FUSION

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Project acronym: FUSION

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Project Coordinator Name: Damian A. Mooney

Project Coordinator Organisation Name: University College Dublin

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Contents

1 Final Publishable Activity Report

1.1 Contractors Involved

#	Participant name	Country
1	University College Dublin [UCD]*	Ireland
2	University of Edinburgh [UEIN]	United Kingdom
3	Delft University of Technology [TUD]	The Netherlands
4	Warsaw University of Technology {WUT}	Poland
5	National Center for Scientific Research “Demokritos” [DEMO]	Greece
6	Technical Research Centre of Finland [VTT]	Finland
7	EcoCeramics B.V. [ECO]	The Netherlands

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1.2 Logo

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1.4 Introduction

FUSION represents a problem-based approach to the development of ultra-high performance, high temperature, gas separation materials based on newly emerging porous, inorganic materials, associated fabrication processes and, in a key way, fundamental molecular-level phenomena. In this latter case, very important theoretical advances made in laboratories associated with this project have provided insights into the controlling, molecular-level phenomena important in ultra-thin, nano-porous, inorganic material (NPIM) performance. To fully and rapidly exploit these and other fundamental advancements, there exists a need to develop a framework for the design and performance testing of porous inorganic membranes for selected gas separations.

To leverage the maximum impact of these new discoveries and developments for ultra-thin NPIMs, major gas separation challenges will be taken as case studies for investigation, including the high temperature separation of CO2/Air, SOX/Air, NOX/Air, O2/N2 and H2/CH4 gas mixtures. Taking the case of the separation of CO2/Air as an example, the successful removal of CO2 from gas streams has, not only, huge commercial implications in the production of a purified CO2 gas stream as a product or raw material, but it necessarily has very significant environmental ramifications, particularly in the light of EU obligations under the Kyoto Protocol.

1.5 Project Objectives

The core S&T objectives of this project can be summarised as follows

- **General**: to provide a coherent picture of the molecular mechanisms controlling the structure and function of novel, ultra-thin (~10 nm), nanoporous,inorganic materials.
- **Particular**: the application of controlled-structure, ultra-thin, nano-porous inorganic materials (in either membrane or coated powder form) to high temperature (500 – 1000K) gas separation activities of major importance, i.e. the high temperature separation of CO2/Air, SOX/Air, NOX/Air, and H2/CH4 gases.

The materials chosen for such high temperature applications are Amorphous Metal Oxides (AMOs), Structured Mesoporous Silicas (SMSs) and Zeolites, chosen by virtue of their unique high temperature resilience, amenability to thin film processing and the promise of nano-structure architecture control. More specifically, these objectives can be described as follows:

- the development and application of simulation tools for the accurate modelling of the deposition process of ultra-thin, nano-porous inorganic deposited materials (NPIMs),
- the development of structural characterisation procedures for these materials and forms,
- the development of fabrication techniques for the generation of ultra-thin, NPIMs with controlled architectures,

- the development of simulation tools for the accurate modelling of the high temperature gas sorption and transport properties of ultra-thin, NPIMs,
- the development of experimental techniques for measuring the gas separation performance of ultra-thin, NPIMs,
- the development and application of experimental *in-situ* characterization procedures to determine the stability of these novel material forms to extended operation,
- the assessment of the performance of these novel material forms under "real" process and economic constraints.

The oveall project structure, designed to achieve the aforementioned objectives is shown in

