there are two options for the removal of VOCs, viz. adsorption and catalytic combustion to carbon dioxide and water. In both of these areas, nanoporous solids are of



utmost importance, viz. as adsorbents and as carriers for the catalytically active components, respectively. The latter mostly consist of noble metals such as platinum.

Like adsorptive VOC removal from air streams, catalytic combustion will be studied in detail and constitute a reference case for round robin experiments. In the new developments of improved catalysts for VOC combustion, the NoE will mostly rely on activated carbons and zeolites or zeolite-like materials as carriers, and the selection of these materials will occur in a close cooperation between the adsorption and catalysis pillars.

It must be borne in mind that, in air streams contaminated with VOCs, water vapor almost always occurs as an additional component. While water vapor is not itself a noxious constituent of such streams, it is expected to have a pronounced influence on the performance of a catalyst for VOC combustion. This influence is to be systematically investigated by varying the relative humidity of the VOC-contaminated air streams. It is anticipated that the sensitivity of a catalyst for VOC combustion towards water vapor depends largely on the surface hydrophilicity or hydrophobicity of its carrier. These correlations are important for optimizing processes for VOC removal and will hence be investigated in detail in this NoE.

#### *3.4.2.4 Isomerization and hydrocracking of model hydrocarbons for various fuels*

Skeletal isomerization and hydrocracking of petroleum fractions or Fischer-Tropsch wax are industrially important reactions. From a chemical point of view, their mechanisms are closely interrelated, and similar types of bifunctional catalysts are usually employed. In such catalysts, a hydrogenation/dehydrogenation function and a Brønsted acid function are combined, and in addition, the principle of shape-selective catalysis is exploited in some instances. Proven processes relying on bifunctional catalysts include hydrocracking of heavy gas oils for making high-quality diesel and jet fuel, isomerization of C<sub>5</sub>/C<sub>6</sub> hydrocarbons for enhancement of the octane number of light gasoline, catalytic dewaxing of middle distillates or lube base oils by shape-selective hydrocracking or skeletal isomerization and mild

hydrocracking of Fischer-Tropsch wax as the final processing step in the emerging gas-to-liquids technology.

While these processes can be looked upon as mature state-of-the-art technologies in the wide field of fuels manufacture, various additional applications of catalytic isomerization or hydrocracking have been identified as potential tools for making clean fuels of the future, in particular if the mandated aromatics content in motor fuels will be further reduced (current limiting value in the EU 35 vol.-%). Before this background, the NoE intends to include into its strategic lines of research three items which are briefly described below:

### ***Isomerization of heptane isomers***

Today, the high octane numbers of commercial gasoline are mainly due to branched alkanes in the light ( $C_5/C_6$ ) fraction and to aromatics in the heavy ( $C_7$  to ca.  $C_{10}$ ) fraction. Benzene has essentially been phased out from gasoline due to its carcinogenicity. Should the aromatics content of gasoline be further reduced in the future to values below 35 vol.-%, refiners have various options for responding. One of these is skeletal isomerization of the  $C_7$  alkanes. The predominating heptane isomers in straight-run gasoline are n-heptane (research octane number  $RON = 0$ ) and its monobranched isomers 2-methylhexane, 3-methylhexane and 3-ethylpentane ( $RON \approx 50$ ). Isomerization of these low-octane heptanes into their dibranched isomers 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane and 3,3-dimethylpentane ( $RON \approx 85$  to 95) could bring about a significant gain in the octane number. Hurdles to be overcome for an economically viable heptane isomerization stem from a) equilibrium limitations and b) undesired hydrocracking reactions at elevated conversions. Possible solutions include a) a limited conversion per pass through the reactor combined with novel technologies for isomer separation downstream of the catalytic reactor, followed by recycling of the low-octane isomers to the reactor; and b) the preparation of novel bifunctional catalysts with an as high as possible isomerization activity but a reduced hydrocracking activity. It is evident that the expertise from all four pillars of the NoE is needed for executing such a demanding project.

### ***Selective ring opening (hydrocracking) of cyclic C<sub>7</sub> hydrocarbons***

Highly branched isoalkanes are the most desirable gasoline components because they possess high octane numbers, are rich in hydrogen (low specific carbon dioxide emissions) and show clean burning characteristics in the spark ignition engine. In case of a severe reduction of the maximal aromatics content of gasoline, a situation may even arise where the rings in aromatic and naphthenic hydrocarbons must be partially opened to form alkanes without degradation of the carbon number. Since aromatic carbon-carbon bonds are quite stable, a hydrogenation to naphthenes is required prior to catalytic ring opening. So far, no good catalysts are known for the selective ring opening of naphthenes into highly branched isoalkanes with the same carbon number. Based on the combined experience within the NoE, especially in its synthesis and catalysis pillars, a search for novel selective ring opening of C<sub>7</sub> naphthenes is intended. A critical evaluation of the literature suggests that bifunctional catalysts with a weak and carefully controlled acidity are required for this application.

### ***Selective ring opening (hydrocracking) of aromatics in pyrolysis gasoline***

Ethene and propene are basic raw materials needed in huge quantities (ca.  $110 \cdot 10^6 \text{ t} \cdot \text{a}^{-1}$  and  $65 \cdot 10^6 \text{ t} \cdot \text{a}^{-1}$  worldwide, respectively) for making polymers and a broad variety of chemicals. The primary source of both ethene and propene is steam cracking of various hydrocarbon streams, of which naphtha, i.e., the C<sub>5</sub>/C<sub>6</sub> straight-run fraction of petroleum, is by far predominating in Europe. Besides ethene and propene, a naphtha steam cracker produces large amounts (combined yields  $\approx 50 \%$ ) of by-products among which are the so-called pyrolysis gasoline (yield  $\approx 20$  to  $25 \%$ ) and hydrogen. Pyrolysis gasoline from steam crackers is mainly composed of aromatic hydrocarbons. Today it is mostly sent back to refineries where it is used as a component of the gasoline pool.

If the maximum allowable aromatics content of motor gasoline is further reduced, other (chemical) uses of pyrolysis gasoline are likely to be more attractive. Probably, one of the most reasonable scenarios is a novel catalytic process that converts pyrolysis gasoline together with hydrogen generated in the steam cracker into a synthetic hydrocarbon stream which, upon being recycled into the steam cracker, gives particularly high yields of the

primarily desired olefins ethene and propene. The net effect of converting pyrolysis gasoline and hydrogen into such a synthetic steam cracker feed would be a drastic saving in the main feedstock to the steam cracker, i.e., naphtha.

It has previously been shown that with modern nanoporous catalysts, based especially on zeolite ZSM-5, a conversion of pyrolysis gasoline into a synthetic steamcracker feed consisting of ethane, propane and n-butane is feasible. It is planned to improve and optimize the nanoporous catalysts for this process route within the NoE. Besides, it is aimed at identifying novel catalysts that allow a selective ring opening of the cyclic hydrocarbons occurring in pyrolysis gasoline *without* a consecutive degradation of the carbon number. Note that these catalysts will be fundamentally different from those described above for the selective ring opening of cyclic C<sub>7</sub> hydrocarbons: Whereas in motor gasoline, the resulting alkanes should be as highly branched as possible, alkanes in a synthetic steam cracker feedstock are desirably unbranched, because n-alkanes give the highest yields of ethene and propene under steam cracking conditions.

Another development worthy to be mentioned in the present context is the efficient separation of hydrogen from the light steam cracker by-product methane. While hydrogen is needed for the catalytic conversion of pyrolysis gasoline, methane is usually burnt for supplying the endothermic heat of reaction of steam cracking. Tailored hydrogen/methane separations will be sought for in a joint endeavor with the adsorption and membrane pillars.

#### *3.4.2.5 Catalytic dehydrogenation of light alkanes*

The importance of light alkenes as raw materials for the chemical industry has been addressed above along with steam cracking of naphtha as the main source of ethene and propene. Today, ca. two thirds of the demand for propene are supplied by steam crackers, the remaining one third being produced in refineries as a by-product of fluid catalytic cracking (FCC) of heavy petroleum fractions. Unfortunately, the coupled production of ethene and propene is not entirely in balance, the demand of propene rising at a higher rate than that of ethene. These supply and demand trends give rise to a so-called "propene gap"

which, in turn, creates an increasing incentive for processes that make propene as the sole product ("on-purpose manufacture" of propene). The most important of these are metathesis of ethene and 2-butene, and dehydrogenation of propane.

The NoE has identified the latter reaction as an industrially relevant, future-oriented research topic that is ideally suited for being jointly investigated: Not only dispose several partner groups of long-lasting experience with this catalytic system, but its adequate investigation also calls for expertise and contributions from all four pillars of the NoE. Propane dehydrogenation is an endothermic, equilibrium-limited reaction which is today usually carried out at high temperatures around 550 °C on bimetallic solid catalysts consisting of platinum and tin on a porous oxidic support. Instead of tin, metals like germanium, zinc, rhenium, bismuth and others have been explored, but preference appears to be given in all processes offered for licensing to the platinum-tin system.

In the NoE's pertinent work, emphasis will be placed on the synthesis of novel catalysts for the dehydrogenation of light alkanes. For the most part, these catalysts will be based on nanoporous solids as carriers. In another approach, catalytic membranes that withstand the high temperatures required for this endothermic reaction are envisaged, thereby shifting the equilibrium towards the desired product propene. While propane will be the feed hydrocarbon in the focus of this project, catalytic dehydrogenation of isobutane to isobutene will also be studied.

#### *3.4.2.6 Direct alkylation (dehydroalkylation) of aromatics with alkanes*

In the first half of the 20<sup>th</sup> century, industrial organic chemistry was largely based on coal-derived alkynes, mostly ethyne, as raw materials. Thereafter, with the advent of cheap and easy-to-transport petroleum and thanks to the rapid progress in catalysis, a technical revolution took place during which ethyne was almost completely replaced by ethene and, to a lesser extent, propene as raw materials. As ethyne, however, alkenes do not occur as such in nature, but they must rather be made from naturally available hydrocarbon sources like

petroleum fractions or natural gas liquids through processes like steam cracking or alkane dehydrogenation (*vide supra*).

