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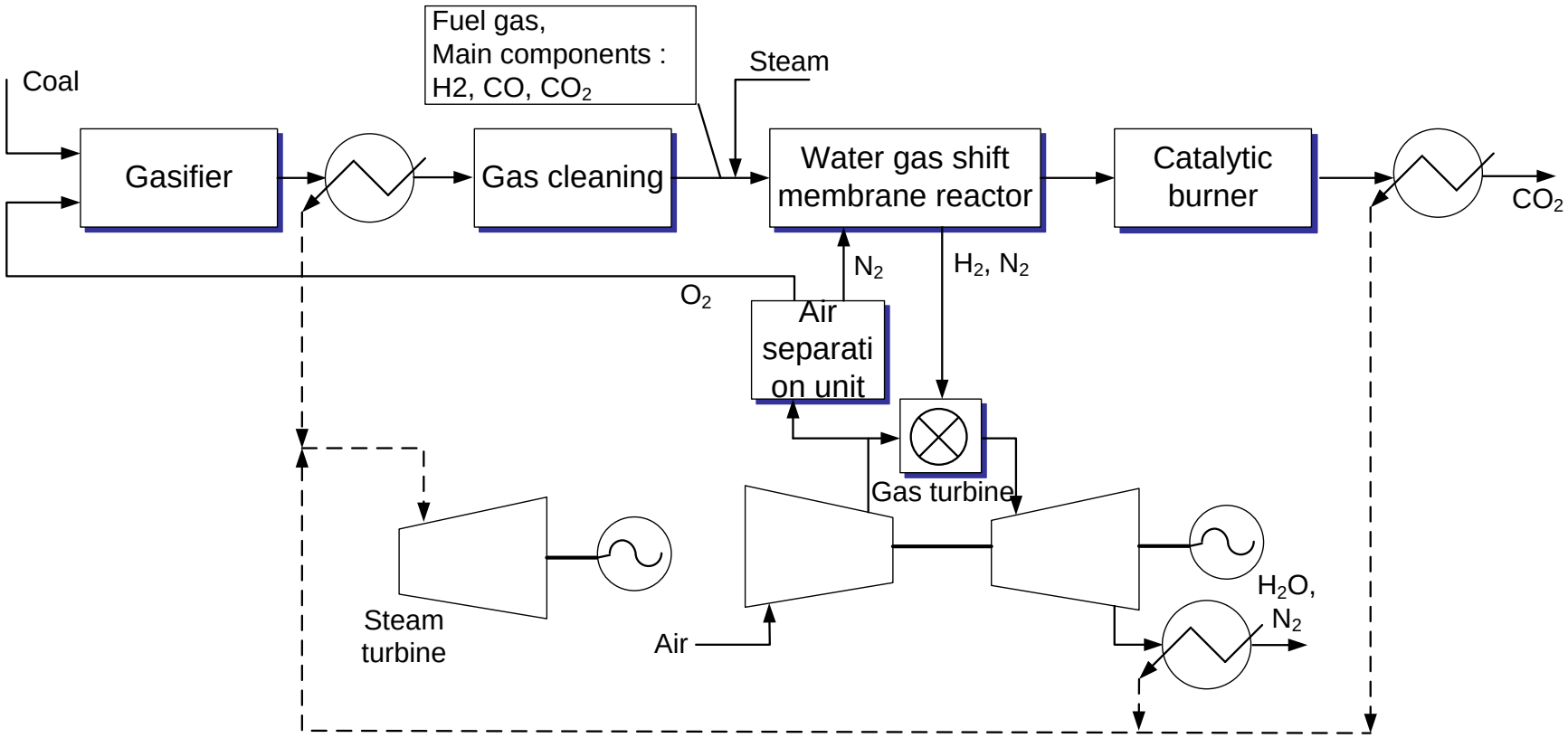
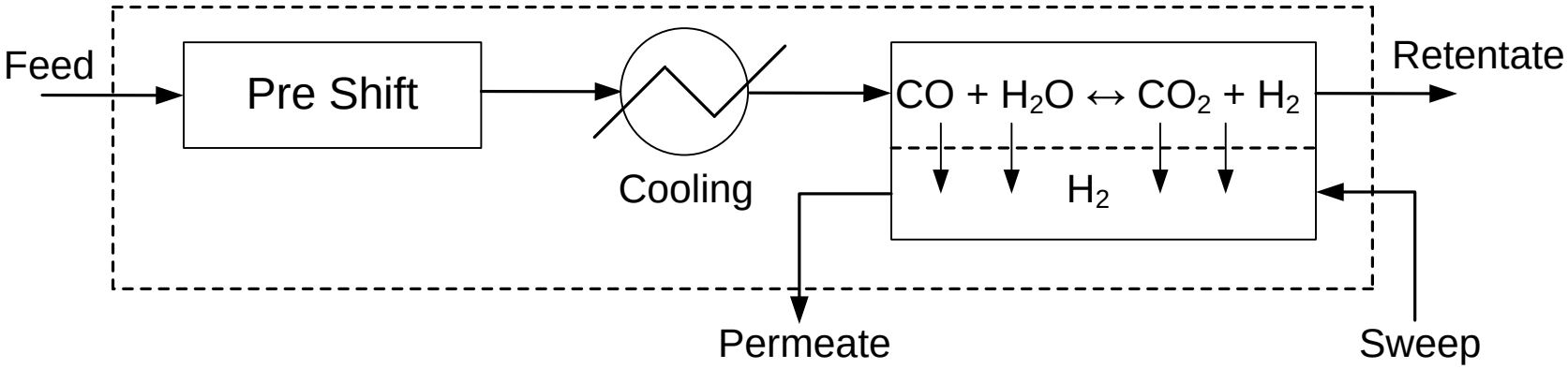
DE-FE001322 Hydrogen Selective Exfoliated Zeolite Membranes
Proposal in response to Funding Opportunity NO. DE-PS26-08NT00699-01
Pre-combustion carbon capture technologies for coal-based gasification plants
Topic Area 1 – High-Temperature, High-Pressure Membranes

Project Overview: H_2-selective membranes for IGCC w/ WGSMR



Bracht et al., **Energy Convers.Mgmt** 38, S159-164 (1997)

IGCC w/ WGSMR



IGCC efficiency
Without CO_2 capture: 46.7%
With conventional CO_2 removal: 40.5%

With WGSMR and CO_2 recovery: 42.8% based on
35atm feed, 20atm permeate (15atm pressure drop)
330°C in the feed
hydrogen/carbon dioxide selectivity = 15
hydrogen permeability = 0.2 mol/m^2-s-bar
Membrane Area Needed: 2,200 m^2 (400MW)

Bracht et al., **Energy Convers.Mgmt** 38, S159-164 (1997)

Table 1: More detailed summary of the findings in (Bracht, et al., 1997)

IGCC Configuration	Net electric efficiency [%]	Overall CO_2 recovery[%][1]
No CO_2 removal	46.7	
Conventional CO_2 removal[2]	40.5	88
WGS-MR + conventional gas cleaning	42.8	80
WGS-MR + dry gas cleaning	43.4	80
1: based on coal input; 2: CO_2 removal by Rectisol wash		

IGCC case	base-case	Conventional CO_2 removal	WGS-MR CO_2 removal with conventional gas cleaining
CO_2 recovery [1]		88	80
CO_2 state		gaseous (1.3 bar, 38 °C)	gaseous (1.0 bar 74 °C)
Net power [MW]	379	355	433
Net efficiency [% LHV]	46.7	40.5	42.8
Specific investment [2] [ECU/kW]	1560	1869	1594
COE[3] (6000 h/a) [ECU / kWh]	0.0787	0.0867	0.0835
1: based on coal input; 2: European Currency Unit, 1ECU=.27 US$, 30 July 1996; 3: Cost of electricity generation.			

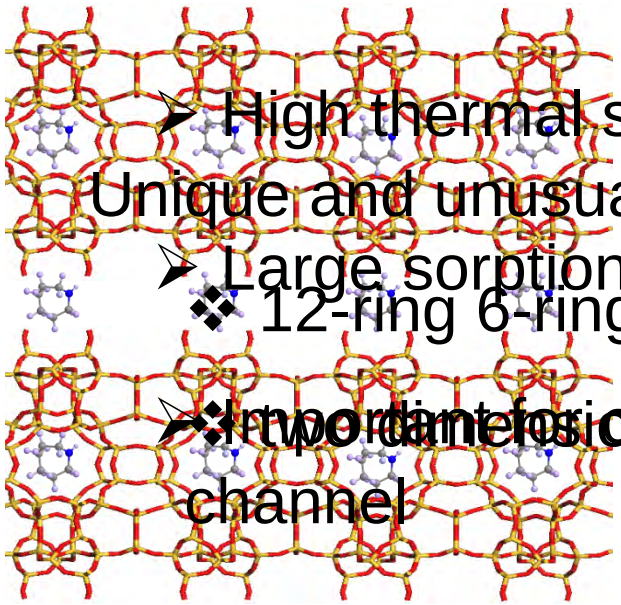
Membrane operates stable at 500 C; Membrane H_2/CO_2 selectivity: 15;
Membrane permeance: 0.1 mol/m^2-s-bar (200 SCFH/ft^2-100psi deltaP);
Membrane tube length 2 m; Total membrane surface area 2176 m ^{2}; Total number of membrane tubes 3300; Membrane tube diameter 10.4 cm; Total catalyst volume 25.3 m^3;
Estimated membrane cost (for proposed exfoliated zeolite membranes): ~$6,000,000

Project Overview: Previous Work and Novel Approach

- **Synthesis of molecular sieve membranes by using thin anisotropic plate-like zeolite crystals and exfoliated zeolites dispersed in an inorganic (e.g., sol gel silica) or polymeric matrix <u>was attempted for the first time</u> with activities supported by DOE Award Number: DE-FG26-04NT42119 (08/01/2004-04/30/2008)**

- **The potential advantages of our approach compared to other technologies that are currently under development include:**
  - **No need to grow (hydrothermally or by chemical vapor/fluid deposition) the selective layer/film on the support. The formation of the selective film is based exclusively on a coating process using pre-made components.**
  - **Potential for high selectivity and flux because, in the case of exfoliated layers or high aspect ratio nanocrystals, very thin layers (ca. 10 to 1,000nm respectively) can, in principle, be made.**
  - **Potential for high stability since the selective components (zeolite layers) are crystalline and more hydrothermally stable than various amorphous oxides used in similar membrane applications.**

Prototype Material: MCM-22(P) A Layered Zeolite Precursor

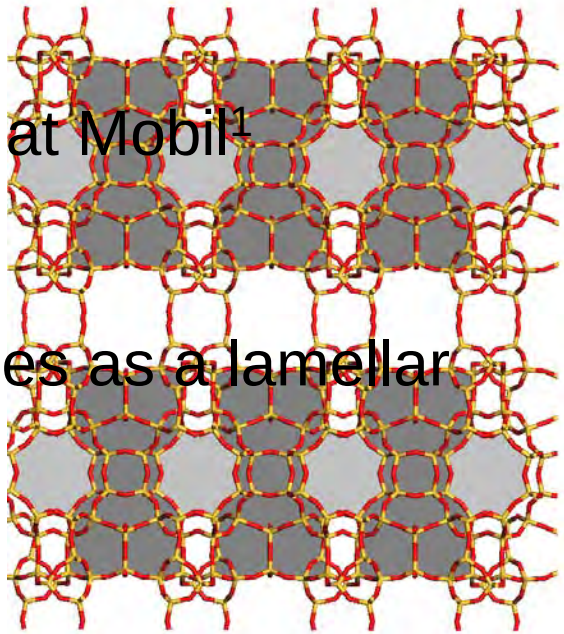


- High thermal stability
- Unique and unusual pore structure
- Large sorption capacity
  - 12-ring 6-ring cups
- Important for catalysis
  - Two dimensional sinusoidal channel

MCM-22(P)

Calcination
540 °C

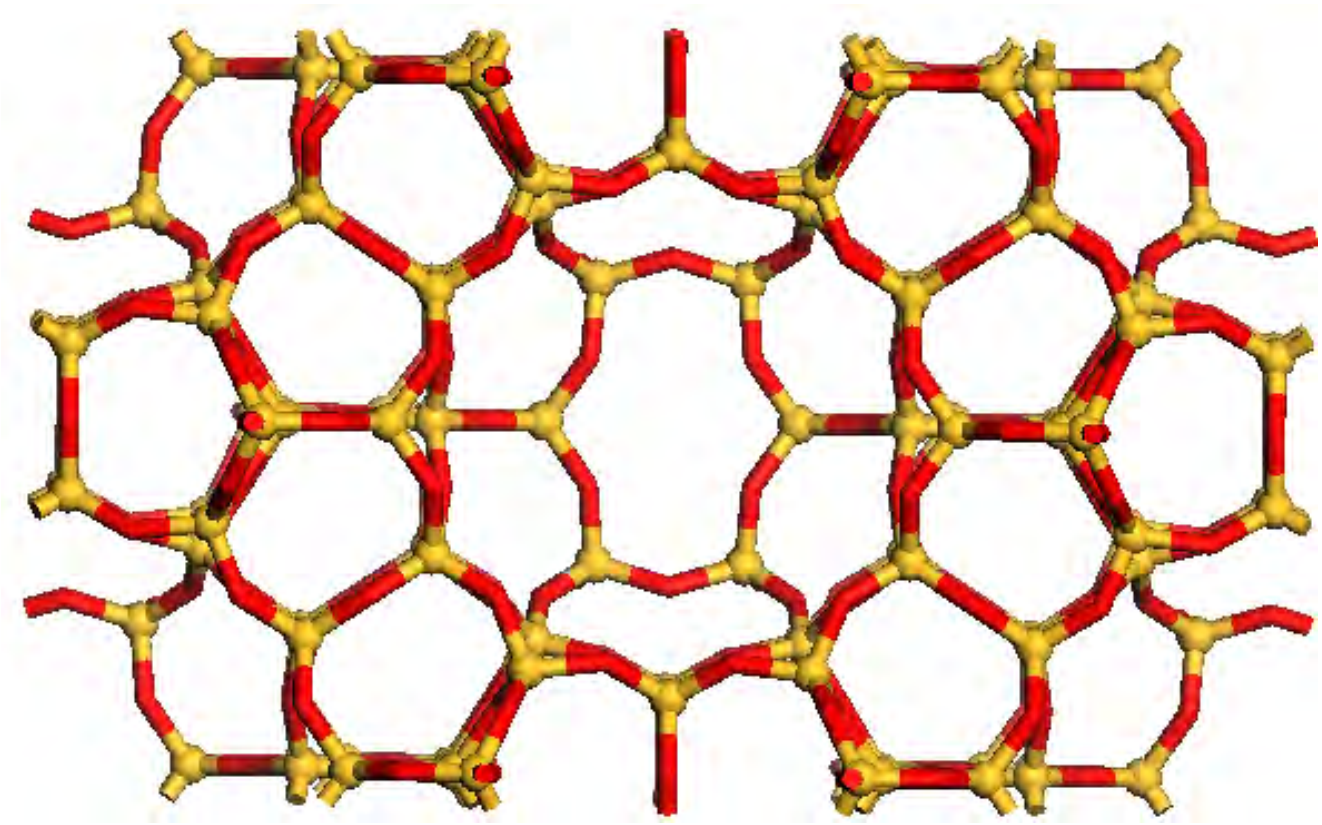
- Invented at Mobil[1]
- Crystallizes as a lamellar structure