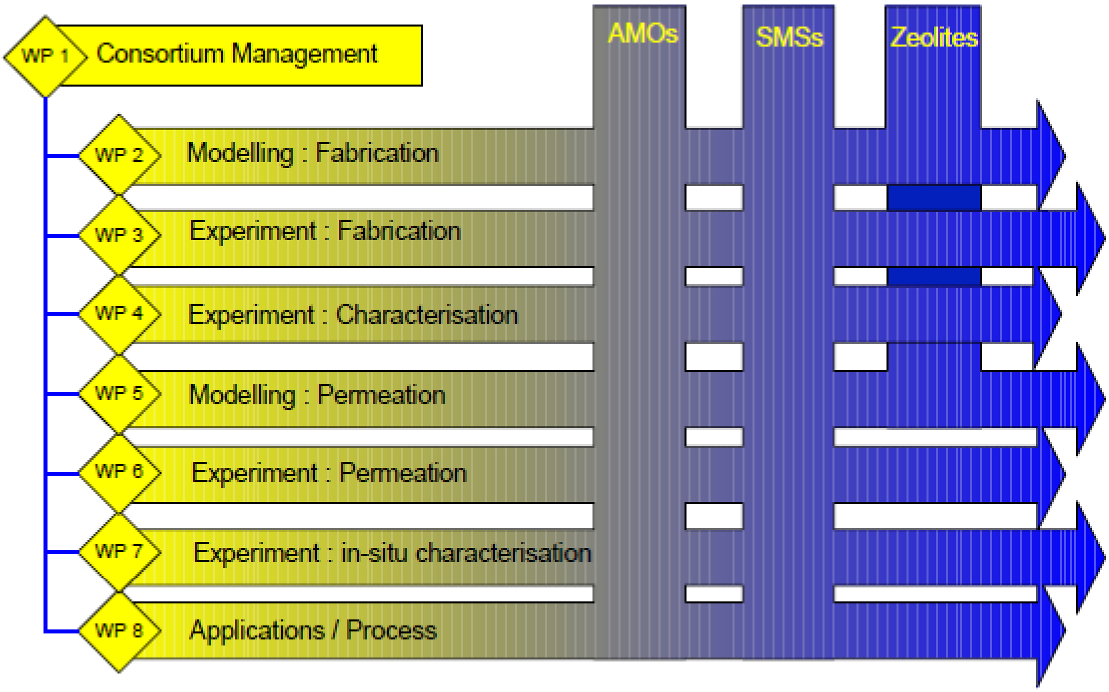

Figure 1: Schematic diagram of the overall project structure. The horizontal arrows represent the possible extension of the methodologies applied to possible future materials. AMOs = amorphous metal oxides. SMS = Structured Mesoporous Silica.

The state-of-the-art is under constant review as part of this project. In light of this, and the reports generated as part of **Del. 8.1, 8.2**, and now **Del. 8.3** it is clear that the core objectives of the project still represent a clear scientific and technological advancement. It is clear from the literature that high temperature gas separation remains a key challenge, particularly for the separation of molecular species very similar in size (CO_2/N_2, for example, which have kinetic diameters of 3.3 Å/3.64 Å, respectively) where molecular size, and not sorption effects, is key for separation. The aforementioned reports also highlight the fact that while systems for the selective separation of CO_2 has been on-going for nearly 10 years, the progress has been slow with no clear high temperature candidate emerging, not to mention the technical difficulties in the preparation of existing membranes. The theoretical developments that underpin this work provide an alternative means to this end, whereby non-percolating effects for ultra-thin nano-porous membranes leverage significantly small molecular size differences.

1.6 Scientific Achievements and Results

As a result of the work performed during this project, the following scientific achievements may be highlighted

1. The development of computational routines for the simulation of supported membrane synthesis via CVD:
    a. A novel technique has been developed for the simulation of the formation of boro-silicate glass (Vycor), extendable to the modelling of other etched amorphous metal oxides (see Figure Figure 2(a)).
    b. A novel kinetic Monte Carlo (kMC) routine has been developed which replicates the experimental synthesis method of CVD for $Si(OH)_4$ and TEOS. This can be easily extended to other precursor agents (see Figure Figure 2(b)).

(a) (b)