It is a fascinating idea to move on in the 21<sup>st</sup> century towards a new era in which alkenes are gradually replaced by alkanes as raw materials for the chemical industry. However, since alkanes are generally much less reactive than alkenes, such a fundamental shift will generally require significantly improved catalysts and/or catalytic reactors. Additional obstacles may arise from the fact that, in some instances, thermodynamic limitations exist for the conversion of alkanes into valuable chemicals.

As an example, the direct alkylation of toluene with ethane as the alkylating agent has been studied on bifunctional forms of nanoporous catalysts. In the desired reaction, toluene reacts with ethane to the three isomeric ethyltoluenes (of which the para-isomer can be looked upon as an intermediate for para-methylstyrene, a monomer for high-value polystyrene analogs) plus hydrogen, hence the term dehydroalkylation. In these studies, catalysts like Pd/H-ZSM-5 zeolite turned out to be active at temperatures around 300 to 350 °C and pressures of the order of 10 to 20 bar. In-line with the results of equilibrium calculations, the dehydroalkylation was found to be equilibrium-limited. The moderate reaction temperature and pressure could make dehydroalkylation an ideal candidate for being studied in a palladium membrane reactor. Such reactors on a laboratory scale are commercially available.

It is planned for the near future to push the conversion of dehydroalkylation of toluene with light alkanes to industrially relevant conversions and product yields by use of a membrane reactor and further improved nanoporous catalysts. This work will be jointly executed in a research program between the catalysis and membrane pillars.

On a more extended time scale, additional catalytic reactions will be studied in which the potential of alkanes for replacing alkenes in industrially relevant syntheses will be explored.

#### 3.4.2.7 *Miscellaneous catalytic reactions*

A number of additional catalytic reactions are currently being studied by various partner groups within the NoE, and a broad variety of nanoporous catalysts find application in these investigations:

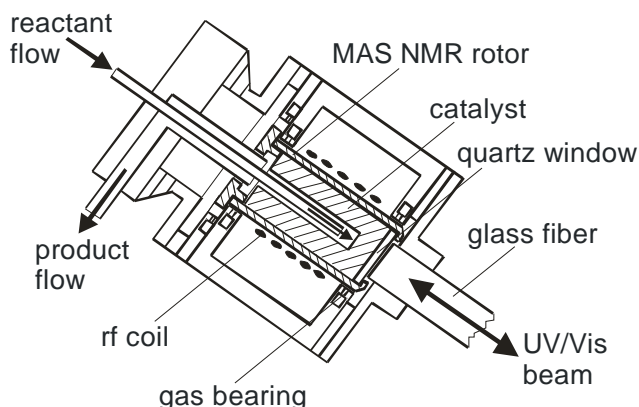
- Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to obtain the corresponding unsaturated alcohols
- Preferential oxidation (PROX) of carbon monoxide in an excess of hydrogen
- Steam reforming of ethanol and methanol for the manufacture of hydrogen

#### 3.4.2.8 *Investigation of nanoporous catalysts by in-situ MAS NMR spectroscopy*

Most atoms contributing to the framework of nanoporous catalysts and adsorbents consist of isotopes with a nuclear spin  $I$ . These isotopes open the way for the application of solid-state NMR spectroscopy for studies of the local structure of framework atoms and surface sites. In these cases, e.g. the oxygen coordination, atom-atom distances, bond angles, spin concentration, and spin dynamics are characterized. Application of two-dimensional techniques of NMR spectroscopy is a suitable way to separate solid-state interactions and to study their influence on resonating nuclei. One of the strongest line-broadening mechanisms is the quadrupolar interaction of nuclei with a spin  $I > 1/2$ , which are characterized by an electric quadrupole moment interacting with the electric field gradient caused by the charge distribution in the vicinity of the resonating nuclei. By analyzing this quadrupolar interaction, e.g. the nature and location of framework aluminum atoms and of extra-framework cations in dehydrated zeolites can be investigated. In cross polarization and TRAPDOR experiments, magnetization is transferred between neighboring atoms coupled *via* dipolar interactions. By application of the above-mentioned techniques, framework atoms in the vicinity of hydroxyl groups and adsorbate complexes can be selectively studied. These approaches allow the study of the local structure of active sites on the surface of catalysts and adsorbents. At one of the partner groups of the NoE such investigations are being performed on activated samples, which are sealed in glass ampoules or gas-tight rotors. The above experimental

techniques make solid-state NMR spectroscopy a modern analytical tool with a high sensitivity for the short-range order of nanoporous catalysts and adsorbents.

In the past decade, this group developed a number of novel *in-situ* NMR techniques, which are suitable for investigating working catalysts under continuous-flow (CF) and stopped-flow (SF) conditions. Recently, the solid-state NMR technique was combined with *in-situ* UV/Vis spectroscopy in a single probe (see Figure 7). In this case, the MAS NMR rotor, acting as a microreactor, is equipped with a quartz glass window at the bottom. A glass fiber, fixed at the bottom of the stator, is connected with the UV/Vis source and a fiber optics spectrometer. Utilizing this technique, simultaneous *in-situ* solid-state NMR and UV/Vis investigations of catalytically active sites, adsorbate complexes, intermediates, and deposits formed on the surface can be performed, and reaction mechanisms and deactivation processes occurring under industrially relevant conditions on nanoporous catalysts can be elucidated.



**Figure 7:** Scheme of the upper part of an *in-situ* MAS NMR-UV/Vis probe.

Examples for the application of *in-situ* CF MAS NMR, SF MAS NMR, and MAS NMR-UV/Vis spectroscopy are investigations of the synthesis of Methyl-*Tert.*-Butyl Ether (MTBE), the conversion of methanol to light olefins on acidic catalysts, and the alkylation of toluene, aniline, and phenol on basic and acidic zeolites. Studying the synthesis of MTBE on zeolites H-Y, H-Beta, and H-ZSM-5, the formation of alkoxy species at framework oxygen atoms was



observed by *in-situ* MAS NMR spectroscopy. It was found that the signal intensity of these alkoxy species correlates with the yield of MTBE determined by on-line gas chromatography. *In-situ*  $^{13}\text{C}$  MAS NMR spectroscopy of the conversion of methanol on zeolite H-ZSM-5 and on the silicoaluminophosphates SAPO-18 and SAPO-34 under continuous-flow conditions indicated the formation of a hydrocarbon pool consisting of a mixture of branched aliphatics and alkylated aromatic compounds. After a strong purging of the working catalysts with dry carrier gas, polymethylaromatics were preferentially found on the catalysts. These investigations gave experimental evidence for the so-called "carbon-pool" mechanism discussed in the literature. According to this mechanism, carbonaceous species exist inside the zeolite pores, which add reactants and split off reaction products such as light olefins.

It is evident that these advanced techniques for characterizing nanoporous catalysts under working conditions furnish most detailed and valuable information about the nature of adsorbates, intermediates and catalytic reaction mechanisms.

### **3.4.3 Long-term (> 10 years) development of nanoporous catalysts and techniques for their *in-situ* characterization**

Among the unique strengths of the NoE are (i) the very broad assortment of experimental techniques for synthesizing, characterizing and testing nanoporous solids and (ii) the close and ongoing cooperation of leading European groups with research profiles that are interrelated with and complementary to each other. This is an ideal prerequisite for developing synergisms between the four pillars, and over the years, making use and deepening of these synergisms will be systematically trained and advanced.

More specifically, emerging and novel nanoporous materials will be made available from the synthesis pillar to the catalysis pillar where their catalytic properties can be systematically tested. Likewise, we expect strong synergistic effects between the adsorption and catalysis pillars, because unravelling adsorption properties of porous materials often yields valuable insight into the catalytic action of solid surfaces. A good example is the

hydrophobicity/hydrophilicity of solid surfaces, the precise role of which in heterogeneously catalyzed reactions is often poorly understood. Within the next few years, we will place a focus of the collaboration between the two pillars on such topics, for a maximal mutual benefit. After all, adsorption of the reactants and desorption of the products are essential steps in the series of events forming altogether a heterogeneously catalyzed reaction. Finally, mere adsorption and heterogeneous catalysis sometimes overlap, and it is difficult to draw a clear-cut borderline, as in the so-called "reactive adsorption". Similarly, there is a wealth of potential synergisms between the catalysis and the membrane pillars, as demonstrated for several examples in Section 3.4.2.

Even though forecasting the long-term developments of a field like heterogeneous catalysis is a difficult task, we expect the following scenarios and challenges to dominate catalysis research within the NoE.

#### *3.4.3.1 Ever cleaner fuels from more-difficult-to-handle and lower-quality fossil raw materials*

In most current scenarios, today's high-quality crude oils will be available for another four or five decades. However, as the reserves dwindle, conventional oils will steadily increase in price, thereby creating a strong incentive for the production and use of non-conventional fossil raw materials. These include heavier, more viscous oils, oil sands and oil shales. In addition, a renaissance of coal is predicted by many experts, since coal is available on the Earth in significantly larger amounts than oil and, geographically, these abundant reserves are much more evenly distributed. However, quality-wise, all these non-conventional raw materials are inferior to conventional petroleum. In particular, they tend to be richer in undesired heteroelements, such as sulfur, nitrogen, vanadium, nickel or other metals. At the same time, they are poorer in hydrogen and more difficult to transport and handle in chemical processes, because they are high-viscosity fluids or even solids.

Making tomorrow's clean fuels from such raw materials will inevitably require a more intense and far-reaching chemical upgrading. The importance of processes by which the molecular

size is reduced (cracking), hydrogen is added (hydrogenation) and undesired heteroatoms are removed (hydrotreating) will steadily increase. Perhaps, completely new value chains will emerge. An example could be the production of vanadium and nickel from the ash residue of refining ultra-heavy, metal-rich oils. Furthermore, new and improved processes for making hydrogen without an excessive co-production of carbon dioxide are urgently needed. Catalysis will be an indispensable tool in mastering the new challenges associated with the production of ever cleaner fuels from fossil raw materials with ever lower quality. The NoE will actively take part in the development of new catalysts for making clean fuels in forthcoming decades.

#### *3.4.3.2 Chemicals from readily available and cheaper raw materials*

The dehydroalkylation of aromatics with alkanes, as described in more detail in Section 3.4.2.6, stands for an entire class of catalytic transformations, which aim at making existing bulk chemicals from cheaper and more readily available starting materials than in the currently existing technologies: Today, alkenes, especially ethene and, to a lesser extent, propene, are used as reactants in countless large-scale processes. Alkenes, however, do not occur in nature, neither in crude oils nor in natural gas, they must rather be made artificially by processes like steam cracking of naphtha or as a by-product of fluid catalytic cracking of heavy gas oils. By contrast, light alkanes are directly available in large quantities, especially in wet natural gases and crude petroleum, and hence much cheaper chemicals than alkenes.