MCM-22

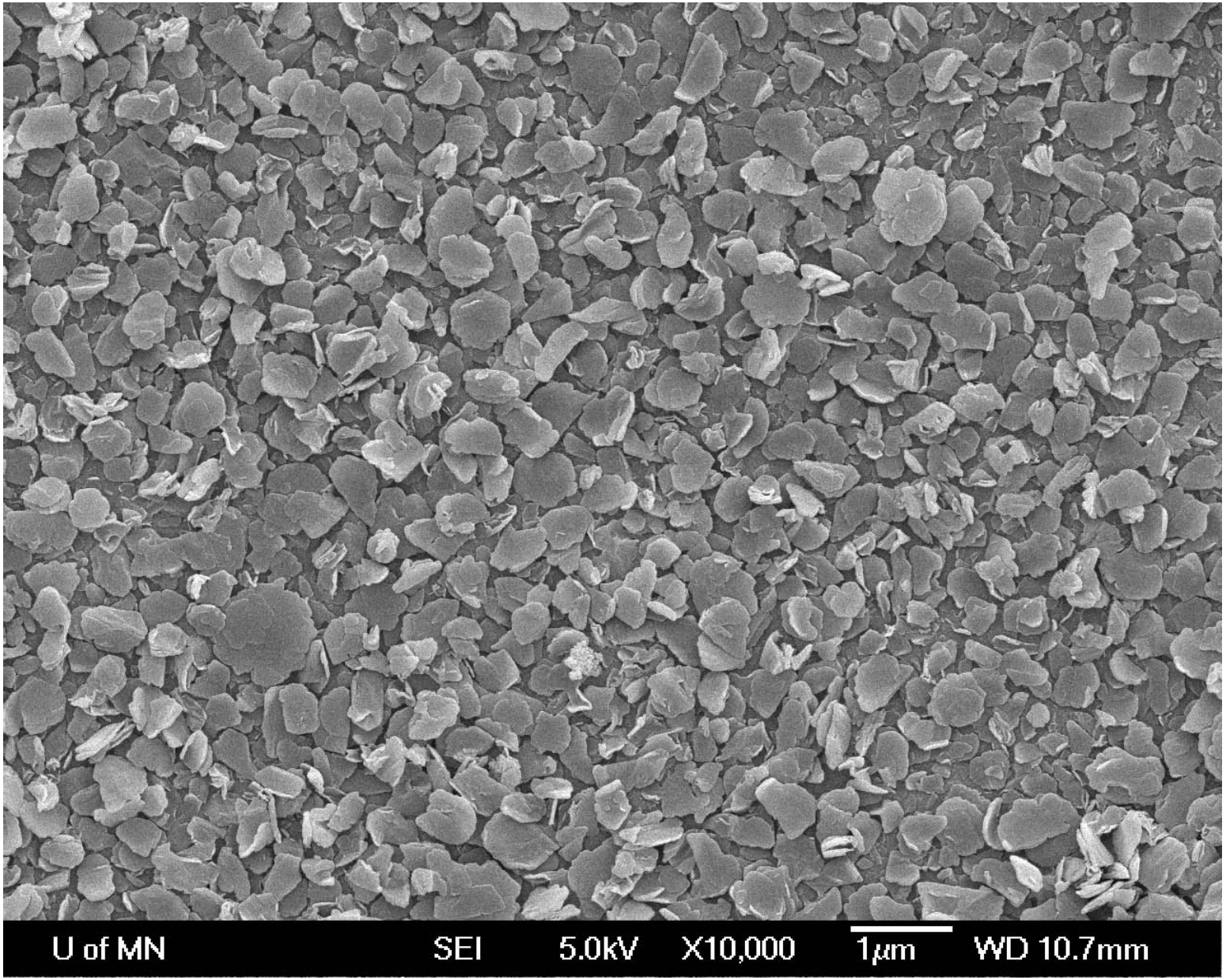
[1]*Rubin and Chu, US Patent 4954325,* ***1990***

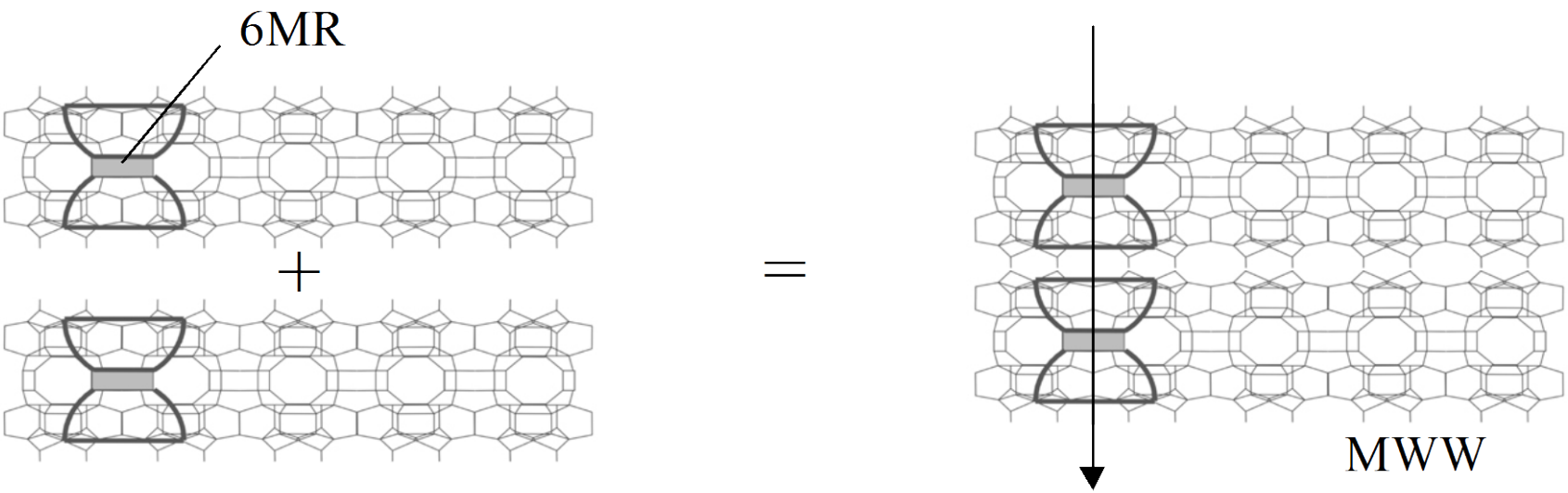
Prototype Material: MCM-22 Layers with H_2-selective pores across



- 6-membered-ring (6MR) transport limiting apertures
- may allow access to hydrogen but will exclude carbon dioxide, nitrogen, carbon monoxide and possibly to a large extend water
- siliceous material is expected to be hydrothermally stable

MCM-22(P) and MCM-22 crystals are plates with aspect ratio of 10

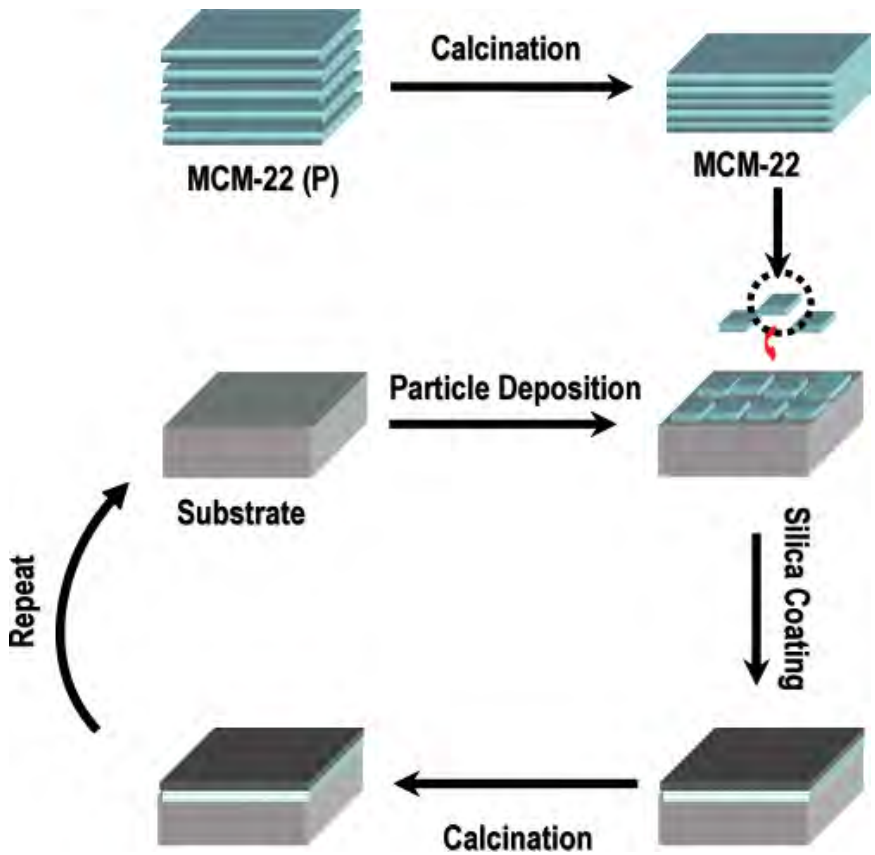




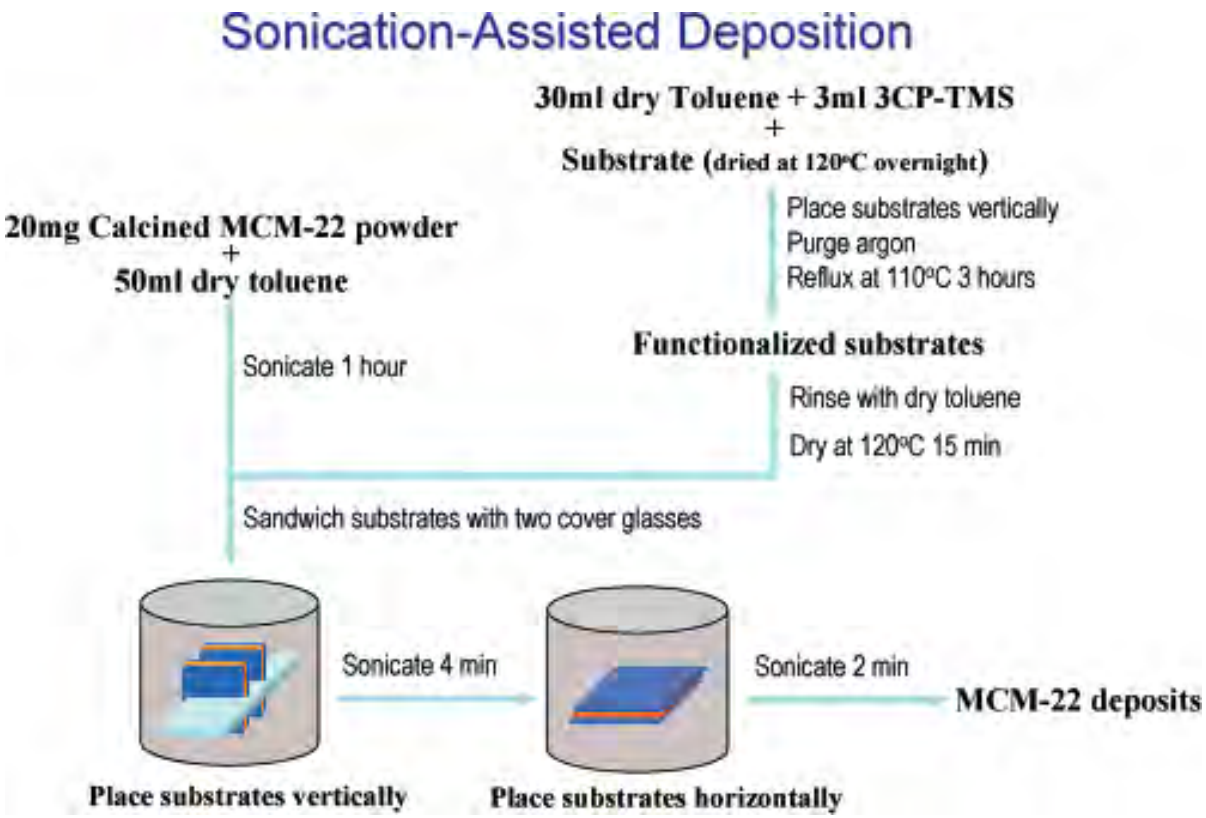
50-100nm thick MCM-22 crystals → 50 6MR transport limited apertures