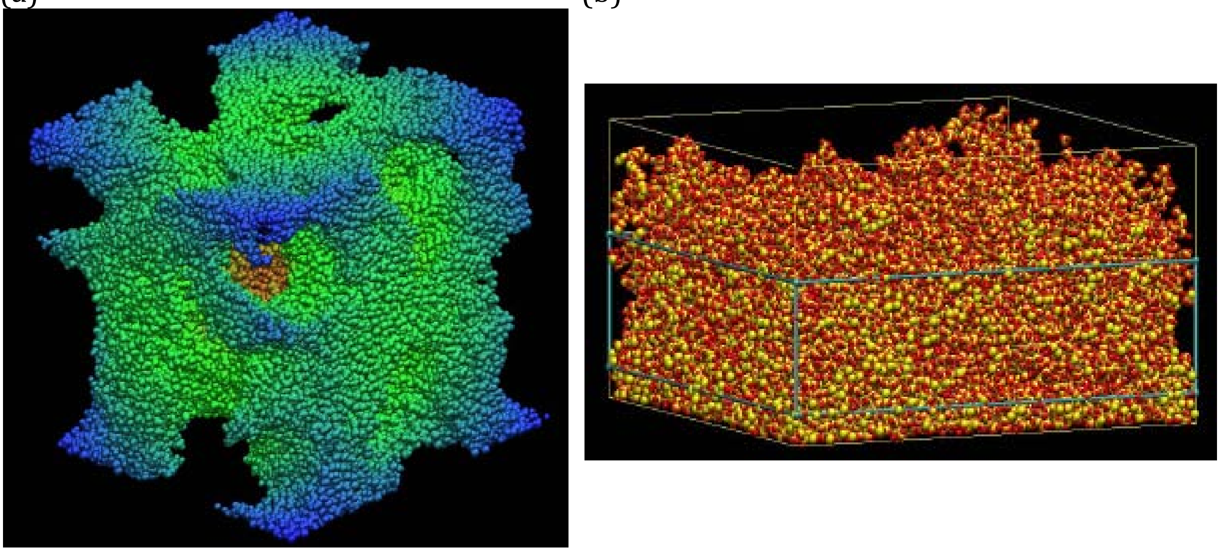

Figure 2: (a) Model porous substrate (Vycor). Coloured spheres indicate hydroxyl surface groups. (b) Image of Si(OH)4 deposited onto Vycor. Yellow indicates silicon, red oxygen. Hydrogens are not show for clarity.

2. The development of routines for the modelling of the synthesis of MCM-based materials including functionalisation
    a. Techniques have been developed which can mimic the synthesis routes for a variety of MCM materials

Techniques have been developed for the surface functionalisation of MCM-based materials, thus allowing the rapid testing of these materials for CO_2 and other gas capture technologies (See Figure 3).

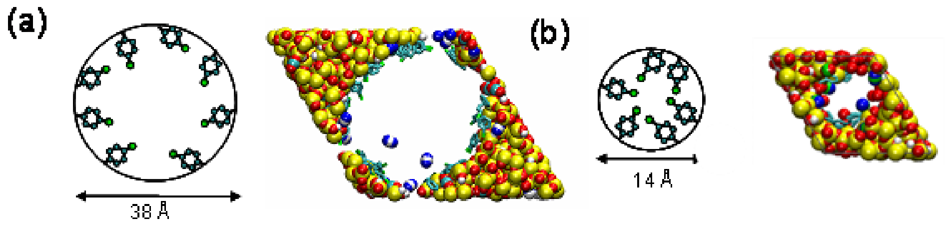

Figure 3 Schematic and snapshot of flue gases adsorbed in (a) Chlorphenyl functionalized MCM-41 of 38 Å pore diameter, (b) Chlorphenyl functionalized of 14Å pore diameter.

3. The development of molecular models for ZSM-5 zeolites, including accounting for the presence of different ions in zeolite cages.

4. A number of techniques have been tested for their application in the preparation of nano-thin selective layers of amorphous metal oxides for high temperature gas separation
   a. Physical Vapour Deposition (PVD) in the form of Magnetron sputtering proved inadequate for membrane formation, producing layers of too high a density and low integrity.
   b. Atmospheric Pressure Plasma Liquid Deposition (APPLD) provided for smooth coatings, well controlled thickness and several optimisation parameters for membrane development (see **Figure** 4)

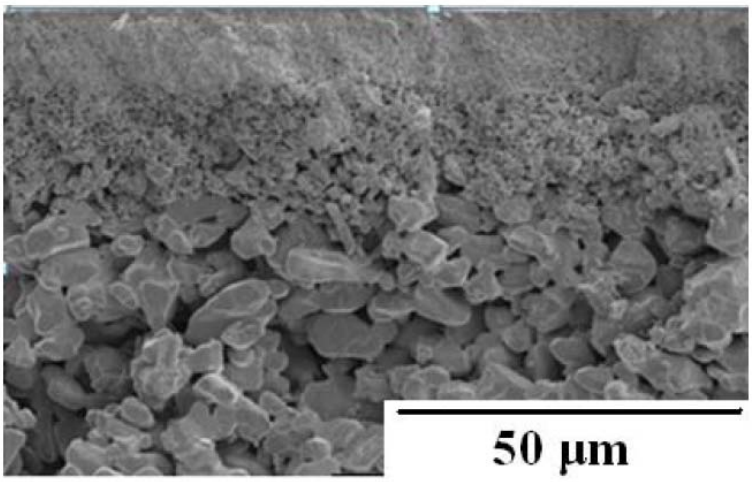

Figure 4: Cross-sectional image of $SiO_2/\alpha Al_2O_3$ composite support membranes used in this work, where the top layer is 1nm SiO_2, supported on 3 μ m αAl_2O_3.