Making chemicals from alkanes instead of from alkenes is kinetically more demanding on account of the reluctance of alkanes to undergo chemical transformations. To compensate for this lack of reactivity, advanced and more active catalysts are required. It can be anticipated that modern materials science will make such improved catalysts available within the next few decades. The NoE is excellently structured and fully prepared to recognize such developments and to play a leading role in using cheap alkanes for synthesizing important chemicals.

Carbon dioxide is another chemical that is abundantly available but usually of little reactivity in most chemical transformations. With the advent of significantly more active catalysts in the future, novel large-scale syntheses starting from carbon dioxide could become feasible. Looking for such syntheses is a highly attractive sub-field of catalysis research due to the low (essentially zero) cost of carbon dioxide. It should be noted, however, that introducing such new syntheses will not solve the global warming problem originating from carbon dioxide emissions, because only a small portion of these could be utilized for chemical synthesis purposes.

#### *3.4.3.3 Pushing catalysis beyond traditional limits: Process intensification*

A frequently encountered obstacle in desirable catalytic reactions stems from thermodynamic limitations of the conversion. Catalysis cannot help in this case, since it is a merely kinetic tool and as such unable to shift the position of equilibrium. In favorable cases, however, a significant shift of chemical equilibria can be achieved according to Le Chatelier's principle by selectively removing one product from the reaction mixture. Indeed, as described in Section 3.4.2.6, this is intended for the dehydroalkylation of toluene with ethane: By using a membrane reactor through the walls of which hydrogen can selectively permeate, it is aimed at significantly shifting the equilibrium towards the desired ethyltoluenes. In close cooperation with the membrane pillar, this principle will be systematically studied and exploited.

In the NoE's long-term strategy, such advanced reaction engineering measures, which are often referred to as process intensification, will be studied in a broader context. Besides using membrane reactors, other potential measures for a favorable shift of equilibria are catalytic distillation and Sorption Enhanced Reaction Processes (SERPs, cf. Section 3.2.1). Especially the latter principle will be explored in a cooperative effort of the adsorption and catalysis pillars. Here, removal of one product of an equilibrium-limited reaction is achieved by selective adsorption on a second solid deliberately added to the solid catalyst. Of course, measures must be taken to allow for a periodic or continuous regeneration of the adsorbent after its adsorption capacity is exhausted.

#### 3.4.3.4 *Unravelling mechanisms of heterogeneously catalyzed reactions by means of sophisticated in-situ characterization techniques*

In Section 3.4.2.8, *in-situ* MAS NMR spectroscopy on working solid catalysts was described. With this characterization technique, and particularly so in combination with *in-situ* UV/Vis spectroscopy, most detailed information concerning the catalytic events on the surface of the nanoporous solid can be acquired. It is justified to forecast that, along with the sensitivity enhancement of spectrometers and improvement of computers to be expected within the next ten years, *in-situ* spectroscopy of working solid catalysts will reach such a degree of sophistication that a true chemical understanding of heterogeneous catalysis will be reached at the molecular level. This, in turn, could create the basis for a knowledge-based improvement and tailoring of solid catalysts for a given application. The NoE INSIDE-POReS is an excellent platform for bringing sophisticated *in-situ* characterization techniques and application-oriented real catalysis together.

#### 3.4.4 References

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## 4 ENMIX Capacities

### 4.1 National Centre for Scientific Research Demokritos (NCSR), Greece

The Membranes and Nanoporous Materials for Environmental Separations Laboratory (MESL) at NCSR Demokritos is an internationally renowned specialized center for the pore structure characterization of both materials and membranes. The skills of the research group are aimed at developing and characterizing porous materials, testing and evaluation of the performance of membranes and modelling of the flow through porous systems. The area of interest expands over a wide range of applications but mainly in gas and liquid separations. They participate in the four pillars of ENMIX, the summary of activities being as follows:

#### *Synthesis:*

For the synthesis pillar, the research will be focused on the development of carbon materials, such as carbon nanotubes and activated carbons, e.g. by pyrolysis of polymeric precursors. Moreover, sub-micrometer thick carbon nanotubes are grown in the interior of the pores of oriented aluminophosphate molecular sieve films by techniques such as vacuum pyrolysis of the structure-directing agent or by CVD-assisted growth.

#### *Adsorption:*

- i. To overcome the main problems found in adsorption and diffusion processes, NCSR has developed over the past fifteen years innovative *in-situ* and *ex-situ* static and dynamic techniques and their combinations as a tool to characterize the nanostructure and control the changes of nanostructure and the evolution of properties of nanoporous materials. These changes induced on materials during their utilization in a wide range of applications, although often underestimated, are highly relevant and moreover crucial for the economic viability of the process. Several processes are being developed, e.g. hybrid membrane-PSA gas separation systems, CO<sub>2</sub> removal systems, hydrogen storage and separation systems, hybrid

nanofiltration/membrane distillation desalination systems and hybrid wastewater treatment systems.

- ii. The contributions of MESL to the activities in the area of sorption are:
  - Studies of sorption of mixtures of gases and vapors by real-time combination of gravimetric and flow calorimetric methods.
  - Sorption studies of activated carbon with tailored nanostructure containing Carbon Nanotubes (CNTs).
  - Sorption studies with sorbents grafted with ionic fluids.

*Membranes:*

- i. Systematic characterization and evaluation of the performance of membranes and thin films by combining differential permeability, gas relative permeability (permporometry) and selectivity measurements.
- ii. Preparation and characterization of single-layer or double-layer hollow-fiber polymeric membranes.
- iii. Preparation and characterization of carbon and silicon carbide hollow-fiber membranes.
- iv. Preparation and characterization of carbon nanotube membranes.
- v. Preparation and characterization of zeolitic  $\text{AlPO}_4\text{-5}$  membranes.
- vi. Modification of ceramic membranes for heavy metal ions removal.
- vii. Preparation and characterization of nanoporous ceramic membranes by Chemical Vapor Deposition (CVD).

*Catalysis:*

At the National Centre for Scientific Research Demokritos, several catalytic processes are under investigation. These include:

- i. Catalytic dehydrogenation of propane in different membrane reactor configurations.
- ii. The synthesis of nanocrystalline metal-carbon nanotube composites and an evaluation of their catalytic properties in various reactions.



### Experimental facilities:

The group at NCSR has access to a variety of experimental techniques for characterizing and evaluating porous materials in different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
BET instruments	Adsorption of various gases at different temperatures
SEM-EDX	High-resolution field emission SEM - visualization of surface by secondary electron detection or backscattered electron detection. EDX enables elemental analysis of a specimen
X-ray diffractometer	Identification and determination of crystal structures
Pressure adsorption	High-pressure adsorption (100 bar)
QUANTACHROME mercury porosimeter	Determination of pore diameter, total pore volume, surface area, and bulk and absolute densities - for meso- and macropores
SANS	Small-angle neutron scattering
SAXS-WAXS	Small/wide-angle X-ray scattering
Neutron powder diffraction	Structure determination
Permeability	Gas and vapor permeability
Calorimetry	Calorimeter Calvet C80-Setaram
CVD units	Investigation of chemical vapor deposition
Membrane testing set-ups	Closed-loop membrane testing units with various membrane sites & flow controller membrane testing units for measurement of differential gas relative permeability and selectivity
FT-IR spectroscopy	Identification of functional groups in materials
TGA apparatus	Thermogravimetric apparatus Setsys 16/18-Setaram
VEECO Atomic Force Microscope	High resolution 3-d imaging of surfaces, providing information on surface morphology, pore size, pore surface area, porosity, pore number density, pore shape and surface roughness and hardness

## 4.2 Centre National de la Recherche Scientifique (CNRS), France

CNRS-LAMMI: Agrégats, Interfaces et Matériaux pour l'Energie, Université Montpellier

The laboratory has a remarkable record in the conception and preparation of new functional micro-/mesoporous and intercalation compounds demonstrating particular properties. Furthermore, a large experience exists in the application of synchrotron radiation and neutron scattering and diffraction methods for the characterization of porous materials.

CNRS-MADIREL: Matériaux Divisés, Revêtements, Electrocéramiques, Université de Provence

The laboratory is internationally recognized in the field of the preparation of divided materials and their transformation by thermal methods.

CNRS-CRMD: Centre de Recherche sur la Matière Divisée, Université d'Orléans and CNRS

The Institute is internationally recognized in the characterization and synthesis of nanomaterials including oxide nanotubes, bionanocomposites, metallic aggregates, etc. Studies of the dynamics of confined materials are one of the main research themes using neutron and synchrotron inelastic techniques.

CNRS-IICE: Intermétalliques et Interstitiels Conversion de l'Energie, Université de Grenoble

This research group is internationally renowned for its expertise in intermetallics and magnetic materials and in all aspects of structure determination.

The CNRS research groups participate in the four pillars of ENMIX, the summary of activities being as follows:

*Synthesis:*

CNRS-LAMMI: In the synthesis pillar attention will be given to the development of the synthesis involving amphiphilic systems and particle suspensions giving rise to ordered macroporous solids by transcription from colloidal crystals, solid foams, materials of controlled nanoporosity by transcription and templating by surfactant mesophases and materials for chemical recognition by imprinting. Also, the design and controlled synthesis of nanoporous solids (including aluminosilicates and carbons) incorporating functionality is of great interest.

CNRS-MADIREL: The contribution to the synthesis pillar is focused on the high-pressure hydrothermal synthesis of zeolitic materials and the simulation of their formation conditions.

CNRS-CRMD: In the synthesis pillar their expertise in synthesis, characterization by the neutron scattering technique and the modelling of porous solids will be used. The synthesis effort deals with new methods of fabrication of mesoporous materials based on silica, titania and various forms of porous and nanocarbons and its tailored functionalization towards well-defined applications.

CNRS-IICE: Their contribution is focused on the synthesis of metallic membranes with hydrogen-induced vacancy structures in metal, alloys or oxide nanoparticles in a metal matrix. Also, the synthesis of nanoporous alumina membranes with ordered hexagonal network pores is studied.