exfoliated single layers → 1 6MR transport limited aperture

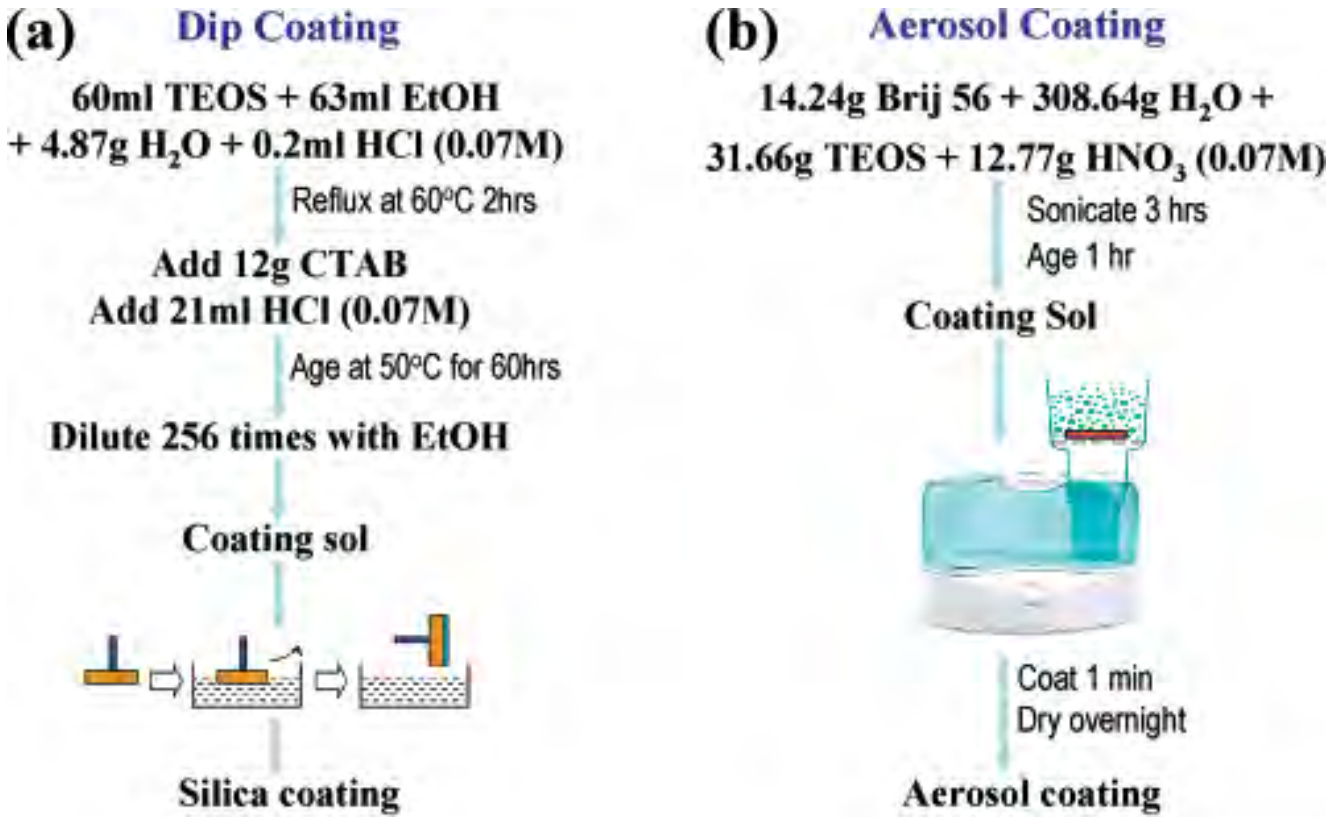
Proof of Concept Demonstartion: Layer-by-Layer Deposition