5. A suite of characterisation routines have been developed specifically for the characterisation of porous, nano-thin layers deposited via a variety of techniques. These include a novel AFM-masking technique for determining coating thicknesses, and surface roughness, SEM and FIB for determining surface and cross-sectional structure and refractive index techniques for determining density

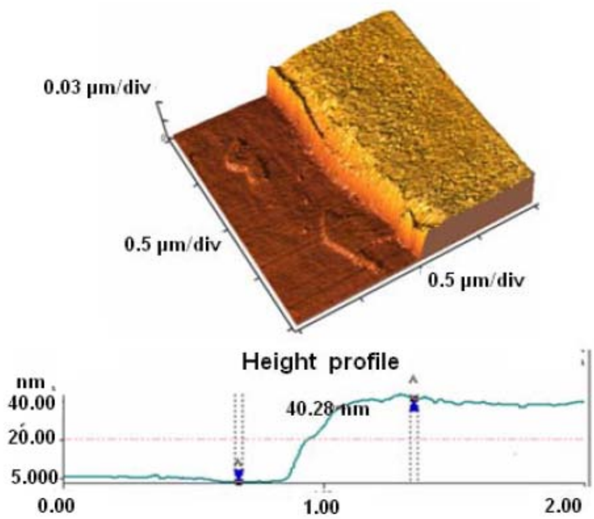

Figure 5: AFM height profile of TiO2 coating coating deposited onto silicon waver. The method of masking is extendable to other deposition routines and deposition materials.

Non-equilibrium molecular dyanamics techniques have been applied to measure the transport properties and mechanism of gases through model membrane materials. The particular model used was that of external-field NEMD, and for carefully chosen external field parameters, it can provide a relatively efficient assessing membrane performance. **Figure 6** shows thru-views from the top-side of deposited structures of SiO_x, while

6. **Figure 7** shows the simulation cell set-up.

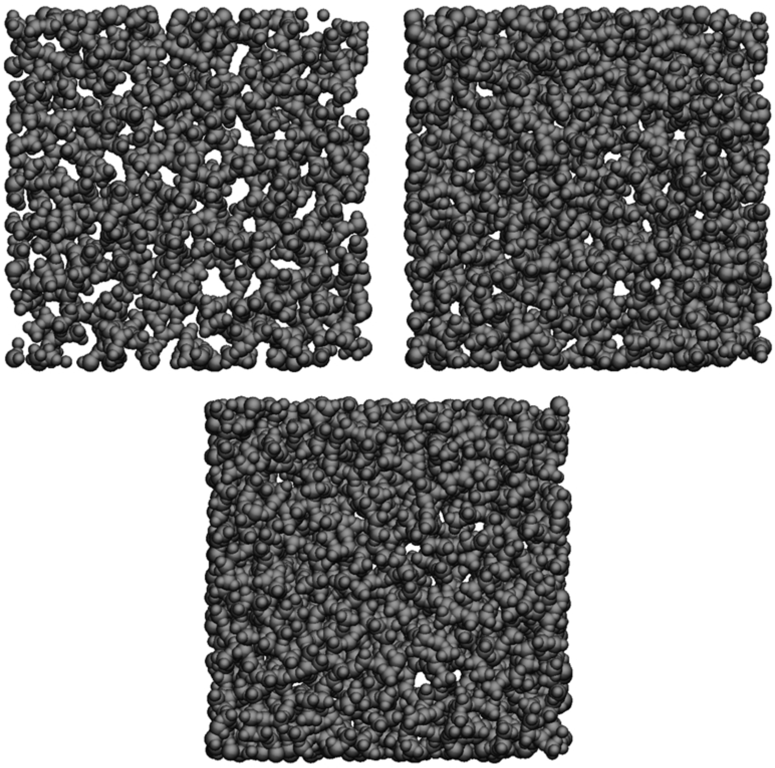

Figure 6: Snapshots of varying thickness from an arbitrarily selected membrane. Top left is the 10°A slice, top right is the 16°A slice and bottom shows the 20°A slice.

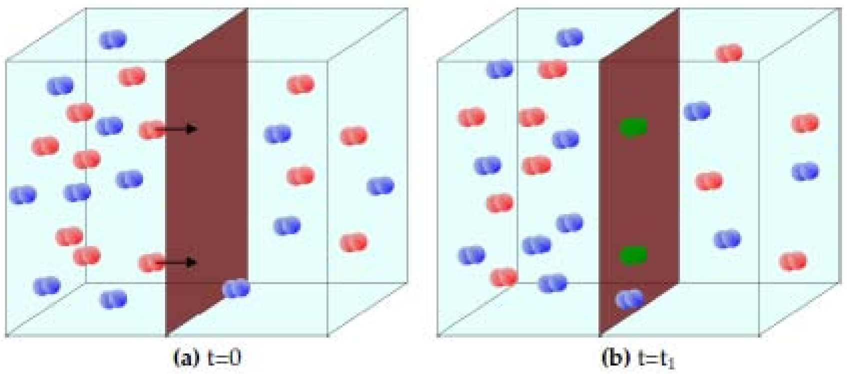

Figure 7: Flux is calculated based on net number of particles passing through a plane. Above shows 2 particles passing through membrane between time 0 and time t1.