*Adsorption:*

CNRS-LAMMI: i) There is extensive expertise in the area of interfacial phenomena and colloidal science. The group offers experimental and theoretical tools for studies in the field of interfacial thermodynamics and, in particular, sorption- and surface tension-based phenomena at solid-gas and solid-liquid interfaces. Methods have been developed and standardized for monitoring changes in the structure of adsorbed layers, nature of the interactions involved, reversibility, selectivity and kinetics of adsorption – desorption phenomena. Individual gas adsorption, individual or composite adsorption of compounds from gas or liquid mixtures, wetting in various liquids or solutions can be investigated with the use of various experimental techniques which are available in the laboratory.

ii) Thermodynamic experimental facilities, quite unique on the world scale, include different types of calorimeters (titration, flow and immersional apparatus, both those developed in-house and commercial equipment), which can be used in studies of the interactions involved in sorption phenomena under batch and dynamic experimental conditions. An original methodology involving the use of  $^{129}\text{Xe}$  NMR diffusion measurements is developed to obtain *in-situ* information about the porous structure of solids, as well as discrimination between hydrophobic and hydrophilic surface domains.

iii) The group is currently developing a new approach to establish the relationship between "local" surface properties of some reference solids and adsorption/wetting mechanisms

involving the use of such solids, as well as a new methodology to study the space-confinement effects on gas-phase or liquid-phase interfacial phenomena in fine-pore solids. CNRS-LAMMI propagates the idea that gas-sorption characterization of porous materials is too restrictive and does not cover all properties that may underlie the action of adsorbents or catalysts in numerous technological processes.

CNRS-IICE: There is a long-lasting experience in metal-hydrogen systems for storage and hydrogen processing of metals at high pressures. IICE also offers a valuable technology for the elaboration of innovative materials (catalysts), namely Plasma-Based Ion Implantation (PBII). Regarding this network, PBII can be used to tailor the surface and physical properties of nanoporous materials. The elaboration of micro- or nanostructures is quite easy by implantation through a mask. CNRS Grenoble is a long-time and well-known user of these facilities (especially ILL) and has developed for this purpose some ancillary equipments dedicated to solid-gas reactions that can be followed in the neutron beam (time-resolved *in-situ* diffraction). These equipments may be shared within the network with groups who express their interest.

At the moment, the available ancillary equipments are

- Solid-gas reaction cells
- Thermogravimetric analysis balance

The operating pressure range is 0-1 MPa at temperatures between 20 and 700 °C. So far, most experiments have been run using hydrogen gas, however any type of gas can be used, provided that the experiment complies to the safety regulations in operation at ILL. Note that these ancillary equipments conform to the appropriate French regulations.

#### *Membranes:*

CNRS-LAMMI: There is experience in:

i) the preparation of supported and self-supported aluminosilicate membranes for selective separation of alkane – alkene gas mixtures through an enhanced sorption mechanism, based on the formation of  $\pi$ -complexes between soft transition metal centers implanted in the membrane and the double bond of the alkene molecules. Mesoporous monoliths and

membranes are prepared by non-ionic surfactant-assisted synthesis following the direct liquid crystal templating pathway conceived and developed previously in the laboratory.

ii) the preparation and optimization of defect-free microporous zeolite membranes. Together, the CNRS-LAMMI group offers home-made rigs equipped with a downstream gas chromatography analyzer or a gas flow microcalorimeter to investigate the gas transport and sorption mechanisms in order to relate pore structure and surface activity of prototype membranes with alkane/alkene selectivity.

iii) development of membrane separators for proton exchange membrane fuel cells (polymer membranes) and proton ceramic fuel cells (ceramic membranes). This research involves ionomer development, elaboration of polymer and organic-inorganic membranes using original methodologies encompassing sol-gel type chemistry and ion exchange routes leading to membranes containing highly dispersed inorganic particles or inorganic networks for hydrogen or direct alcohol fuel cells, in particular for automotive or stationary power generation. Another aspect of this research involves the development of approaches to the preparation of proton conducting perovskites in the form of nanopowders with a core-shell type arrangement designed for high proton conductivity, sinterability, and chemical stability. The group is fully equipped with impedance spectrometers for conductivity measurement and fuel cell test benches for single cell and stack characterization.

#### *Catalysis:*

CNRS-LAMMI develops catalyst materials for the production of clean fuels, in particular clean diesel, either by upgrading of heavy oil fractions in processes including selective mild hydrocracking, hydrogenation and hydrodearomatization of light cycle oil, or the production of synthetic diesel by oligomerization of C<sub>5</sub> olefins. The current preparative approaches in CNRS-LAMMI are based upon the development of hierarchically organized tailored catalyst materials comprising the combinations micro-/mesoporous, supermicro-/mesoporous, meso-/macroporous and even micro-/macroporous. Furthermore, CNRS-LAMMI has previously developed super-microporous silicoaluminates as catalyst supports for sulfur-resistant bimetallic nanoparticles. These supports allow formation of very highly dispersed intermetallic-type particles. The laboratory is well equipped for characterization of surface

properties of the support and the catalyst, as well as structural and spectroscopic characterization. It has long experience also in the application of probe characterization techniques using national and European large facilities, in particular the application of X-ray Absorption Fine Structure (EXAFS) spectroscopy to the characterization of local structures in bimetallic nanoparticles.

### Experimental facilities:

The research groups at CNRS have access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
BET instruments CNRS-LAMMI and CRMD	Adsorption of various gases at different temperatures
FT-IR CNRS-LAMMI and CRMD	Fourier Transform Infrared spectrometry
FT-Raman CNRS-LAMMI	Fourier Transform Raman spectrometry
SEM-EDX CNRS-LAMMI	High-resolution field emission SEM
TEM CNRS-LAMMI and CRMD	Field emission transmission electron microscopy
X-ray diffractometer CNRS-LAMMI and CRMD	Identification and determination of crystal structures
HR TEM CNRS-CRMD	High-resolution transmission electron microscope equipped with a CDD, cooling and heating devices
PFG-NMR CNRS-CRMD	Solid-state NMR
XPS CNRS-CRMD	X-ray photo-electron spectroscopy
AFM CNRS-CRMD	Atomic force microscopy (in vacuum and environmental)
EXAFS CNRS-CRMD	Access to national/European synchrotron radiation facilities for Extended X-ray Absorption Fine Structure
<sup>129</sup> Xe-NMR CNRS-LAMMI	Transport and diffusion phenomena
Particle size characterization	Determination of particle size
ILL Grenoble CNRS-IICE	CNRS has developed solid-gas reaction cells and thermogravimetric analysis balance to be used in the neutron beam
Zetasizer CNRS-CRMD	Measuring Zeta potentials and particle size
Hydrogen absorption CNRS-IICE	Kinetics, equilibrium (PCT measurements) and reversibility up to 7 GPa
Adsorption CNRS-LAMMI	Extent and rate of adsorption at solid-gas and solid-liquid phases (Micromeritics)

TPD/TPO/TPR CNRS-LAMMI	Temperature controlled processes
Calorimetry CNRS-LAMMI	Gas flow and liquid-flow calorimeters (MICROSCAL), batch titration and immersion calorimeters
Contact angle measurements CNRS-LAMMI	Powder-bed capillary rise
Electrophoretic measurements CNRS-LAMMI	Surface electric charge and electrophoretic mobility
Spin- and dip-coaters CNRS-LAMMI and CRMD	Spin- and dip-coaters, coatmaster for membrane solution casting
Membrane selectivity test rigs	With a GC or with a gas-flow microcalorimeter
Electrochemical characterization CNRS-CRMD	Impedance spectroscopy for conductivity measurement up to 700 °C

#### 4.3 University of Leipzig, Department of Interface Physics (UNILEP), Germany

Research topics at the Department of Physics of Interfaces at the University of Leipzig are focused on the study of molecular dynamics and interactions between molecules and interfaces. The main experimental methods of study are Nuclear Magnetic Resonance (NMR) and optical spectroscopy. Among various NMR techniques, the central position belongs to the Pulsed Field Gradient technique (PFG NMR) permitting measurements of self-diffusion and molecular transport in porous materials. This technique has been strongly developed in the department. Due to its unique home-built apparatus and extremely strong magnetic field gradients, the group is one of the leading laboratories worldwide in studies of transport phenomena in nanoporous solids.

The UNILEP research group participates in the four pillars of ENMIX, the summary of activities being as follows:

##### *Synthesis:*

Items concerning mobility and exchange properties, probing fractal pore network, extracting the information about mobility of individual components are especially valuable for the synthesis pillar. Detailed information on transport properties of nanoporous solids on all

relevant length scales is a necessary prerequisite of the optimization of the synthesis processes of the micro-, meso- and combined micro-/mesoporous materials.

*Adsorption:*

i) Probing the mobility in and the exchange between different ranges, such as micro- and meso-/macropores or, more generally, hierarchically organized pore systems. Interesting additional information is accessible by considering diffusant molecules of different size so that, e.g. micropores remain inaccessible by them.

ii) Probing fractal pore networks (e.g. percolation networks close to the percolation threshold) may be shown to give rise to anomalous diffusion (i.e. to deviations from the Einstein relation).

iii) In the special case that in polycrystalline materials the long-range diffusivity is much larger than the intracrystalline diffusivity (both being accessible following item 1), one may easily distinguish whether there are additional transport resistances on the surface of the individual crystallites.

iv) Information about mobility of the molecules in nanoporous crystallites may further be obtained for individual components in multicomponent molecular systems, either by applying molecules with different NMR-active nuclei (in particular fluorine and protons or protons and deuterons) or by high-resolution PFG-NMR, including the most interesting aspect that different molecules may behave quite differently in one and the same sample.

*Membranes:*

i) Membranes are in focus of our co-operative investigations with the Hanover group related to the study of guest-molecule distribution in nanoporous materials in the context of the lattice-gas model.

ii) Interference microscopy can be used for studying sorption kinetics and as a tool of membrane evaluation. In particular, such studies appear to be useful for preparation of supported MOF membranes for molecular sieving.