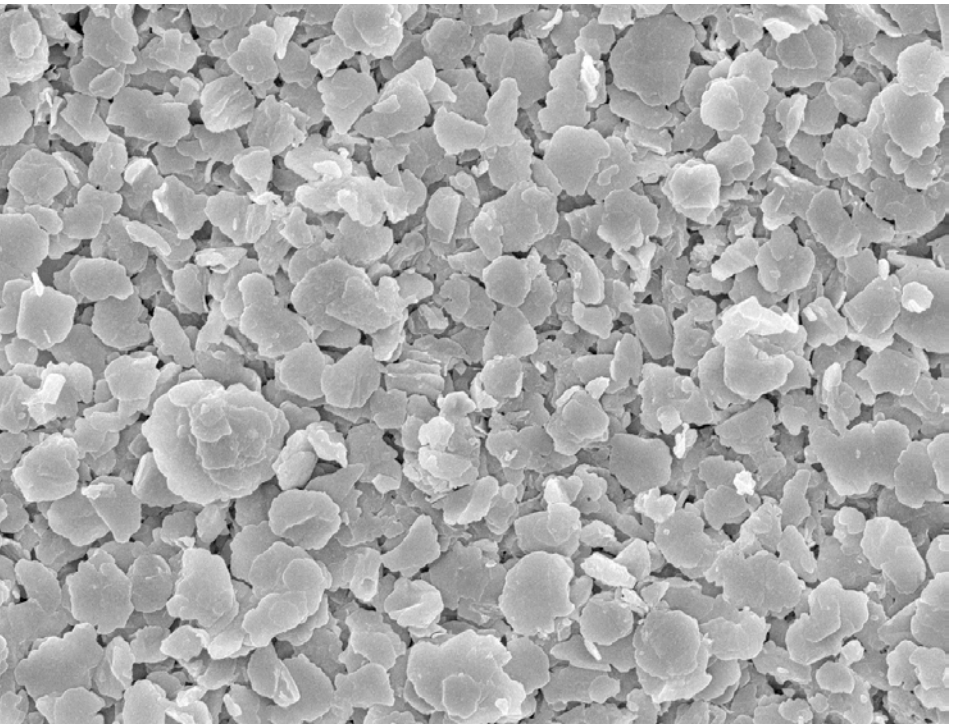
Covalent Attachment of MCM-22 Crystals

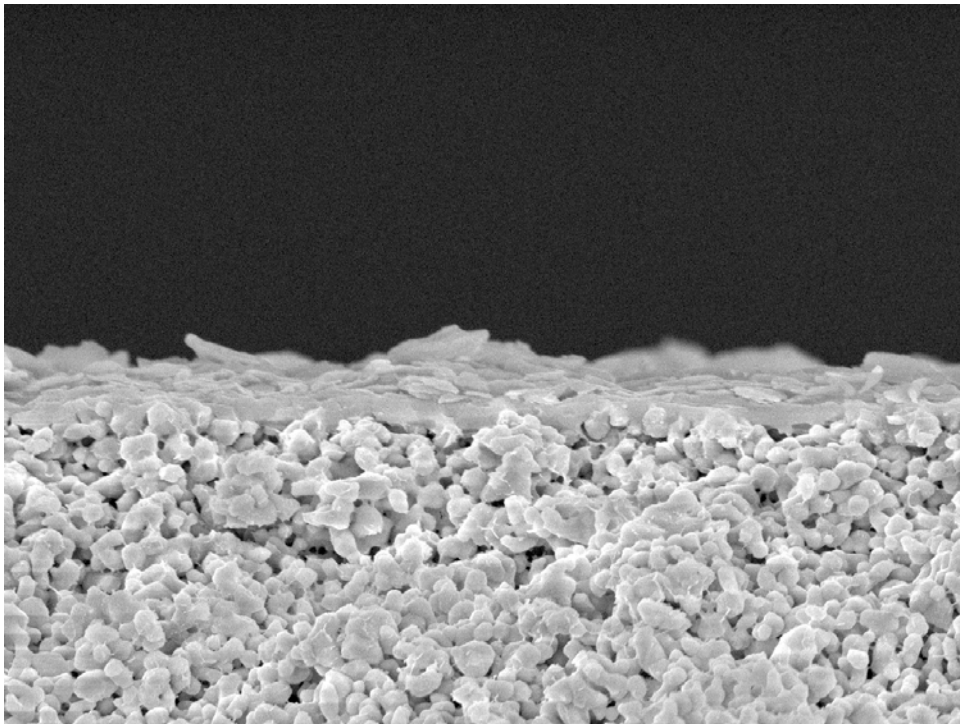


Intermediate Silica Coatings

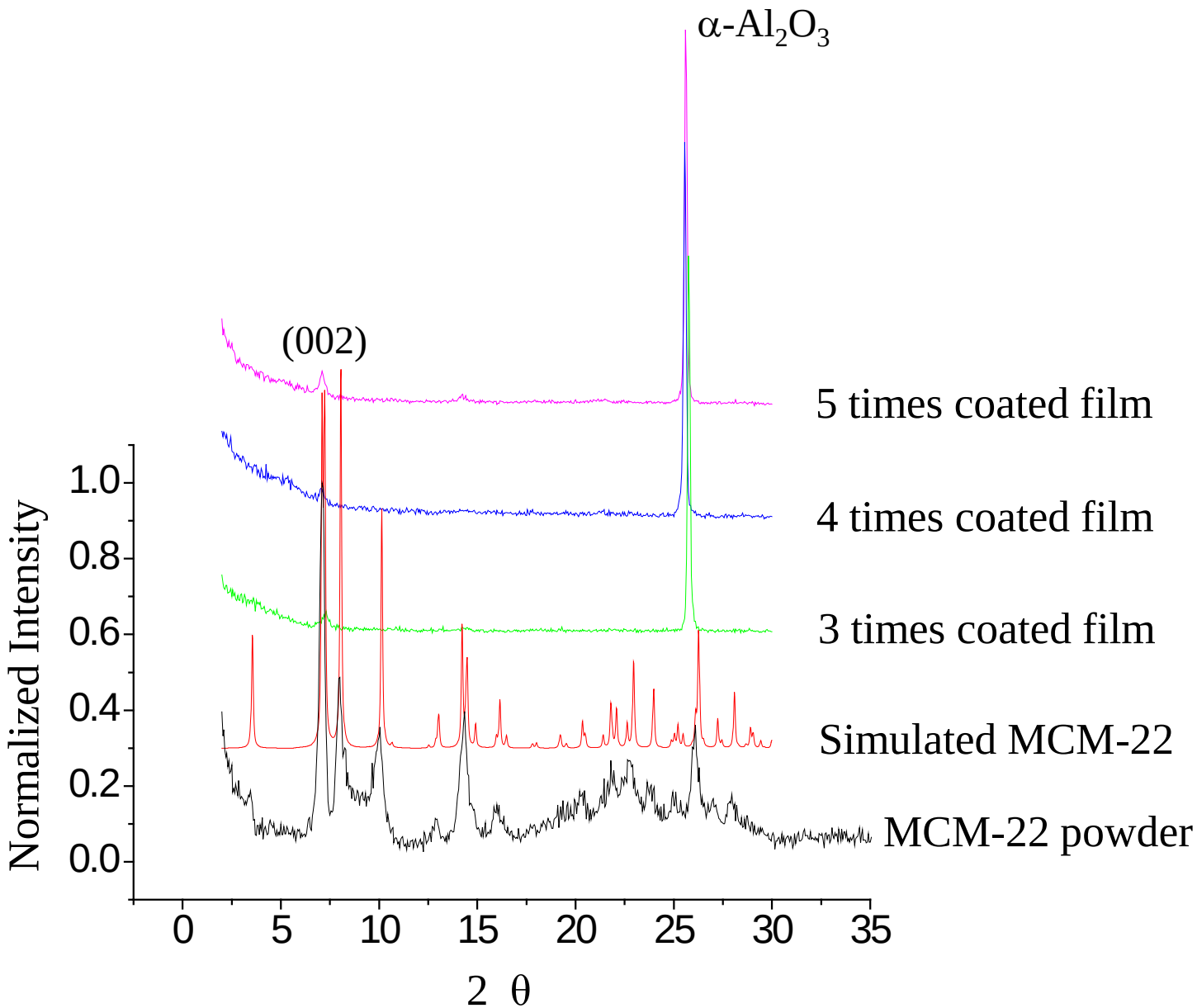


5 times coated MCM-22 /silica film

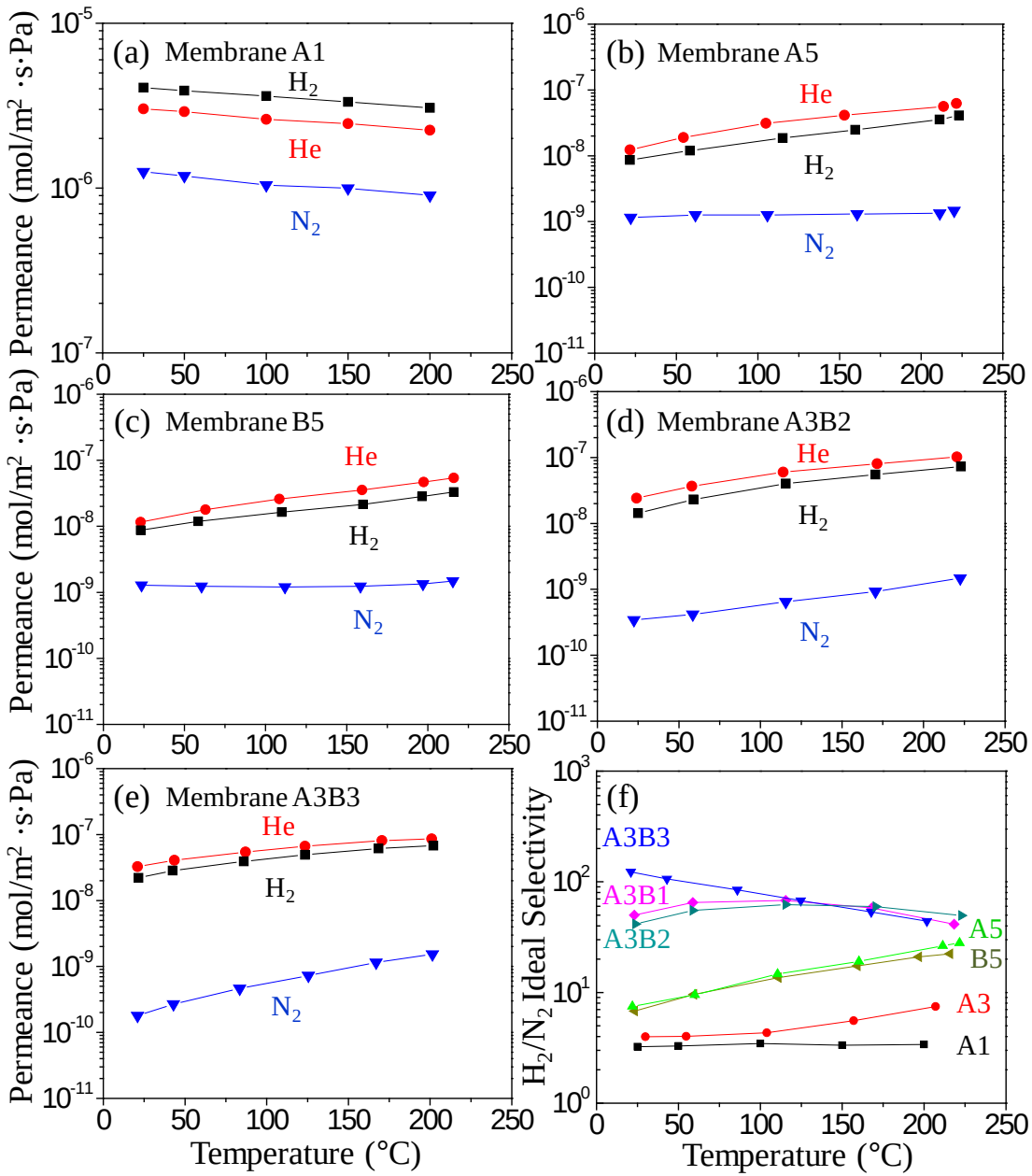




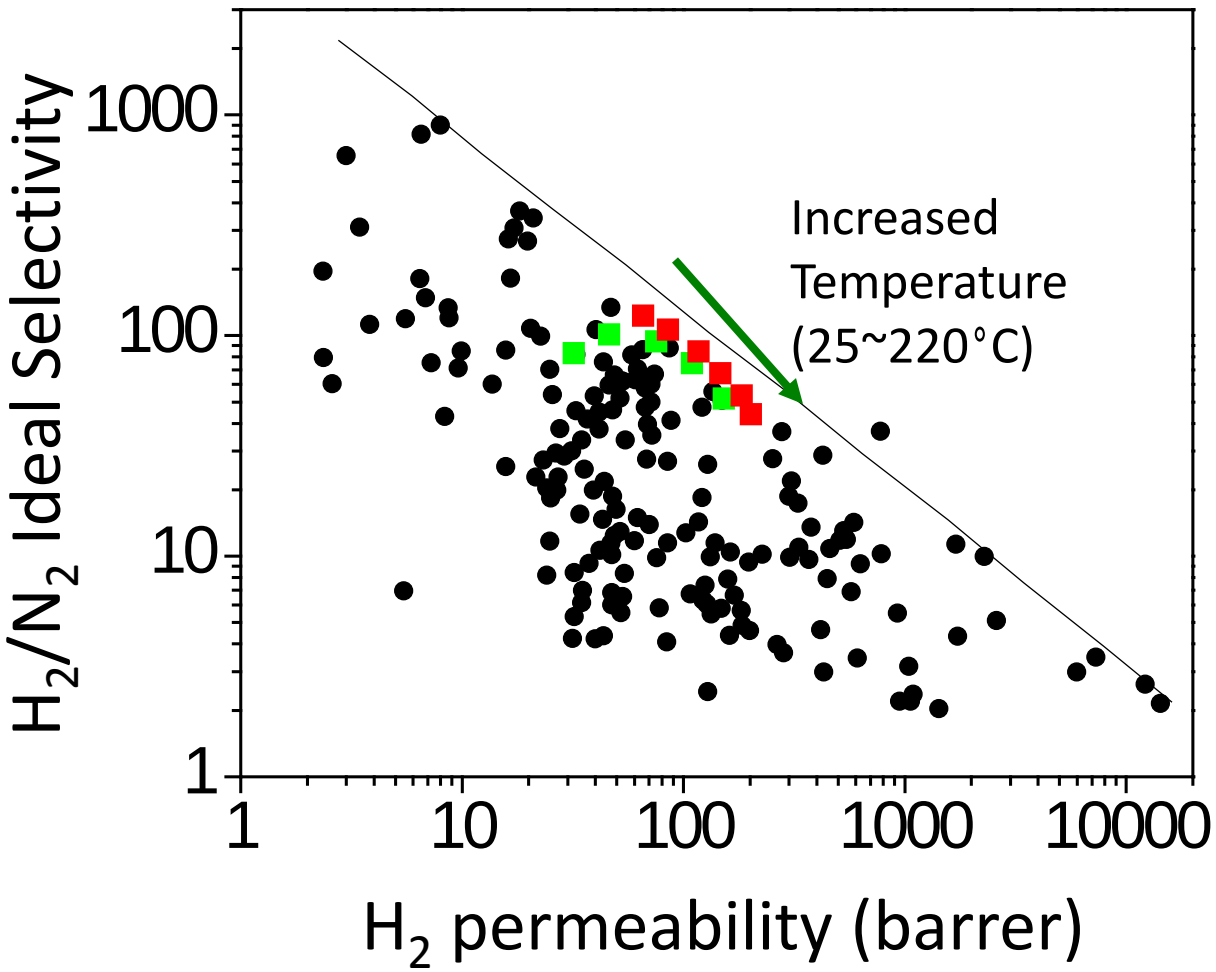
c-oriented MCM-22 Films



Selective Membranes by Deposition of MCM-22 crystals Demonstarted!



Performance is Promising

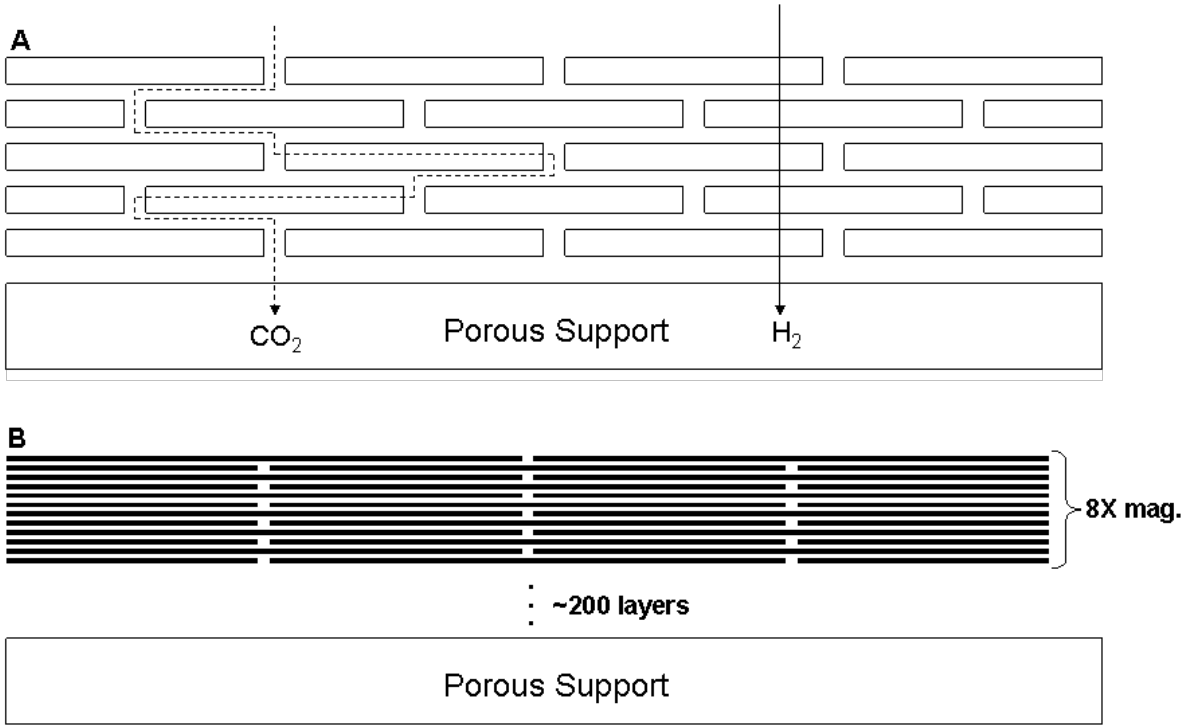


Membrane Microstructure and Separation Performance

- **<u>Target:</u> 0.1 micrometer thick, 50-layer films with**
- **H_2/CO_2 selectivity of 100 and**
- **hydrogen permeance of 0.1 mol/m^2-s-bar at 500°C**

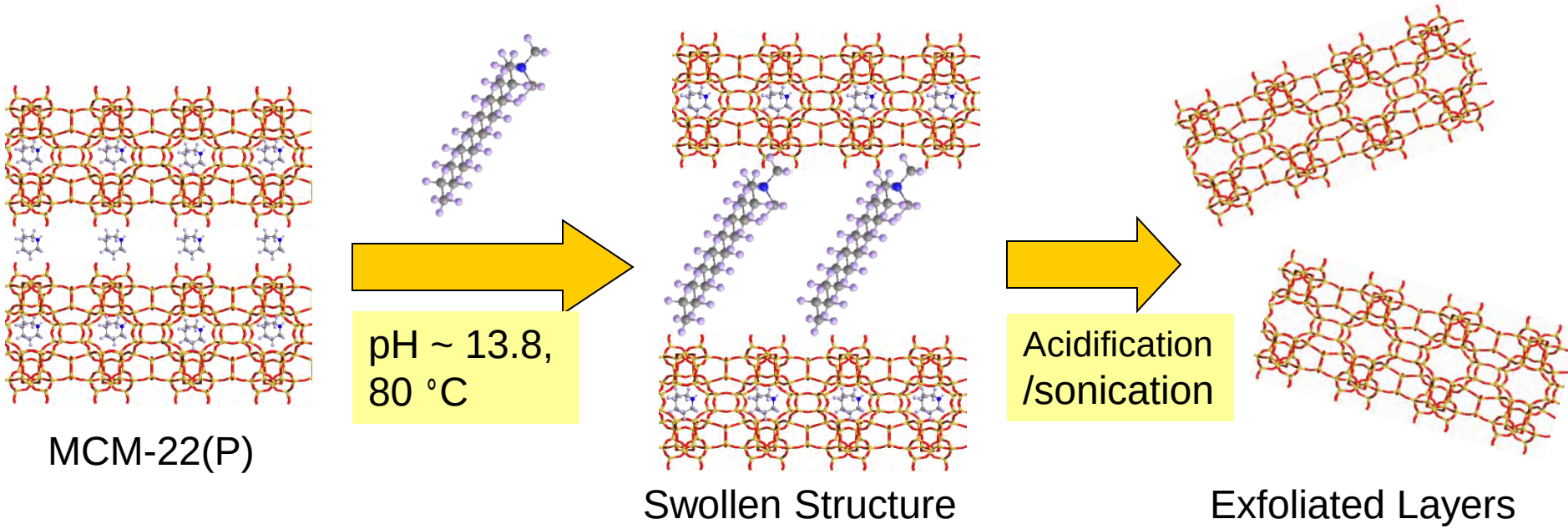
- **<u>Achieved:</u> 1 micrometer thick, 5-layer films with**
- **H_2/CO_2 and H_2/N_2 ideal selectivities of approximately 10 and 50, respectively, with an activated (i.e., increasing with temperature) hydrogen permeance of approximately 0.005 to 0.01 mol/m^2-s-bar**

- **Proof of Concept Achieved. Exfoliation is needed to improve performance.**



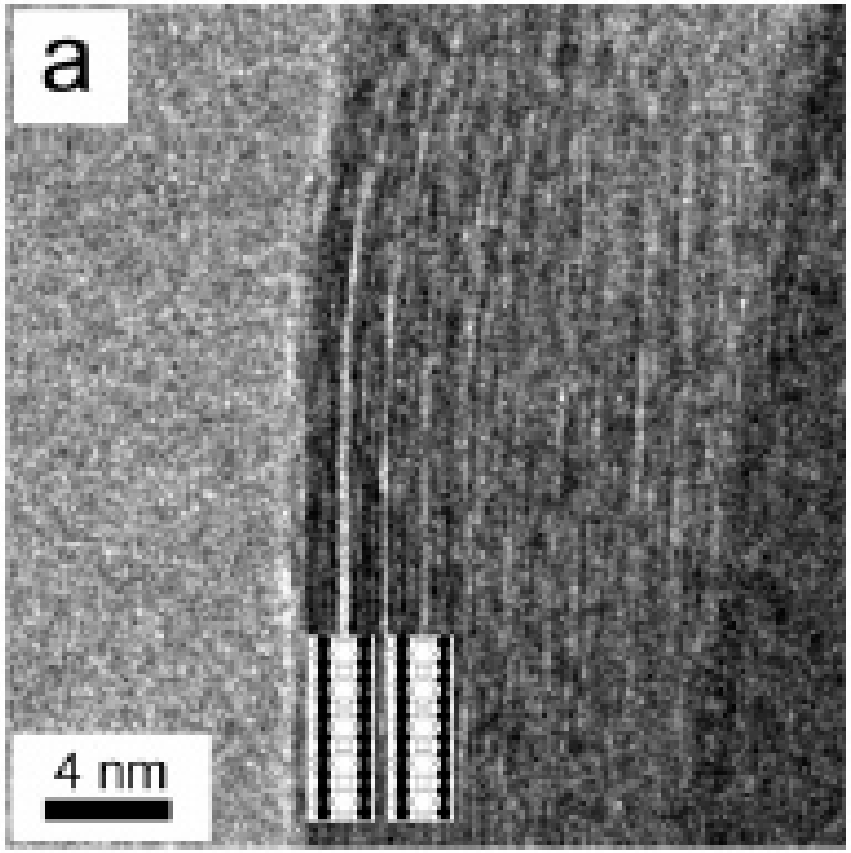
Consider the membrane containing 200 layers of (2.5 nm) x (250 nm) exfoliated tiles
The expected performance of these membranes at 500°C is H_2/CO_2, H_2/N_2 and H_2 permeance of 800, 6,000, and 0.06 – 0.12 mol/m^2-s-bar
(100 – 200 SCFH/ft^2-100 psi deltaP), respectively.