7. A methodology has been devised for the high-through-put screening of functionalised MCM-based materials for gas adsorption properties.
    a. Multiple functionalisations have been tested for CO2 adsorption
    b. A number of candidates have been identified for future developmental work, including experiment, for pressure-swing applications.

8. A specially constructed rig has been developed for the testing of planar, membrane geometries at a variety of temperatures and pressures.
    a. This includes a membrane testing apparatus (see .Figure 8(a)) and
    b. A specially design membrane holder (see .Figure 8(b))

(a) (b)

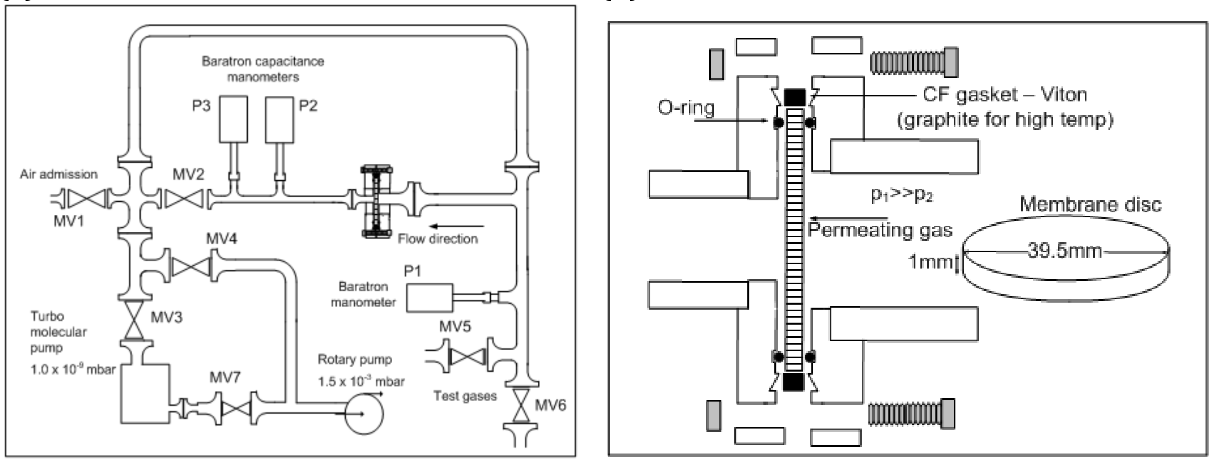

Figure 8: (a) Schematic diagram of permeation rig used for all measurements of gas transport properties; (b) Details of flange design for membrane holder used in this experimental work.

9. Over 500 membrane tests have been conducted on membranes prepared by both PVD and APPLD techniques.
    a. Optimised APPLD deposition conditions have been established for the synthesis of high quality membranes
    b. Selectivities of 8:1 for CO2/N2 and 100:1 for He/N2 at 673 K have been achieved. Currently, no technology is able to achieve this degree of separation at this elevated temperature

1.7 Conclusion

The FUSION project represented an ambitious endeavour aiming to advance the technology for high temperature CO2 capture through membrane technology.

Substantial advancement has been made in the development of techniques for the manufacture of membranes currently representing the state-of-the-art in CO2/N2 elevated temperature capture (8:1 at 673K). We are confident the this can be substantially improved upon with further modification to deposition equipment (APPLD) and process optimisation. Indeed, theoretical predictions suggest that an order or magnitude improvement is possible. This work is currently underway.

A second significant achievement is the development of software tools and techniques for the molecular modelling of deposited layer synthesis (amorphous metal oxides) of membranes (as mentioned above) and the synthesis of functionalised MCM-based materials. Together with techniques applied for modelling sorption and transport properties in these model materials, a suite is now available for the rapid testing of a wide variety of material modification, speeding up the discovery and ultimately the implementation of successful capture technologies.

Currently, a number of IP opportunities are being pursued with a view to commercialisation.

1.8 Acknowledgements:

As the coordinator of FUSION, I would like to personally thank all the partners for their hard-work, enthusiasm and friendship during the course of this project.

We acknowledge the generous support of the EU Commission, which through contract

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gave life to the project.

I would also like to extend my heart-felt thanks for the diligence, professionalism as well as kind help encouragement offered by our Scientific Officer, Dr. Martyn Chamberlain. His exemplary character raises the esteem of Commission for which he works.