*Catalysis:*

Research concerning surface resistance, mobility and exchange properties of individual components are especially valuable for the catalysis pillar. Detailed information on transport properties of nanoporous solids on all relevant length scales is a necessary prerequisite for the optimization of these materials for catalytic applications. It turns out that molecular diffusion tends to be the rate-determining mechanism in such catalytic reactions in which the adsorption rate of the reactants and/or desorption rate of the products become smaller than the intrinsic reaction rates. In particular, deposition of ions inside the nanoporous solids may lead to changes of transport properties of guest molecules. The importance of diffusion studies for catalytic applications was demonstrated in the co-operative work with the Antwerp group. The work was related to the study of the effects produced by deposition of vanadium silicalite-1 nanoparticles on the structure and transport characteristics of SBA-15 materials.

**Experimental facilities:**

The research group UNILEP has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table.

Technique/Facility	Short description
Home-built PFG-NMR spectrometer (400 MHz and 125 MHz)	Determination of diffusion coefficients of gases, liquids, adsorbate-adsorbent systems
Interference microscopy	Monitoring concentration profiles during adsorption/desorption processes

#### **4.4 University of Antwerpen, Laboratory of Adsorption and Catalysis (UA), Belgium**

The Laboratory of Adsorption and Catalysis at the University of Antwerpen is an internationally recognized and specialized research laboratory for (a) the synthesis and characterization of micro-, meso- and combined micro-/mesoporous siliceous and non-siliceous materials, (b) pore size engineering in porous structures by impregnation techniques, ion-exchange processes and chemical modification reactions and (c) the development of chemical activation/deactivation processes in porous materials. Recently, the synthesis and properties tuning of various silica-based mesoporous organic hybrid materials are under investigation. The skills of this research group are focused on the development of new synthesis routes, new chemical modification processes to tune the material properties towards applications in the area of adsorption, separation and catalysis. An extensive experience is present for detailed characterization and evaluation of the performance of porous solids.

The UA research group participates in two pillars of ENMIX, the summary of activities being as follows:

##### *Synthesis:*

By controlling the synthesis methods and the modification techniques of a broad range of porous materials, designed materials are formed for specific applications in the field of adsorption and catalysis. The focus is on microporous, mesoporous and combined micro-/mesoporous materials as well as on organic-inorganic hybrid materials. Both siliceous and non-siliceous materials are developed. Much attention is focused on:

i) Mesoporous siliceous materials with internal nanoparticles: nanoparticles (zeolite precursors, transition metal oxides) are introduced into mesoporous materials (MCM, SBA, MCF,...) by post-synthesis impregnation or *in-situ* synthesis methods. The obtained materials having both open and narrowed sections in their mesopores, exhibit unique properties

(diffusion, stability,...) that can be adjusted to the application (sorption, catalysis, encapsulation, separation,...).

ii) Combined micro- and mesoporous materials. These materials are known to have advantages towards diffusion, stability, multifunctionality to process a wide variety of feeds, capabilities to encapsulation, controlled release,... They are prepared by a templated method using zeolite precursor particles.

iii) Hybrid organic-inorganic materials. The selectivity and stability of mesoporous materials are changed by modifying the inorganic materials with organic functional groups. This can be done by grafting (post-modification) or by co-condensation (*in-situ*) or by synthesizing PMOs (periodic mesoporous organosilicas). Also microporous hybrid materials can be made by grafting or in a direct way (Metal Organic Frameworks, MOFs). Moreover, the modification methods also apply to metal oxides or silica films and membranes.

iv) Mesoporous photocatalytically active transition metal oxides. Mesoporous transition metal oxides ( $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ , ...) are prepared via different synthesis approaches such as sol-gel route, EISA method, carbon replicas or other templated routes. Also template-free, fast synthesis routes of, e.g. nanotubes, is one of the main topics.

#### *Catalysis:*

Among the research activities related to catalysis is the activation, combined with a stabilization, of ordered mesoporous materials with transition metals. Active catalysts can be made from ordered mesoporous materials by:

i) Molecular designed dispersion of the heteroatoms on the surface of the catalyst. To make active catalysts, the metals V, Cr, Ti, Mo, Fe and Al are used.

ii) Plugged Hexagonal Templated Silicas (PHTS materials) containing catalytically active plugs in the mesoporous channels: The obtained materials have a combined micro- and mesoporosity and a high mechanical and hydrothermal stability.

iii) Use of multifunctional chloro- or alkoxy silanes: The obtained materials have an improved mechanical and hydrothermal stability. Furthermore, leaching of the active centers can be drastically reduced in liquid-phase catalytic reactions.

iv) Direct hydrothermal incorporation of active metals during the synthesis of the mesoporous materials or use of starting materials with intrinsically incorporated heteroelements.

v) Hybrid organic-inorganic materials for heterogenization of homogeneous catalytic reactions.

Furthermore, the Antwerp group focuses on liquid-phase reactions and photocatalytic degradation reactions under UV radiation. In a first step, the characteristics of the catalyst, such as leaching, hydrothermal stability, regeneration and mechanical strength are evaluated. The activity and product selectivity will be compared – initially by using a simple test reaction – with commercial and/or conventional catalysts. In a second step, industrially more relevant synthetic reactions from the fields of fine chemicals, pharmacy and petrochemistry can be investigated.

#### **Experimental facilities:**

The research group UA has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
BET instruments	Adsorption of various gases at different temperatures
FTIR	Fourier transform infrared spectrometry
FT-Raman	Fourier transform Raman spectrometry
FT-IR Pas	Fourier transform infrared with photo-acoustic detection
Facilities for synthesis under various conditions	Autoclaves for synthesis on lab-scale and/or large scale
Facilities for modification of nanoporous materials	Set-ups for various modification reactions on porous materials
SEM-EDX	High-resolution field emission SEM
TEM	Field emission transmission electron microscopy
HRTEM	High-resolution TEM
X-ray diffractometer	Identification and determination of crystal structures
AAS	Atomic absorption spectrometry
TGA/DTG/DSC	Thermal analysis/calorimetry
UV-VIS DR	Ultraviolet-visible diffuse reflectance spectroscopy
EPR	Electron paramagnetic resonance

Catalytic batch reactors	Reactors for oxidation (liquid and gaseous phase)
UV-lamps	UV-lamps for photocatalysis
IR and Raman <i>in-situ</i> spectroscopy	<i>In-situ</i> techniques to study calcination processes, stability or adsorption phenomena

#### 4.5 Universität Stuttgart, Institut für Technische Chemie (USTUTT), Germany

The research at the Institute of Chemical Technology at the University of Stuttgart is focused on the synthesis and modification of zeolites and related micro- and mesoporous materials, as well as on their application as catalysts and adsorbents. The institute disposes of a broad assortment of instruments for the characterization and evaluation of solid catalysts. FTIR and MAS-NMR spectroscopy have been successfully applied to gain a deeper understanding of processes occurring on catalytically active sites by *in-situ* monitoring of the working catalysts. The development of catalytic test reactions to probe the acidic, basic and shape-selective properties of nanoporous materials is also a major research interest.

The USTUTT research group participates in the four pillars of ENMIX, the summary of activities being as follows:

##### *Synthesis:*

The Institute of Chemical Technology at the University of Stuttgart has been active in the field of synthesis of nanoporous materials for about three decades. Materials which are in the center of interest include large-, medium- and narrow-pore zeolites with numerous framework types, zeotypes of the AIPO, SAPO, MeAPO and other families, all-silica zeolites and ordered mesoporous materials. Likewise, the characterization of these materials by a variety of physicochemical techniques has been a major activity of the institute. In the majority of the cases, the ultimate goal of synthesizing and characterizing nanoporous materials is their application in heterogeneous catalysis.

*Adsorption:*

i) The Institute of Chemical Technology at the University of Stuttgart (USTUTT) is primarily working in the fields of synthesis and characterization of nanoporous materials and the application of these materials in heterogeneous catalysis. It has, however, previously done research projects in adsorption as well. Typical examples are the separation of benzene and thiophene on ZSM-5-type zeolites and of the two diastereomers of 3,4-dimethylhexane on silicalite-1. Furthermore, the so-called Hydrophobicity Index (HI), was introduced which is based on the competitive adsorption of vapors of a hydrocarbon, e.g. n-octane and water.

ii) Currently, the research interest in the field of adsorption focuses on the removal of volatile organic compounds (VOCs) from air on carbon-based materials, special variants of zeolites and ordered mesoporous materials. Among the factors under investigation are the influence of the hydrophobicity (expressed in quantitative terms by the Hydrophobicity Index, *vide supra*) of the solid surface on the performance in VOC removal, both in the absence and presence of moisture in the air. Another current field of interest is the separation of propane and propene.

*Membranes:*

The Institute of Chemical Technology has a wide background with regard to separation technology and catalysis, especially in the field of zeolites. They are in a favorable position to merge the two topics by applying catalytic membrane reactors for process intensification.

i) One focus of the catalysis research at the Institute of Chemical Technology is the non-oxidative activation of light alkanes using bifunctional zeolite catalysts. These reactions are generally strongly limited by thermodynamic equilibrium, and removal of a reaction product via a membrane to "shift" the equilibrium would be very beneficial. Industrially relevant test reactions studied are especially the dehydroalkylation of aromatics with alkanes, e.g. the reaction of toluene with ethane to the isomeric ethyltoluenes and hydrogen. Here, hydrogen can be removed in a packed-bed membrane reactor via a palladium-based membrane. Such reactions are of interest as it has been shown that, from an economic point of view, membrane reactors for hydrogen production can only be successful if the production of

hydrogen is accompanied by other valuable products, such as bulk chemical intermediates including ethylbenzene and ethyltoluenes.

### *Catalysis:*

The group at the Institute of Chemical Technology of the University of Stuttgart has been active in the field of heterogeneous catalysis for more than three decades. From the beginning, an integrated approach has been pursued, i.e., the synthesis of catalytic materials, their characterization by a broad assortment of physico-chemical techniques, and testing of their catalytic performance in a variety of laboratory-scale apparatuses were of equal importance in the research strategy. Currently, the research interests in the field of heterogeneous catalysis focus on the following topics:

- i) Direct alkylation (dehydroalkylation) of aromatics with alkanes.
- ii) Oxyfunctionalization of alkanes with dioxygen or air on small metal clusters.
- iii) Stabilization of small clusters of noble metals as guests in nanoporous solids as hosts.
- iv) Catalytic combustion of volatile organic compounds in air streams.
- v) Isomerization and hydrocracking of model hydrocarbons for various fuels.
- vi) The observation of working nanoporous catalysts by *in-situ* MAS NMR spectroscopy.