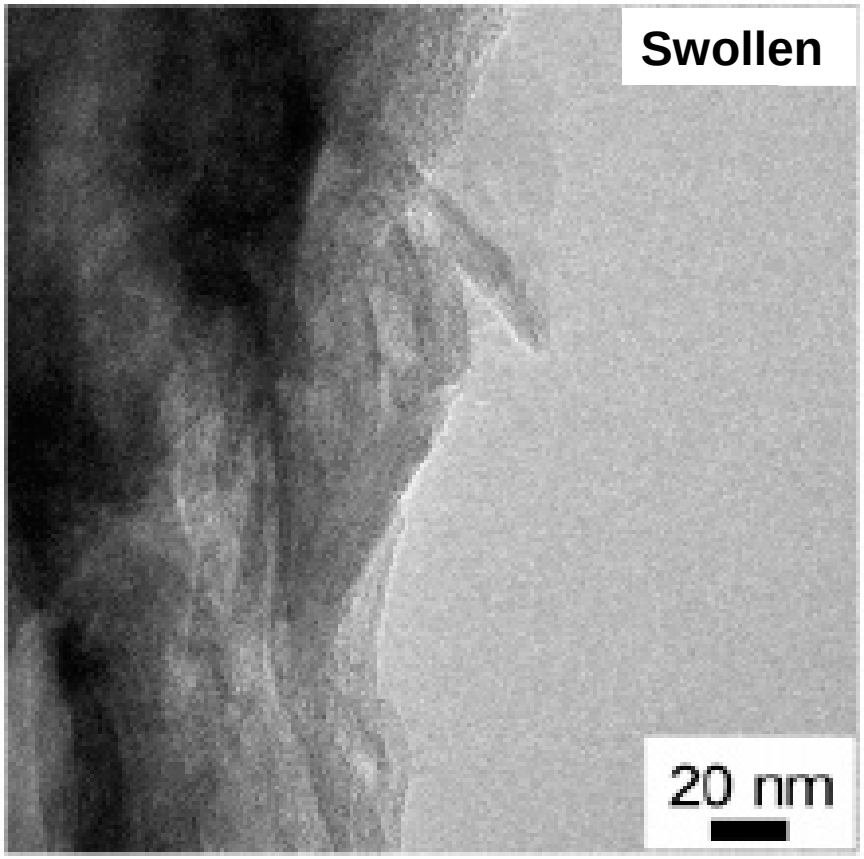
Exfoliated Layers Can be Prepared: ITQ-2



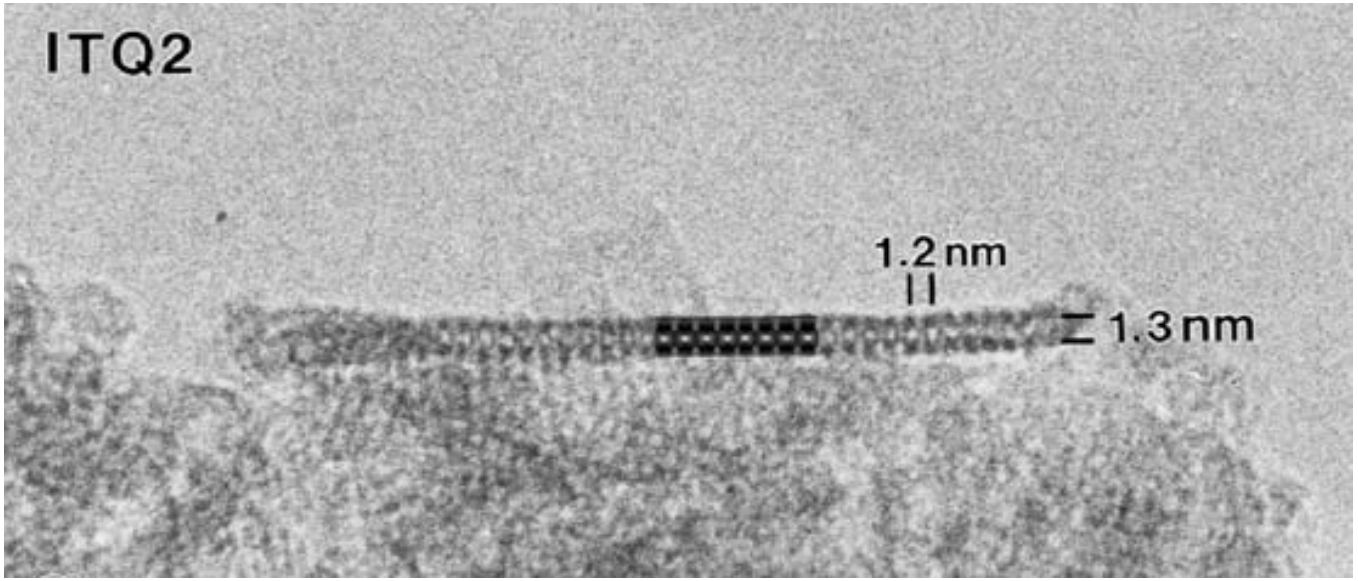
*Corma et al., Nature, **1998**, 396, 353*

Destruction of framework connectivity during swelling and exfoliation





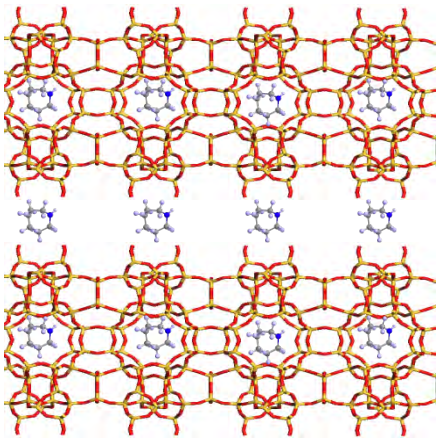
Along with exfoliated layers (ITQ-2) a disordered phase is present



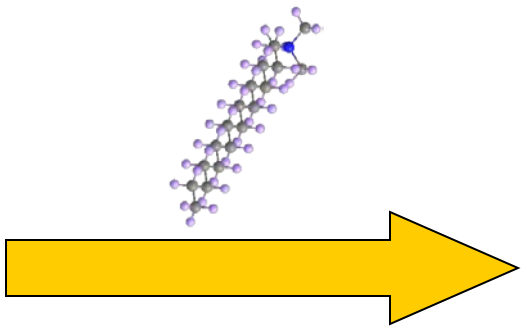
Corma et al.,
NATURE |VOL 396 | 26 NOVEMBER 1998

Milder conditions to swell MCM-22(P)

Swelling MCM-22(P) at Room Temperature instead of 80 C followed by repeated washing with water.

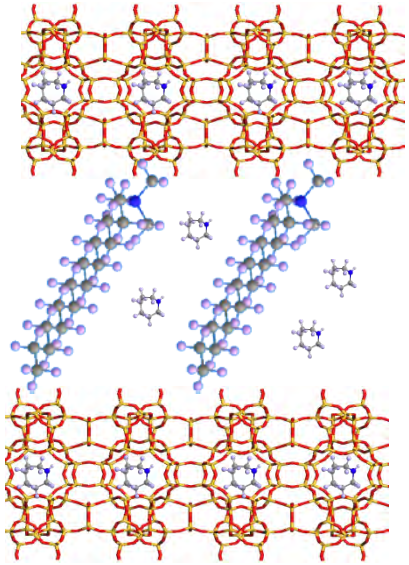


MCM-22(P)



pH ~ 13.8, ~~80~~ °C
RT

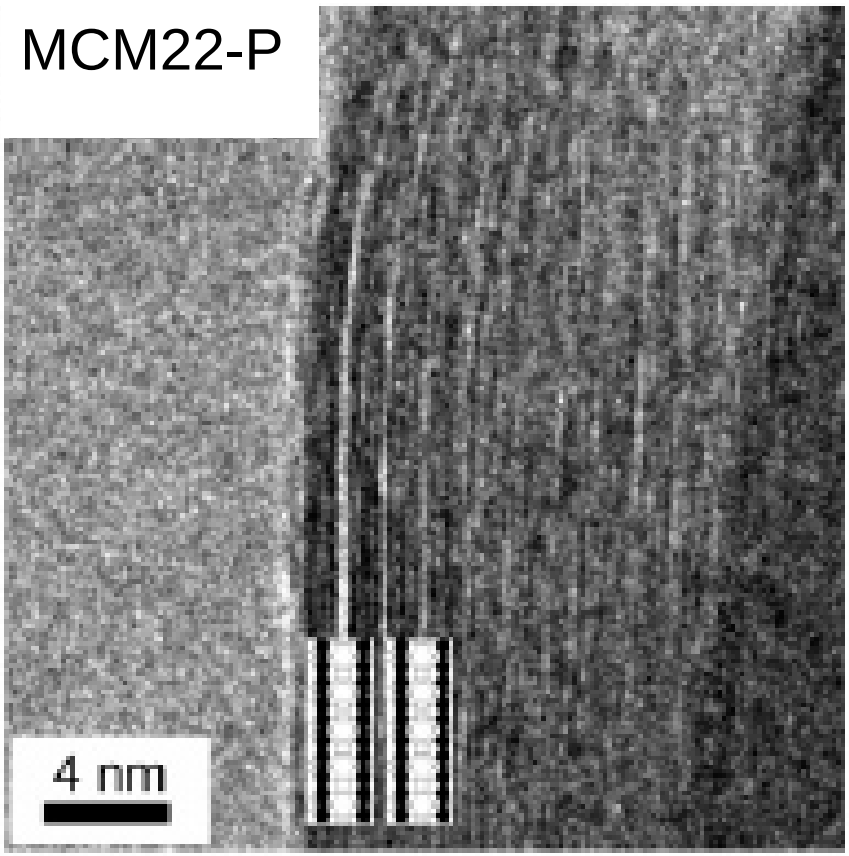
Repeated washing with water to remove weakly associated surfactant