### **Experimental facilities:**

The research group at USTUTT has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
BET instruments	Adsorption of various gases at different temperatures
FTIR	Fourier transform infrared spectrometry
TEOM	Tapered element oscillating microbalance
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
Solid-state NMR	Nuclear magnetic resonance for solids, <i>in-situ</i> studies of catalytic processes
Fixed-bed reactors	Flow-type apparatus with a fixed-bed reactor with mass-flow-controlled gas feeding stations and on-line gas chromatography
Batch reactors	150 cm <sup>3</sup> stainless steel reactor for high-pressure applications

Membrane reactors	Packed-bed reactors, GC- and mass-flow-controlled
Facilities for synthesis under various conditions	Autoclaves for synthesis on lab-scale and/or large scale
X-ray diffractometry	Identification and determination of crystal structures

#### 4.6 Institute for Energy and Technology (IFE), Norway

At the Institute for Energy and Technology (IFE) the Physics Department performs mainly basic research in physics based on IFE's JEEP II neutron research reactor. The IFE research group participates in the sorption pillar of ENMIX, the summary of activities being as follows:

##### *Adsorption:*

- i) The department investigates the physical properties of materials and their potentials in a growing number of applications, such as hydrogen uptake in metals for energy storage, and novel properties of nanocarbon materials. The group also explores the connections between the microscopic and macroscopic properties of soft, complex materials including biomaterials, polymers and biopolymers, colloids and complex fluids. The main tools used in these investigations are neutron scattering, X-ray scattering and optical microscopy. At the JEEP II reactor, advanced neutron diffractometers are tailor-made to explore the properties of the various materials.
- ii) IFE's Physics Department is currently developing an *in-situ* unit for its Small-Angle Neutron Scattering (SANS) instrument. This set-up has been designed especially for studying processes of gas sorption in porous materials. Preliminary studies with water as a sorbent and the carbon reference material Takeda 5 as a sample are planned for September 2007.

##### **Experimental facilities:**

The research group IFE has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
SANS	Small-angle neutron scattering
Neutron diffraction	Neutron powder diffraction



#### 4.7 Technical University of Delft (TUDELFT), The Netherlands

The group at the TU Delft is internationally recognized as one of the leading research groups in the area of the synthesis of nanostructured materials for application in adsorption, catalysis and membranes. They participate in the four pillars of ENMIX, the summary of activities being as follows:

##### *Synthesis:*

For the synthesis pillar, the research will be focused on the mechanism towards hierarchical materials, the preparation of hierarchically structured nanoporous materials for catalysis and separation and the development of multi-structured porous materials. Besides product characterizations, they will evaluate the obtained nanostructured materials in membrane applications. Furthermore, attention will be given to the development of novel porous materials with specific properties.

##### *Adsorption:*

The group offers experimental and theoretical tools for studies in this field, in particular, sorption and separation of light olefin/paraffin mixtures. Breakthrough performance of the NaX and CuCl-NaX materials for propane/propene separation has been measured experimentally. Other interest of the group is in the adsorption of alkanes on zeolites, in general, and their practical applications in isomerization reactions of alkanes. The group is investigating experimentally the selective formation of dibranched isomers in the n-hexane hydroisomerization process. Molecular simulations done showed the possibility of selectively producing dibranched alkanes due to packing entropy effects during the isomerization reaction with a zeolitic catalyst. As a catalyst Pt/HMOR is used (0.4 wt.-% Pt). Therefore, equilibrium and kinetic adsorption data are essential. These data provide key information regarding the catalytic isomerization on zeolites themselves.

### *Membranes:*

The TU Delft group is a world expert in the field of membranes, in particular, zeolitic membranes. Research into the synthesis, characterization, modelling and application currently comprises the following subjects: i) Systematic investigation of the zeolite polarity by tuning the amount of silanol groups within the framework of silicalite-1. The amount of silanol groups within the framework is increased by means of deboronation. The possibility to use ozone detemplation to increase the silanol content is also being investigated. ii) Batch and continuous synthesis of zeolite A membranes (disk and tubular), and their characterization by single-gas permeation. iii) Synthesis, characterization and performance testing of hydroxy sodalite membranes for water removal, focusing on combination with catalytic reactions at elevated temperatures. iv) Batch and continuous synthesis, and characterization of silicalite-1 membranes. v) Development of DDR, Cu-BTC, and membranes of other materials. Applications include gas separation, isomer separation, water removal and membrane reactors (selective product removal).

### *Catalysis:*

Catalysis research within the Catalysis Engineering/DCT group at the Technical University of Delft comprises the application of zeolites, ordered mesoporous materials and classical solid catalysts in single- and multi-phase applications for various processes. Examples are selective hydrogenation, oxidation, fluid catalytic cracking, the Fischer-Tropsch synthesis, hydrotreating and the conversion of renewables. The nature of funding of these projects limits the activities of the group in the catalysis pillar of the NoE, even though certain facilities can be made available.

### **Experimental facilities:**

The group at TU DELFT has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
BET instruments	Adsorption of various gases at different temperatures
FTIR	Fourier Transform Infrared spectrometry
FT-Raman	Fourier Transform Raman spectrometry
TEM	Field emission transmission electron microscopy
Catalytic facilities	Evaluation of catalytic behavior
Mass analyzer	Rupprecht&Patashnick TEOM
Breakthrough	Breakthrough curve set up
TAP	Temporal analysis of products
Quick single gas permeation	A simple set-up for membrane characterization.
O <sub>3</sub> Detemplantation set-up	A2Z ozone generator with a controlled temperature oven.
Catalytic membrane reactor	A home-made set-up with a temperature controlled oven, GC and a liquid pump.
Single gas permeation	Characterization of zeolite membranes by permeation with different gases from room temperature up to 200 °C.
Binary mixtures permeation	Temperature can be controlled from room temperature to 500 °C (strongly dependent on sealing material) and pressures from 1 to 17 bar. The exit flow is analyzed on-line by MS and GC.
Permporometry set-up	Characterization of (zeolite) membranes by permporometry. Maximum temperature 70 °C.
Batch reactors	Reactors for hydrogenation
TPD/TPO/TPR	Temperature-controlled processes
TAP	System for mechanistic studies
Flow set-up	For N <sub>2</sub> O decomposition and diesel soot combustion
Chemisorption	For metal dispersion determination

#### 4.8 Universidad de Alicante (UALI), Spain

The Laboratorio de Materiales Avanzados (Laboratory of Advanced Materials, LMA) at UALI has a long-term international reputation in the area of synthesis, characterization and application of porous solids, especially porous carbons, in adsorption and catalysis. The group participates in thee of the four pillars of ENMIX (synthesis, sorption and catalysis), the summary of activities being as follows:

*Synthesis:*

In the synthesis pillar, the interest of this leading research group ranges from activated carbons and other siliceous/non-siliceous adsorbents to catalysts supported on porous solids (among them activated carbons and zeolitic materials). The expertise of this group includes the synthesis of a large variety of adsorbents based on porous carbons, including some with special physical forms such as binderless monoliths, cloths, felts, etc. Attention is given mainly to the synthesis of carbon-supported catalysts containing metals (Pt, Ru, Sn, Zn), the preparation of nanoporous carbons and lignocellulosic-based carbon molecular sieves.

*Adsorption:*

i) Adsorbents:

A. Activated carbons with very different physical forms, including granular, pellet, cloth, felt or monolith. Also, activated carbons can be prepared in such a way that the porosity may range from essentially microporous to essentially mesoporous, and in most cases the precursor is an agricultural or industrial by-product.

B. Carbon molecular sieves, mainly prepared from fruit stones or shells using a controlled carbonization-activation process. In some cases chemical activation is used in this synthesis.

C. Activated carbon cloth and felt, produced from viscous rayon using a mixed activation procedure (chemical followed by physical activation).

D. Catalytic activated carbons for the selective removal of toxic or harmful chemicals.

The three types of porous carbons are prepared at two different levels, laboratory and pilot plant, using continuous processes for the latter, when possible.

ii) Adsorption processes:

A. Use of carbon molecular sieves in the separation of gas mixtures (mainly  $\text{CH}_4/\text{CO}_2$ ;  $\text{N}_2/\text{O}_2$ ,  $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ )

B. Use of special activated carbons in the storage of natural gas. The storage of hydrogen is also studied in the last year.

C. Selective removal of some specific components from industrial mixtures, using carbons with a pre-determined pore size distribution.

- D. Removal of components from industrial air using special impregnated activated carbons to ensure the decomposition of the compounds and the adsorption of resulting compounds.
- E. Purification of water in food industry for re-use.
- F. Removal of undesirable compounds from industrial water before final disposal.

*Catalysis:*

The Laboratory for Advanced Materials at the University of Alicante works in the synthesis and application of advanced catalysts for different reactions:

- i) Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to obtain the corresponding unsaturated alcohols.
- ii) Dehydrogenation of light paraffins (propane, isobutane) to obtain the corresponding olefins (propene, isobutene).
- iii) Catalytic combustion of volatile organic compounds (ethanol, ethyl acetate, toluene, etc.) in air streams.
- iv) Selective oxidation of CO in the presence of hydrogen (PROX process).
- v) Steam reforming of ethanol and methanol to obtain hydrogen.

Catalysts for these reactions are mainly based on platinum and bimetallic Pt-M (M= Sn, Zn, etc.) systems supported on different materials (activated carbon, alumina, mesoporous silica, TiO<sub>2</sub>, CeO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, SnO<sub>2</sub>-TiO<sub>2</sub>, ZnO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub>, etc.). The synthesis techniques are chosen to tailor the catalytic properties for obtaining high activity, selectivity and durability. The catalytic tests at the laboratory scale are carried out both in the gas/vapor and in the liquid phase at high pressure. The relationships between the structure and composition of the active phase, the interaction of the active phase with the support and the effect of promoters on catalytic activity and selectivity in the different reactions are among the main interests.

**Experimental facilities:**

The group at UALI have access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
TEM	Field emission transmission electron microscopy
XR diffractometer	Identification and determination of crystal structures
Facilities for synthesis under various conditions	Autoclaves for synthesis on lab-scale and/or large scale
MAS-NMR	Solid-state NMR
XPS	X-ray Photo-electron Spectroscopy
TGA/DTG/DSC	Thermal analysis/colorimetry
Adsorption facilities	Evaluation of adsorption performance
TPD/TPR-MS	Temperature controlled processes coupled with MS
TMA	Thermomechanical analysis
FTIR/DRIFT	<i>In-situ</i> DRIFT
Microcalorimeter	Adsorption microcalorimeter (Setaram)
Breakthrough	Breakthrough dynamic system
Climatic	Climatic chamber (controlled temperature and humidity)
PSA	Pressure swing adsorption
Calorimetry	Adsorption microcalorimetry and immersion calorimetry
Microreactor systems	Several flow microreactor systems and one batch system able to work at high pressure
Batch reactor	Reactor for high-pressure experiments

**4.9 Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche (CNR), Italy**

This is a research governmental (> 100 permanent staff) Institute with interest in layered materials, composites, porous materials for industrial applications, semiconductors including epitaxial nanostructured semiconductors for optoelectronic and photonic, superconductors, molecular electronics and spintronics, functionalization of surfaces by biomolecules for biodiagnostic. The section of Rome (*ca.* 40 permanent staff) is located on a medium-sized research area (*ca.* 360 staff) also housing related laboratories with common site services and considerable interaction between Institutes. The ISMN group participating in the NoE was the

first to develop complex-pillar chemistry, to prepare oxide-pillared layered phosphates and mildly acid restructured clays as catalysts.

*Synthesis:*

The group has expertise in the synthesis of clays (montmorillonite, beidellite, bentonite, laponite) restructured and subsequently metal-loaded, and pillared with a variety of metal and non-metal oxides including combinations of two or three of them and also subsequently metal-loaded again with up to three metals; layered materials, in particular group IV metal phosphates, which are also pillared; zeotypes including MCM-41, MCM-22 and MCM-48 and the entire series of FSMs, all of which are also produced with mixed silica/metal frameworks and subsequently metal-loaded. The structural and spectroscopic characterization of these materials is also routinely performed utilizing the techniques and instrumentations listed in the experimental facilities.

*Adsorption:*

The ISMN group also has expertise in ion-exchange specialist chromatographic separations also through the preparation of zeotype-modified chromatographic columns both capillary and packed. The group is also involved in the study and testing of industrial scale reactors for the sorption and recovery of VOCs by utilization of commercial carbons and in-house prepared zeolitic sorbents. Selective sorption of specific, more value-added VOCs from industrial polluted air mixtures, is achieved with multi-layered sorption beds composed of both zeolite and carbon components of appropriate pore sizes.

*Catalysis:*

The group applies the materials developed in the synthesis section to different reactions at micro- and small-scale level. The following are some of the reactions/processes of interest:

- i) Plastic waste degradation for monomer(s) recycling and/or energy production;
- ii) FTS process conducted under supercritical conditions for maximizing overall yield and selectivity to the C<sub>11</sub>-C<sub>19</sub> cut from syngas feed derived from lignite.
- iii) Catalytic combustion of volatile organic compounds after concentration from air streams.
- iv) Butenes dimerization.

As mentioned above catalysts for these reactions are mainly bimetallic M(I)-M(II) (M= Fe, Co, etc.). The catalytic tests can be carried out at microscale through an apparatus directly connected to a GC-MS system and at lab-scale (up to 5 g) including in liquid phase at high pressure.

### Experimental facilities:

A summary of experimental techniques and facilities accessible to the group is given in the following table:

<i>Technique/Facility</i>	<i>Short description</i>
UV-VIs -NIR spectrometer including reflectance and glancing angle	UV-visible analysis of metals electronic transition and state in solid frameworks
FTIR including cells for following gas-solid interactions	IR spectroscopy for organic molecules-inorganic substrates interaction analysis
Raman spectrometer	RAMAN Spectrometry
Photoluminescence	Optical characterization of materials
XPS/Auger and related spectroscopies	X-ray Photo-electron Spectroscopy
XRPD diffractometer	Identification and determination of powder crystal structures
AFM	Atomic Force Microscopy for morphological, magnetic and friction and electric analysis of sample surface
UHV-STM/STS	Ultra High Vacuum Scanning Tunneling Microscopy and Spectroscopy
SEM and FEG SEM	Scanning Electron Microscopy and Field Emission Gun SEM
Combined GC/MS	Separation and identification of catalysis products
BET porosimeter	Adsorption of liquid N <sub>2</sub> , BET and Langmuir porosity
Facilities for synthesis s conditions	Autoclaves for synthesis on lab-scale
High field and MAS-NMR	Solid-state NMR
e.p.r.	Electron paramagnetic resonance
TGA/DTA	Thermal analysis
AAS	Atomic absorption spectrometry for quantitative metal analysis
Adsorption facilities	Evaluation of adsorption performance
Climatic	Climatic chamber (controlled temperature and humidity)
Microreactor system	Microreactor system connected with GC-MS
Batch reactor	Reactor operating with up to 3 gases + 1 liquid, catalyst bed up to 5 ml and pressure up to 100 bar



#### **4.10 Chemical Process Engineering Research Institute - Centre for Research and Technology (CERTH-CPERI), Greece**

The Laboratory of Inorganic Materials of the Centre for Research and Technology-Hellas is doing applied research in ceramic materials and in particular:

##### *Synthesis:*

This participating group aims at the synthesis, characterization (both experimental and theoretical) and evaluation of porous materials with applications (at the bench- and pilot plant scale) in the areas of gas and liquid separations and heterogeneous catalysis. A large expertise is present in the development and characterization of porous adsorbents for gas separation, theoretical modelling of microstructures and the simulation of equilibrium and transport properties on these structures. In the synthesis pillar, they will contribute to the preparation of nanostructured micro-/mesoporous materials (hydrothermally stable mesoporous materials, crystalline zeolites and partially crystalline, nanosized zeolite-based materials) and layered double hydroxides. Also, attention will be given to the synthesis of ceramic porous (micro-, micro-/meso- and mesoporous) membranes.

##### *Adsorption:*

The group is working on porous materials such as: i) in meso- and microporous ceramics in the form of membrane layers used for gas or liquid separations. Current activities involve the development of microporous membranes for olefin-paraffin and carbon dioxide or hydrogen separations, ii) in catalytic ceramic materials for reactions leading to the production of hydrogen. Current activities involve the development of spinel or perovskite materials for the redox water decomposition.

##### *Membranes:*

The Laboratory of Inorganic Materials of the Centre for Research and Technology-Hellas focuses on applied research in ceramic materials and in particular:

i) electronic and optical bulk polycrystalline, or in the form of nanoparticles, ceramics used for telecommunications, space, lighting and medical applications. Current activities involve the development of materials for wireless tagging, materials for satellite signal processing and development of new concepts in light emitting diodes

ii) meso- and micro-porous (IUPAC-definition) ceramics in the form of membrane layers used for gas or liquid separations. Current activities involve the development of microporous membranes for olefin-paraffin and carbon dioxide or hydrogen separations

iii) catalytic ceramic materials for hydrogen production. Current activities involve the development of spinel or perovskite materials for the redox water decomposition.

Membrane processes are in particular of importance for activity ii) mentioned above.

#### *Catalysis:*

(i) Production of fuels and chemicals from biomass: The catalytic pyrolysis of biomass and the upgrading of biomass pyrolysis products with the use of catalysts based on micro- and mesoporous materials will be a major activity in CERTH-CPERI in the next five years. Focus will be placed on optimizing yields and selectivity of desired products, such as high-quality biooil as fuel, increased concentration of high-value compounds in biooil (e.g. phenols), increased production of hydrocarbon streams, etc. For this purpose classical acidic micro- and mesoporous aluminosilicate catalytic materials (such as zeolites silicalite-1, H-ZSM-5, USY, H-Beta, MCM-41, HMS, SBA-15, foams) with varying Si/Al ratio will be synthesized and characterized. In addition, new stable aluminosilicate mesostructures will be developed that can combine both the zeolitic and mesoporous materials characteristics. The crucial catalytic properties will be tailored in order to control yields and selectivity of the desired products.

(ii) Selective oxidation reactions: Selective oxidation reactions, such as propene epoxidation or oxidative dehydrogenation of propane, will be another major activity within CERTH-CPERI in the next years, focusing on the development of effective and economic catalytic processes for the production of propene, propene oxide and other useful chemicals. Silver (Ag), vanadia ( $V_xO_y$ ), and other metal/oxide catalysts will be supported on micro- and mesoporous structures in order to promote dispersion of the active metal phase, inhibit deactivation via

sintering and facilitate diffusion of reactants and products, thus minimizing secondary oxidation reactions.

(iii) Optimization of FCC catalysts against deleterious metals: Tolerance of FCC catalysts against deleterious feed metals is a major research target for both refineries and catalyst vendors as metal poisons are more and more abundant in heavier FCC feeds. Thus, CERTH-CPERI research interests will include applied research in development or optimizing FCC catalysts against poisonous feed metals. FCC catalysts are porous materials in powder form, comprising a mixture of different components (mainly a zeolitic component and a porous, amorphous support), each one of them affecting differently the behavior and performance of the aggregate catalyst. The research efforts will focus on clarifying complex deactivation mechanisms due to feed metals.

**Experimental facilities:**

The group at CERTH-CPERI have access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
BET instruments	Adsorption of various gases at different temperatures
Facilities for synthesis under various conditions	Autoclaves for synthesis on lab-scale and/or large scale
SEM-EDX	High-resolution field emission SEM
HRTEM	High-resolution TEM
XR diffractometer	Identification and determination of crystal structures
ICP- OES	Inductively Coupled Plasma/Optical Emission Spectrometry
TGA/DTG/DSC	Thermal analysis/calorimetry
UV-VIS	Ultraviolet-visible spectroscopy
Particle size characterization	Determination of particle size
Multi-component gravimetric analyzer	Dynamic sorption operation
TPA/TPD/TPO/TPR	Temperature-controlled processes
Spin coating device of disk-shaped substrates with frequency control	Synthesis of meso- and micro- porous multilayer membrane systems
Unit for single or binary component mixture	Computerized unit for mixture permeability equipped with GC
Membrane liquid filtration unit	Unit with back flushing capabilities, maximum useful membrane area 500 cm <sup>2</sup>

#### 4.11 University of Hannover (UNIHAN), Germany

At the Leibniz University Hannover, Germany, detailed expertise on porous and non-porous (dense) inorganic membranes for gas separation and catalytic membrane reactors exists at the Institute of Physical Chemistry and Electrochemistry. This important group participates in the synthesis and membrane pillars, their activity being as follows:

##### *Synthesis:*

The experience of this partner laboratory is focused on the controlled synthesis of solids under mild hydrothermal conditions using organic and metal organic molecules as templates. Special expertise is available in the field of EXAFS, XANES and in the structural modelling of porous materials to support their controlled preparation. Attention will be given in the synthesis pillar to structure formation at organic-inorganic interfaces, large single crystals as reference materials (LTA, FAU, AFI), the preparation of inorganic nanotubes ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ) and the synthesis of organic-inorganic hybrid materials.