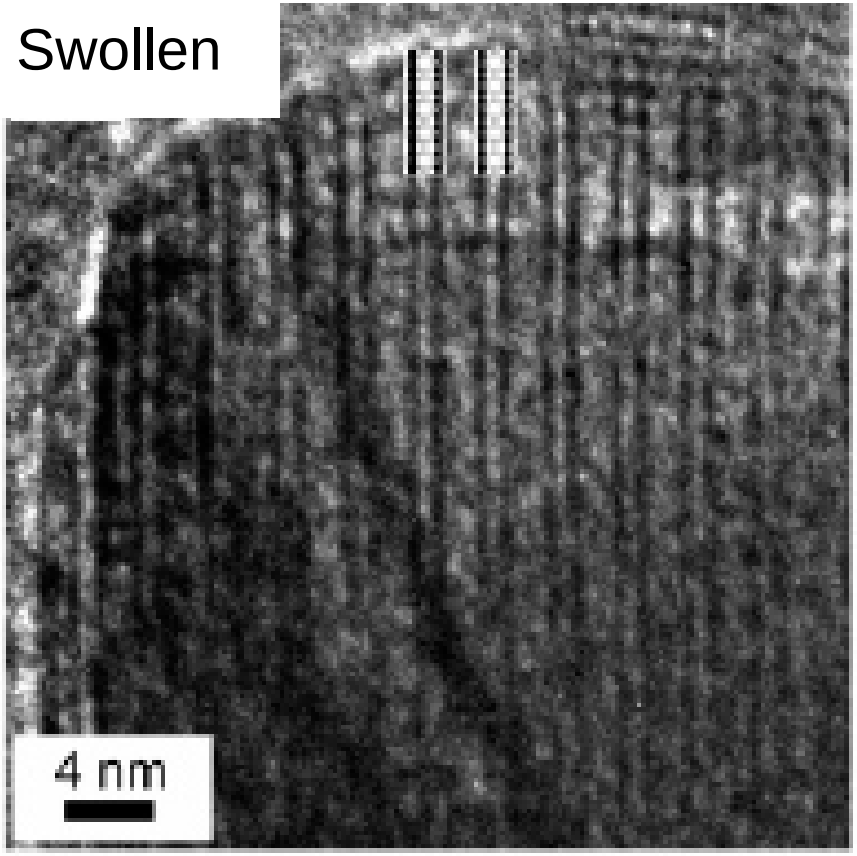


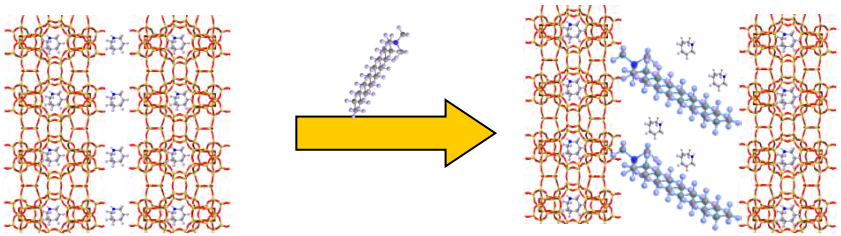
Swollen Structure

Swelling MCM-22 at RT

Swelling without structural degradation

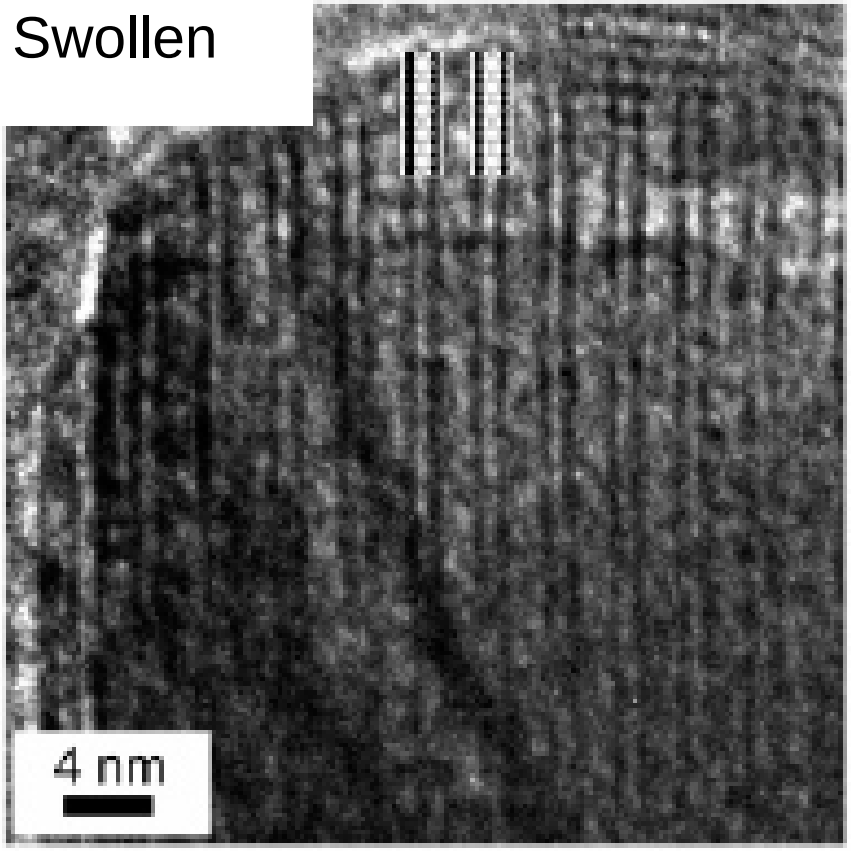


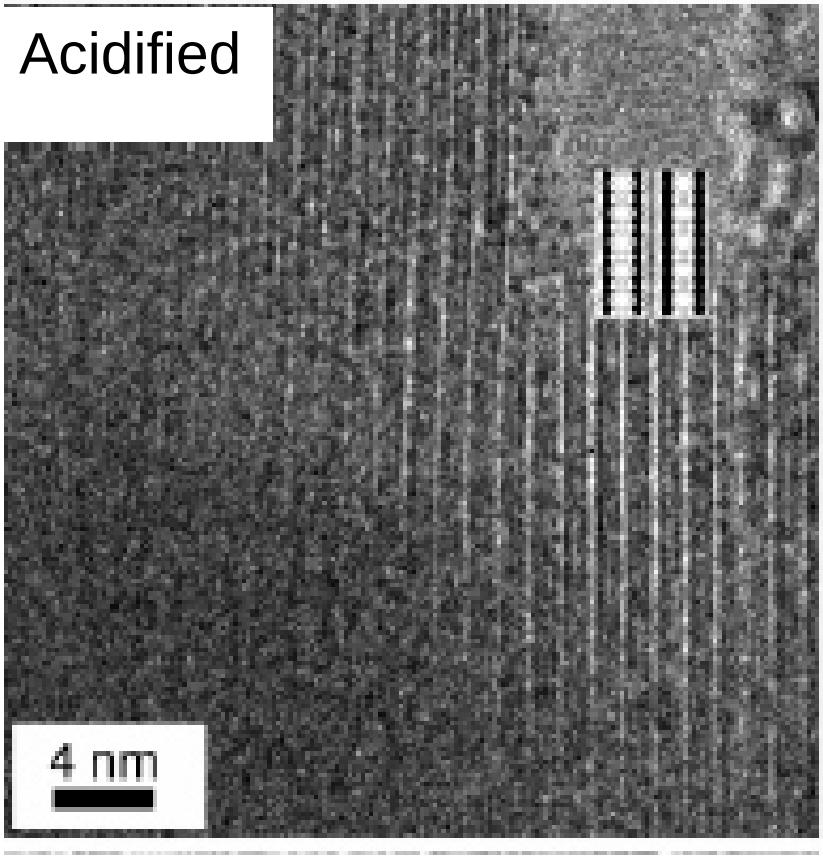


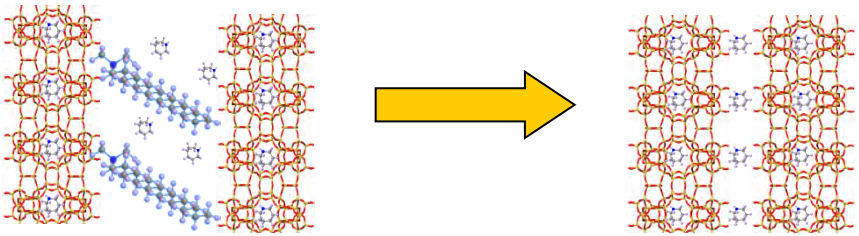


Deswelling by acidification

Reversibility of swelling to give back starting material !!



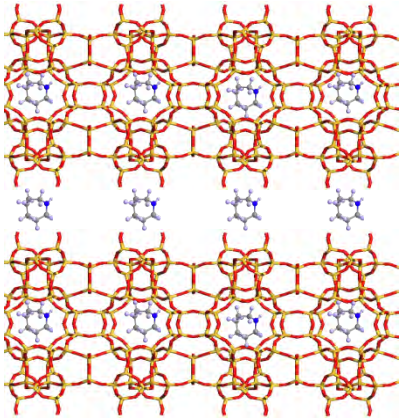




Combining XRD, TGA and TEM

*Maheshwari et. al., JACS, **2008**, 230, p1507*

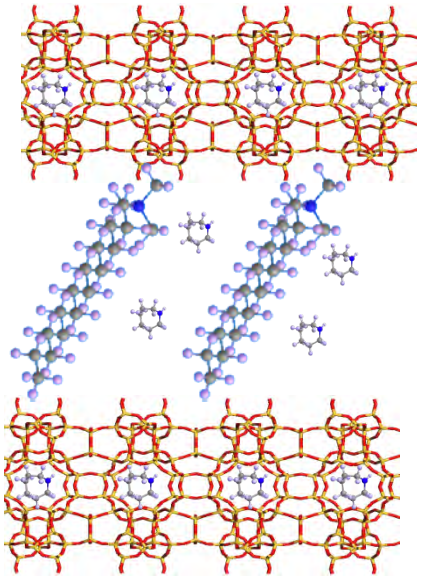
XRD, TEM and TGA results are consistent with the following picture:



MCM-22(P)

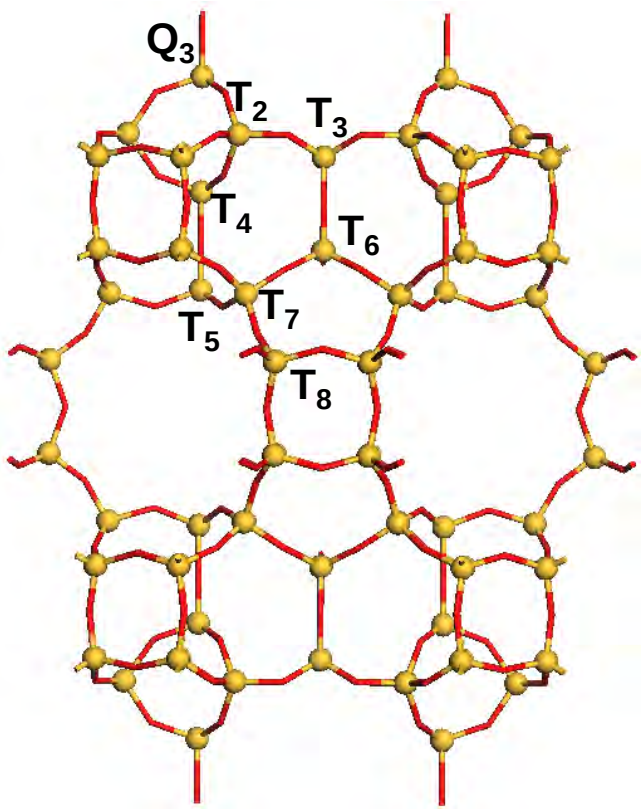
Swelling

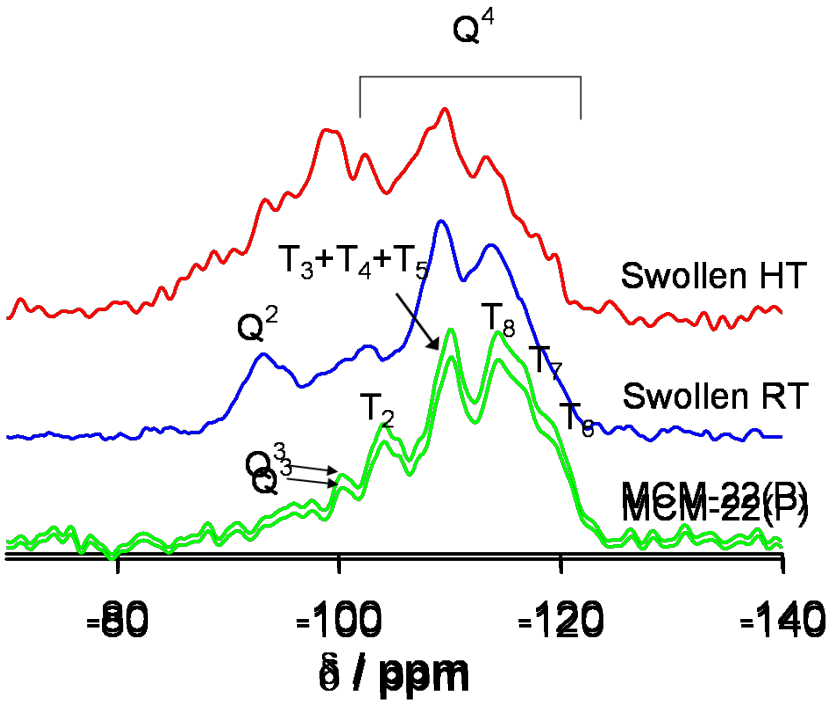
Acidification



Swollen Structure

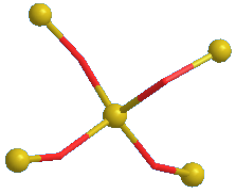
Local environment investigation by Si NMR