##### *Membranes:*

- i) Development of high-temperature-stable full- $\text{SiO}_2$  membranes of the type silicalite-1 (MFI) on stable ceramic tubular supports for the shape-selective separation of gases with a critical cut-off of 0.55 nm.
- ii) development of the worldwide first hollow-fiber perovskite membrane by a novel spinning process, co-ordinated by Hannover University. This perovskite hollow-fiber allows the continuous separation of oxygen from air as an alternative to the well-known Linde process. Further, in catalytic membrane reactors oxygen separated from air can be used for the partial oxidation of methane to synthesis gas ( $\text{CO}$ ,  $\text{H}_2$  mixture). The latter development takes place within the frame of a "Lighthouse Project" of the German Federal Ministry of Science and Technology and is co-financed by a consortium of European industries.
- iii) bridging the borders of separation and reaction leading to the development of novel membranes and sophisticated membrane reactors, a.o. catalytic membrane reactors.

### Experimental facilities:

The group at UNIHAN has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
SEM-EDX	High-resolution field emission SEM
TEM	Field emission transmission electron microscopy
XR diffractometer	Identification and determination of crystal structures
EXAFS	Extended X-ray absorption fine structure
XANES	X-ray absorption near-edge structure
TEM	Field-emission transmission electron microscopy lattice resolution in STEM < 0.2 nm, Energy resolution in EELS < 0.7 eV.
SEM	With the resolving data: 1.0 nm at 15 kV and 2.2 nm at 1 kV.
Permeation apparatus	3 on-line-gas chromatography (HP) coupled devices, mixture and single-component permeances, up to 3 bar, up to 900 °C

#### 4.12 Stiftelsen SINTEF (SINTEF), Norway

SINTEF is a private, non-profit foundation, which performs contract research for industry, private organizations as well as public authorities. The field of research and development covers the entire range of applied science and technology. SINTEF is one of the largest European research institutes having around 2 000 employees with an annual turnover of about 220 million €, mainly originating from bilateral industrial research contracts and participation in European or National research projects. The research group participates in three pillars of ENMIX and their participation is as follows:

##### *Synthesis:*

The contribution of SINTEF to the synthesis pillar can be summarized as the synthesis of new ordered mesoporous hybrid materials, hydrothermal synthesis and dealumination of

functional zeolites and the preparation of metal-modified mesoporous materials and nanocomposites of micro- and mesoporous materials. Furthermore, various characterization techniques are available to evaluate the obtained nanostructured materials with tuned properties in the field of catalysis.

*Adsorption:*

i) The Department of "Hydrocarbon Process Chemistry" is part of the Materials and Chemistry Institute of SINTEF. This department exhibits a long-term competence within material science, catalysis and process development. The Department has during the recent years been involved in a number of different projects related to upgrading of oil and natural gas, including Fischer-Tropsch technology, methanol-to-olefins, catalytic cracking, single-site catalysis, fuels cells technology, desulfurization, oligomerization and polymerization technologies, dehydrogenation reactions, synthesis and characterization of micro- and mesoporous materials, metal oxides, zeolites, different carrier materials, perovskites etc., separation and purification technologies, among others.

ii) The group can utilize their materials expertise for development of novel materials on a small scale. We are well equipped with synthesis and characterization techniques as well as with test and high-throughput facilities, dedicated to materials science, catalysis and sorption.

*Catalysis:*

The Department of Hydrocarbon Process Chemistry of the Materials and Chemistry Institute of SINTEF possesses long-term competence in materials science, catalysis and process development. In recent years, the department has been involved in a number of different projects related to:

i) The synthesis and characterization of micro- and mesoporous materials, metal oxides, zeolites, different carrier materials, perovskites etc.

ii) Upgrading of oil and natural gas, including Fischer-Tropsch technology, methanol-to-olefins, catalytic cracking, single-site catalysis, fuel cell technology, desulfurization, oligomerization and polymerization technologies and dehydrogenation reactions.

**Experimental facilities:**

The group at SINTEF has access to a variety of experimental techniques in order to characterize and to evaluate porous materials in the different applications. A summary of experimental techniques and facilities is provided in the following table:

Technique/Facility	Short description
Facilities for synthesis under various conditions	Autoclaves for synthesis on lab-scale and/or large-scale
Facilities for modification of nanoporous materials	Set-ups for various modification reactions on porous materials
SEM-EDX	High-resolution field emission SEM
TEM	Field emission transmission electron microscopy
XR diffractometer	Identification and determination of crystal structures
MAS-NMR	Solid-state NMR
XPS	X-ray Photo-electron Spectroscopy
TGA/DTG/DSC	Thermal analysis/calorimetry
Catalytic facilities	Evaluation of catalytic behavior
Solid-state NMR	Nuclear magnetic resonance for solids
Catalytic reactors	Small-scale test facilities for catalytic testing (fixed-bed, fluidized-bed, microactivity test (MAT), slurry reactor, pulse reactor)

**4.13 First Elements (FE), Cyprus**

First Elements was founded in 2000, under the name First Elements Ventures Ltd, with the vision to build upon its unique business model of fully integrated/complementary services and leverage upon its first mover advantage, accumulated know-how, network and access to risk capital, to emerge as the SE European region's premier service provider in relation to activities which foster entrepreneurship, innovation, competitiveness and technology transfer. In 2006 the company was renamed to First Elements Euroconsultants Ltd (FE), after it was acquired by Euroconsultants S.A., one of the biggest consultancy companies in Greece with offices and collaborators in Eastern Europe, the Mediterranean and in countries of the Persian Gulf.

First Elements is active primarily in three core business sectors around which the company is structured as follows:

- Grants and Research Division which focuses on European and national funded projects relevant to research. First Elements is partner in a number of research projects relevant to Information and Communication Technologies, and also supports public authorities in submitting proposals at EU at national level. The main focus areas are FP6&FP7, Competitiveness and Innovation Framework Programme, Leonardo Da Vinci Pilot Projects, national funded research programmes, INTERREG.
- Public Tenders Division services to public bodies and SMEs, especially in relation to State- and EU-funded programmes aimed at improving competitiveness, innovation and technology transfer. It focuses on business development and capacity building of public organizations as well as on promoting entrepreneurship on a European level.
- SME support Division, especially for developing and supporting new-founded, entrepreneurial, technology-based companies. FE operates on a regional, national and supranational level both within the EU and outside in designing, managing and potentially investing in SME support mechanisms such as Science and Technology Parks, Business Incubators and SME financing schemes/funds. In this aspect of its operation FE works with both the private and the public sector as well as academia in the framework of the triple helix approach to developing entrepreneurship.

The three sectors present significant overlap and synergies; indeed, many of the company's activities cut across all three sectors, which require similar skill-sets, know-how and network.

FE applies hands-on, business-type management methods and is actively involved in the strategic development, operational and financial management of projects and companies/organizations under its supervision. In supporting these entities, the FE team immerses itself in their operations retrieving data and acknowledging their "modus operandi" (mode of operation), mapping the environment and establishing their needs. Having successfully done so, FE prepares strategic roadmaps and feasibility studies that will shed light to their future prospects. Finally, business/strategic plans are prepared that are dynamic



in nature, as the environment and the factors surrounding the company and its operations are also dynamic and ever changing.

FE maintains an international network of strategic partners and associates that assist in the implementation of all the types of activities/projects that the company participates in. These partners come from a wide range of fields ranging from academia to consultancy and from financial organizations to Non-Governmental Organizations and International Industry Associations.

The staff of First Elements comprises a mixture of educational and experience backgrounds, ranging from finance/economics, to psychology, political sciences, and European studies. The majority of the staff members have a master degree in related fields, i.e. Master of Business Administration. Currently, First Elements employs eleven staff members, all of which consultants who undertake different projects according to their interests and specialization.

Within INSIDE-POReS, FE is the only non-research partner of the network responsible for the financial management as well as the commercialization of the project's outputs and legal integration of the network, in formulating a new legal structure business plan that entails consortium partners and will constitute the vehicle for continuation of research after the project ends.

## 5 Conclusions

The roadmap described in the previous chapters provides a framework for future R&D activities related to the synthesis and application of nanoporous materials in sorption, membranes and catalysis. It defines the objectives of the ENMIX and focuses on R&D challenges for the short (< 10 years) and longer (> 10 years) term and provides goals, directions and technologies needed to address these challenges.

The drivers for the defined challenges are diverse, but determined by the issues our society and economies are faced with. Increased energy demand, limited fossil feedstocks, global warming and environmental pollution call for reduced energy consumption, a more efficient utilization of resources and a change for renewable resources of energy and chemicals, thus enabling clean and sustainable processing. Application of nanoporous materials through catalysis, sorption, storage and separation can play a pivotal role in reaching these targets.

The strength of ENMIX lies in the proposed integrated approach covering all fields from the synthesis and characterization of materials to their final application. In this respect the NoE INSIDE-POReS was already unique; it brought together European top groups with a different background. This roadmap includes an overview of the expertise and facilities of the participating groups, which form the basis of the future activities within ENMIX.

These future challenges should not be limited to ENMIX itself. A concerted effort between ENMIX and other European partners is needed to address these challenges in an even more powerful and appropriate way. As the activities of ENMIX are complementary to and may partially overlap with those of two related legal entities, ERIC (European Research Institute of Catalysis) and EMH (European Membrane House), it is advised to explore the common interests and objectives and to investigate what level of collaboration and integration can be achieved. Combination of the strengths of these entities will ultimately lead to a powerful

European institution and may eliminate duplicate efforts. Eventually, this could lead to the erection of a (virtual) European Institute of Nanoporous Materials.