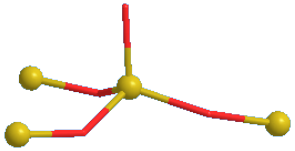


^{29}Si MAS NMR

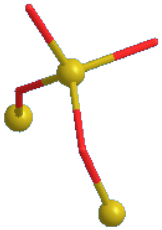
Q^4

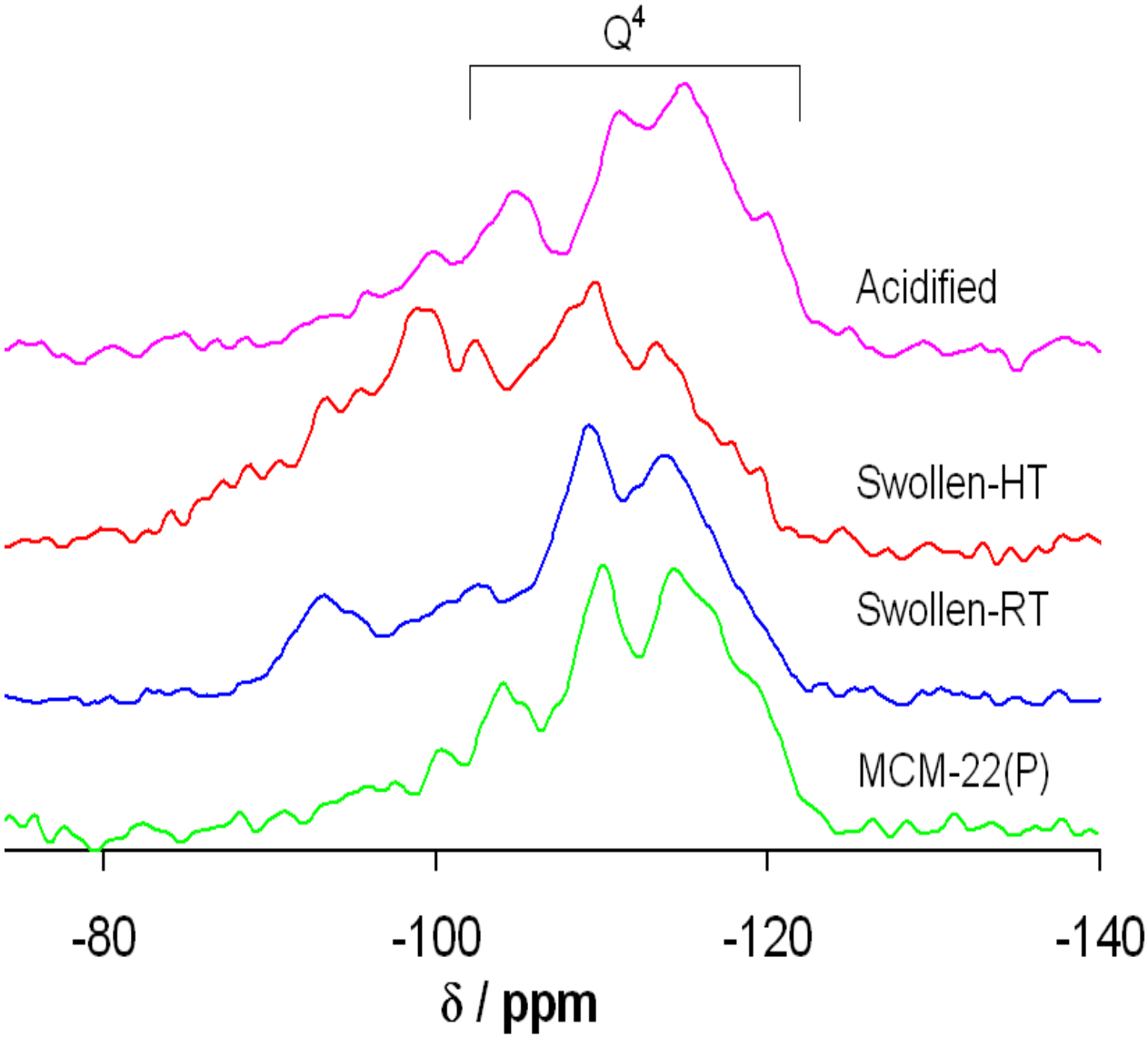


Q^3

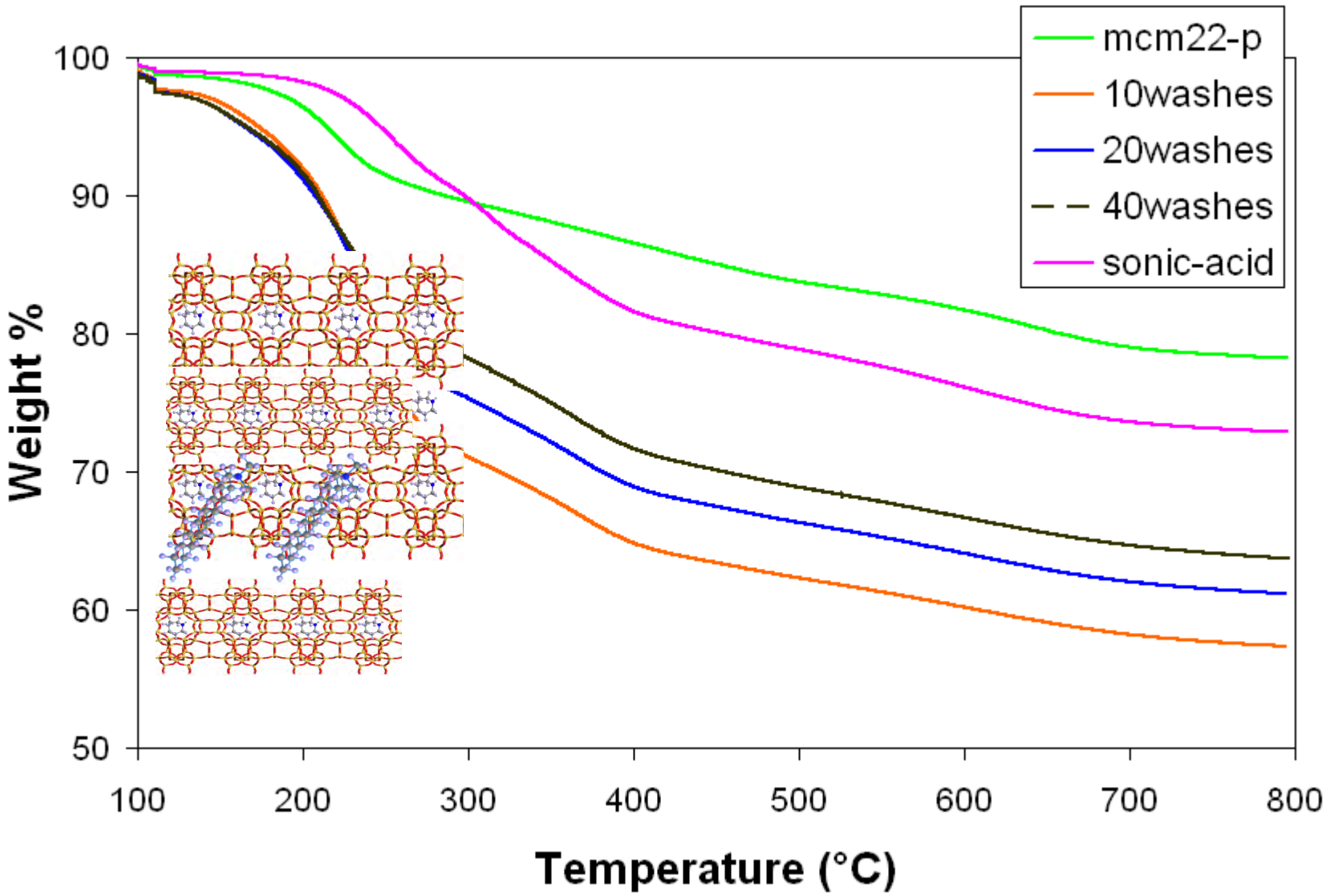


Q^2

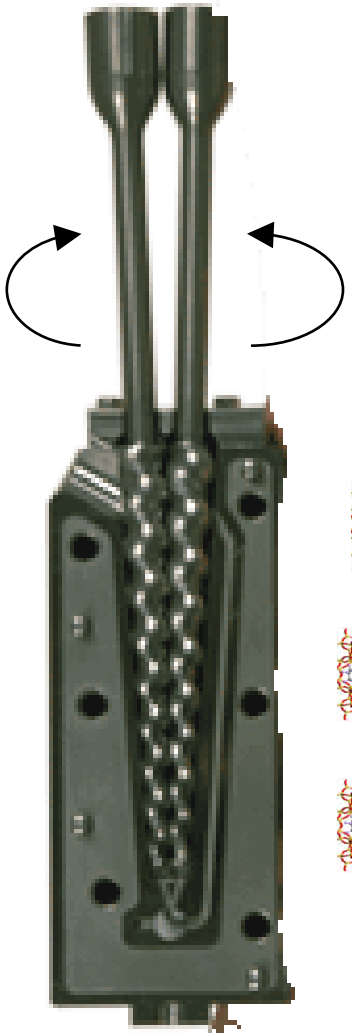



Q4
Acidified
Swollen-HT
Swollen-RT
MCM-22(P)
-80
-100
-120
-140
δ / ppm

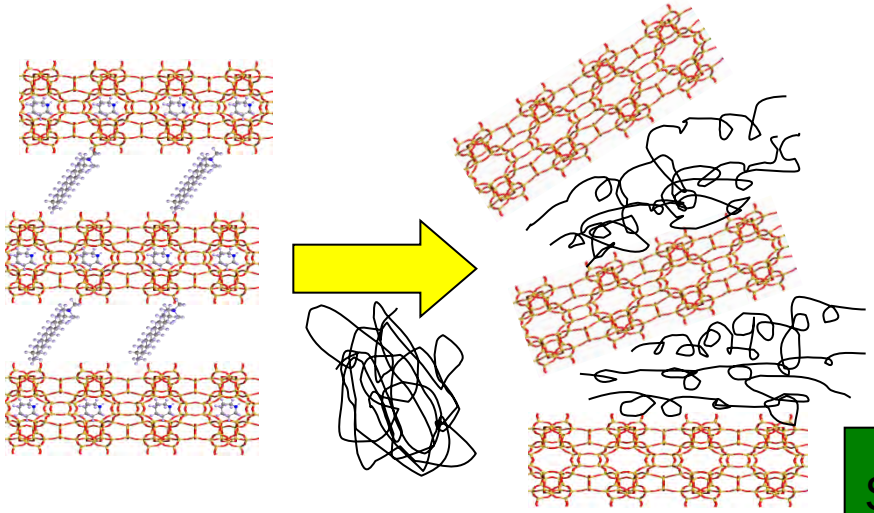
TGA to investigate effect of washing and acidification



Polystyrene nanocomposite by melt compounding



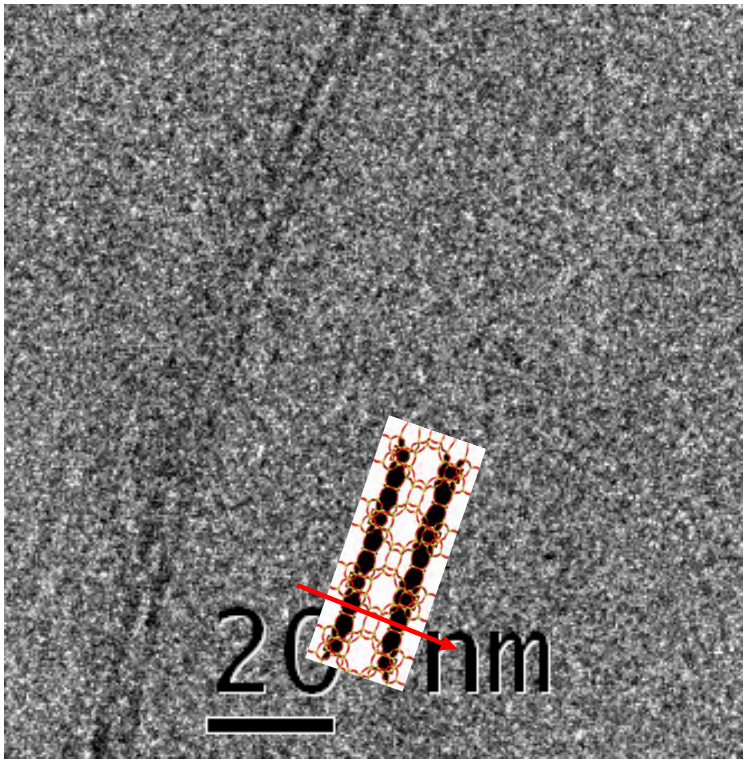
- Mixing of molten polymer and swollen zeolite layers
- Separation of layers by combined effect of shear forces and polymer diffusion between the layers

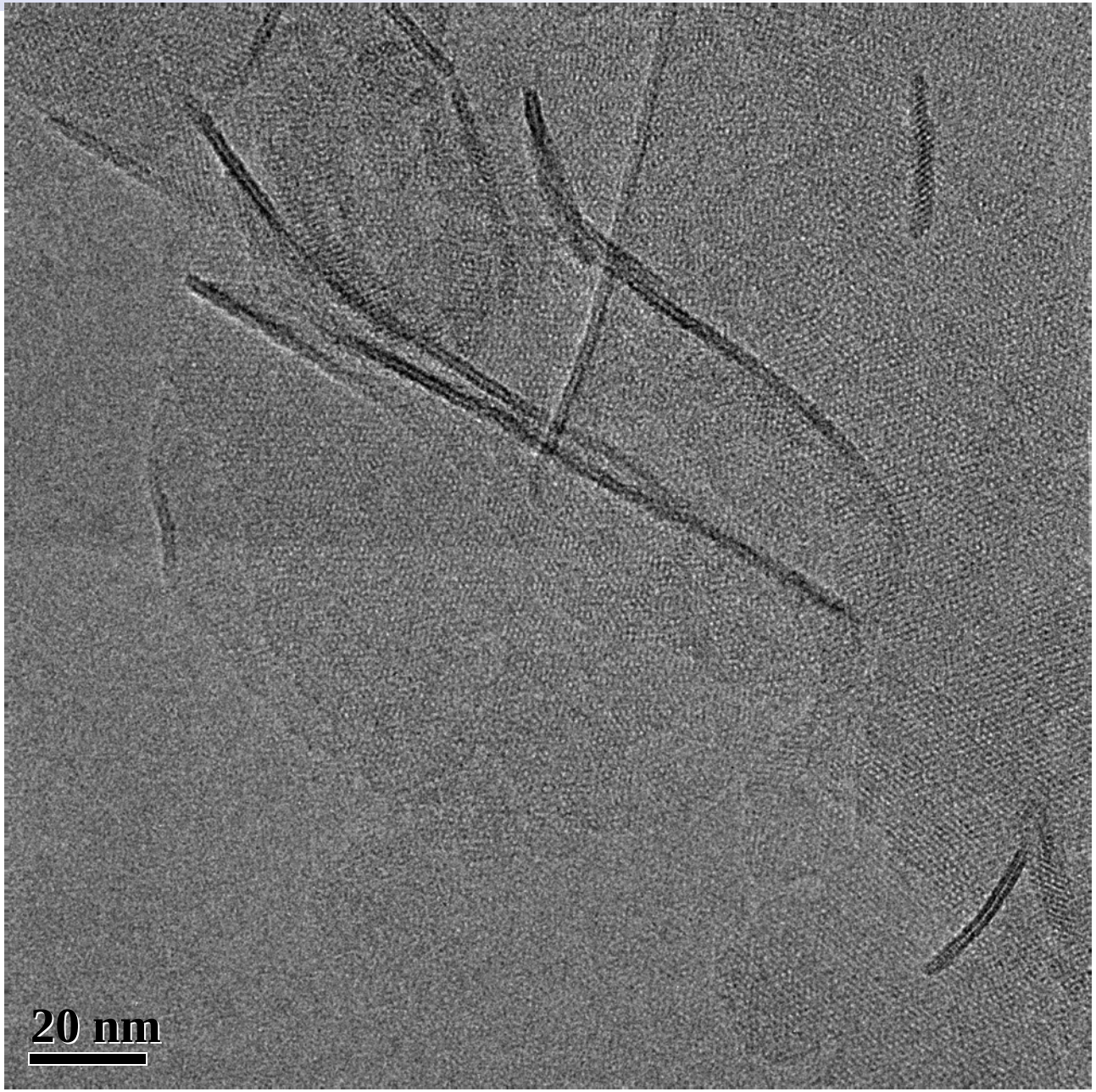


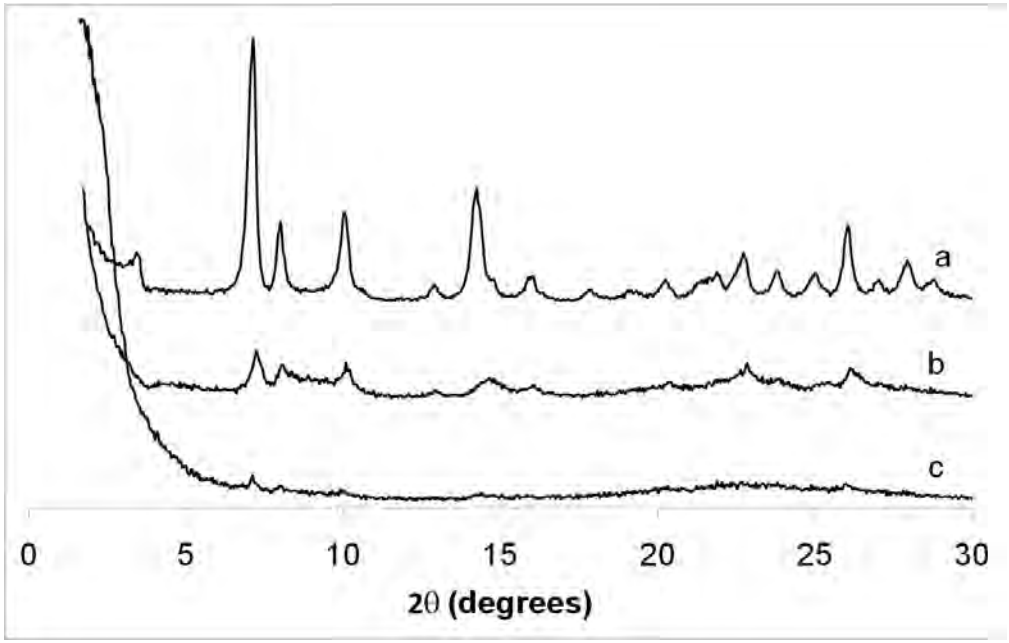
Polystyrene (Mn 45000)
+
Swollen MCM-22(P) powder

Sample extruded from a circular die

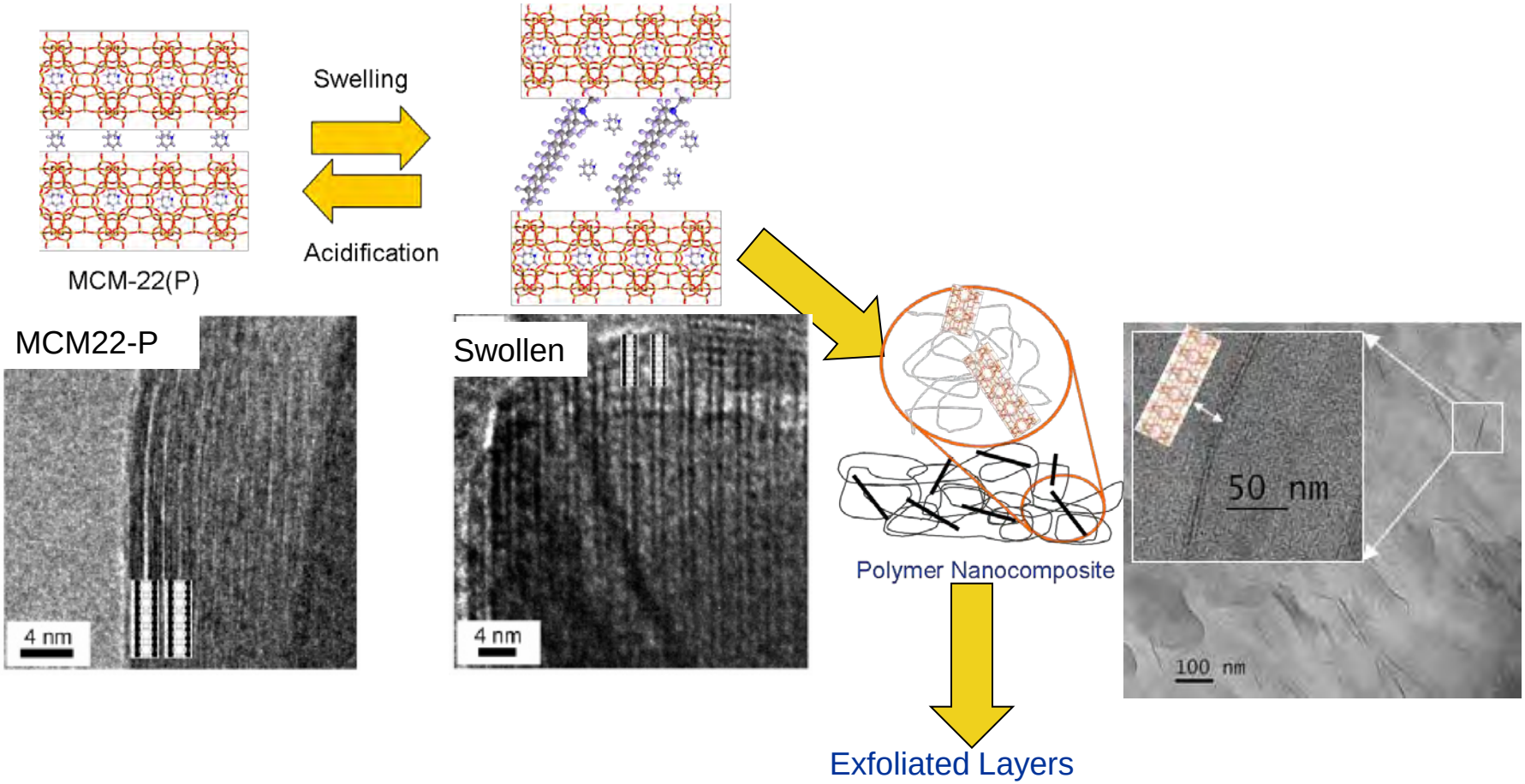
Preservation of pore structure of layers after exfoliation

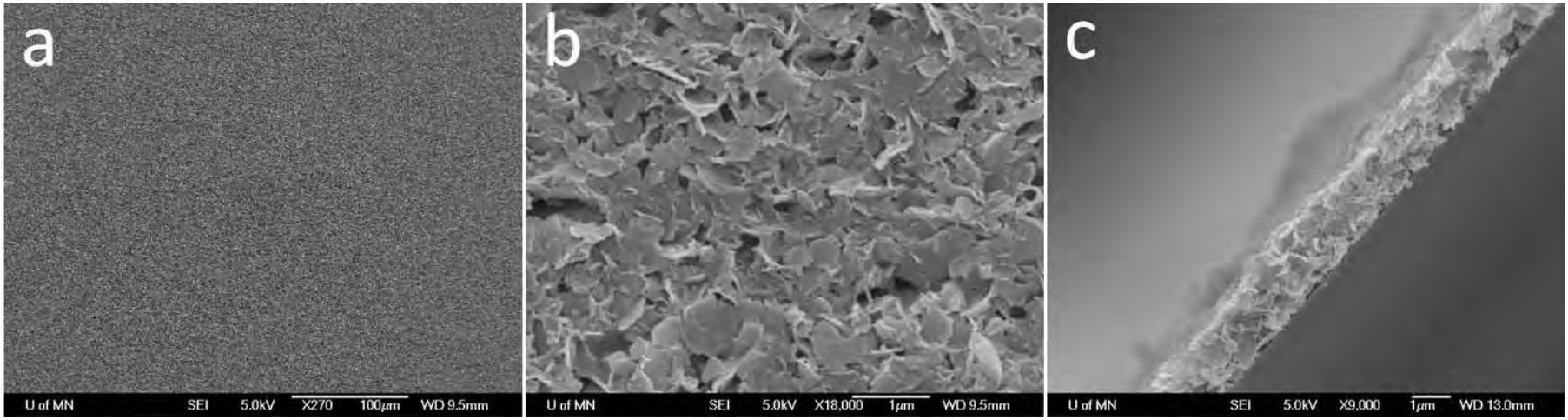



20 nm



XRD patterns of
a) MCM-22
b) Exfoliated nanosheets
c) ITQ-2


Swelling
Acidification
MCM-22(P)
MCM22-P
4 nm
Swollen
4 nm
Polymer Nanocomposite
50 nm
100 nm
Exfoliated Layers


a
U of MN SEI 5.0kV X270 100μm WD 9.5mm
b
U of MN SEI 5.0kV X18,000 1μm WD 9.5mm
c
U of MN SEI 5.0kV X9,000 1μm WD 13.0mm

- **We now have expertise in procedures that allow us to prepare high aspect ratio intact single layers in pure powder form. This is a breakthrough in the area of exfoliated zeolites and an enabling discovery for the realization of the proposed concept.**

- Maheshwari, Sudeep; Jordan, Edgar; Kumar, Sandeep; Bates, Frank S.; Penn, R. Lee; Shantz, Daniel F.; Tsapatsis, Michael. **Layer Structure Preservation during Swelling, Pillaring, and Exfoliation of a Zeolite Precursor.** Journal of the American Chemical Society (2008), 130(4), 1507-1516
- Tsapatsis, Michael; Maheshwari, Sudeep; Bates, Frank S.; Koros, William J. **Layered zeolite materials and methods related thereto.** PCT Int. Appl. (2009), 58pp. CODEN: PIXXD2 WO 2009108166 A2 20090903

Task 1. Synthesis of exfoliated MCM-22 layers and optimization of the process

Subtask 1.1. Synthesis of siliceous MCM-22(P)

Subtask 1.2. Swelling of MCM-22(P) with structure preservation

Subtask 1.3. Melt compounding optimization for high exfoliation yield

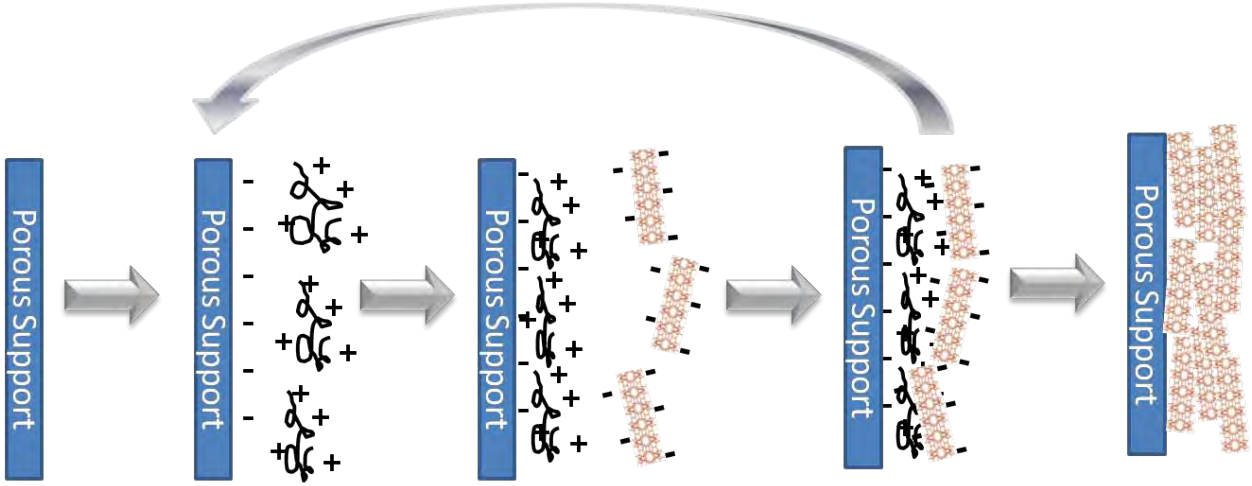
Subtask 1.4. Polymer removal and recovery of exfoliated MCM-22 layers

Task 2. Preparation of layer-by-layer coatings of the exfoliated MCM-22 layers

Subtask 2.1. Dispersion of MCM-22 exfoliated layers in water and alcohol

Subtask 2.2. Layer-by-layer coating process optimization

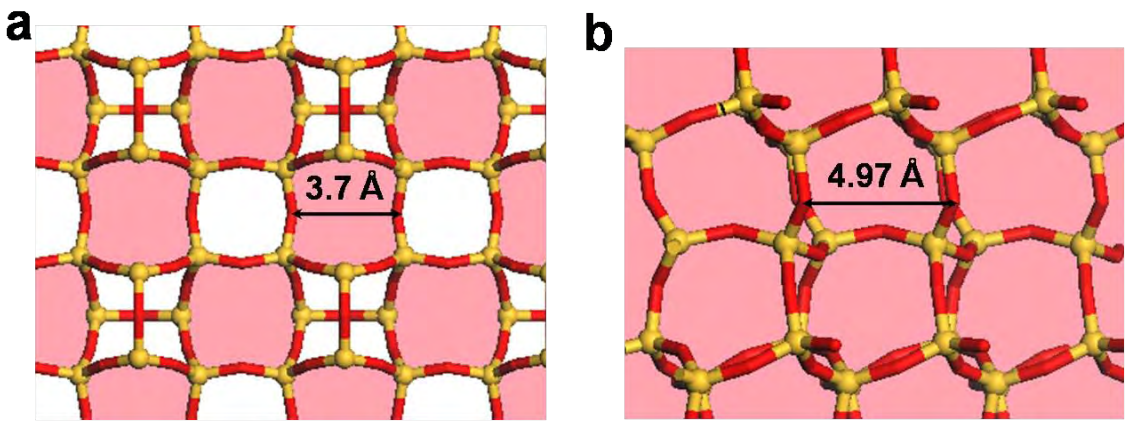
Subtask 2.3. Alternative deposition processes (if needed)



Layer by layer assembly to make a multilayered coating on a support surface.
In case of polyion-inorganic coating, polyions can be eliminated in the final step by calcination at high temperature.

- Task 3. Determination of membrane separation performance
- Subtask 3.1. Membrane screening tests on flat alumina supports up to 220°C
- Subtask 3.2. Tubular membrane testing using single gases up to 600°C
- Subtask 3.3. Tubular membrane testing using simulated feeds up to 600°C
- Subtask 3.4. High temperature, high pressure testing of tubular supports

- Task 4. Determination of membrane stability in a water gas shift environment
- Subtask 4.1. Stability tests in steam containing simulated feeds for exfoliated powders
- Subtask 4.2. Stability tests in steam containing simulated feeds for alumina supported films
- Subtask 4.3. Stability tests in steam containing simulated feeds for stainless steel supported films



Schematic of the layer structure of the siliceous layered zeolite precursors a) RUB-18 and b) NU-6(1). Both, like MCM-22(P), contain 6MR transport limiting apertures. However, the SiO_4 tetrahedra connectivity and the openings of the 6MR are different (see representative oxygen center to oxygen center distances depicted in the figure and compare with the corresponding 0.5nm distance in the 6MR of MCM-22 layers). Si atoms are yellow, O atoms are red. 6MR are highlighted by pink color.

Task 5. Evaluation of the other layered materials RUB-18 and NU-6(1)

Subtask 5.1. Synthesis, swelling and exfoliation

Subtask 5.2. Stability tests in water gas shift environment for powders

Subtask 5.3. Layer-by-layer coatings

Subtask 5.4. Membrane separation performance in simulated dry feeds

Subtask 5.5. Stability tests in water gas shift environment for films

Task 6. Modeling, simulation and techno-economic evaluation

Subtask 6.1. Membrane reactor modeling

Subtask 6.2. Integration of membrane reactor model in IGCC process

Subtask 6.3. Techno-economic analysis and optimization

Subtask 6.4. Operability and control analysis

6.1 – Reactor Modeling

Goal: correlate reactor performance and membrane performance as function of operating conditions (T,P, feed conditions)

Desired conversion and % recovery →membrane surface → reactor cost

Optimization of reactor design

1-D plug flow model (initially)

2-D steady state model (later)

Isothermal (at mean T) vs. non-isothermal

Different flow configurations

Effect of reactor design on reactor performance

6.2 - Integration of reactor in IGCC process

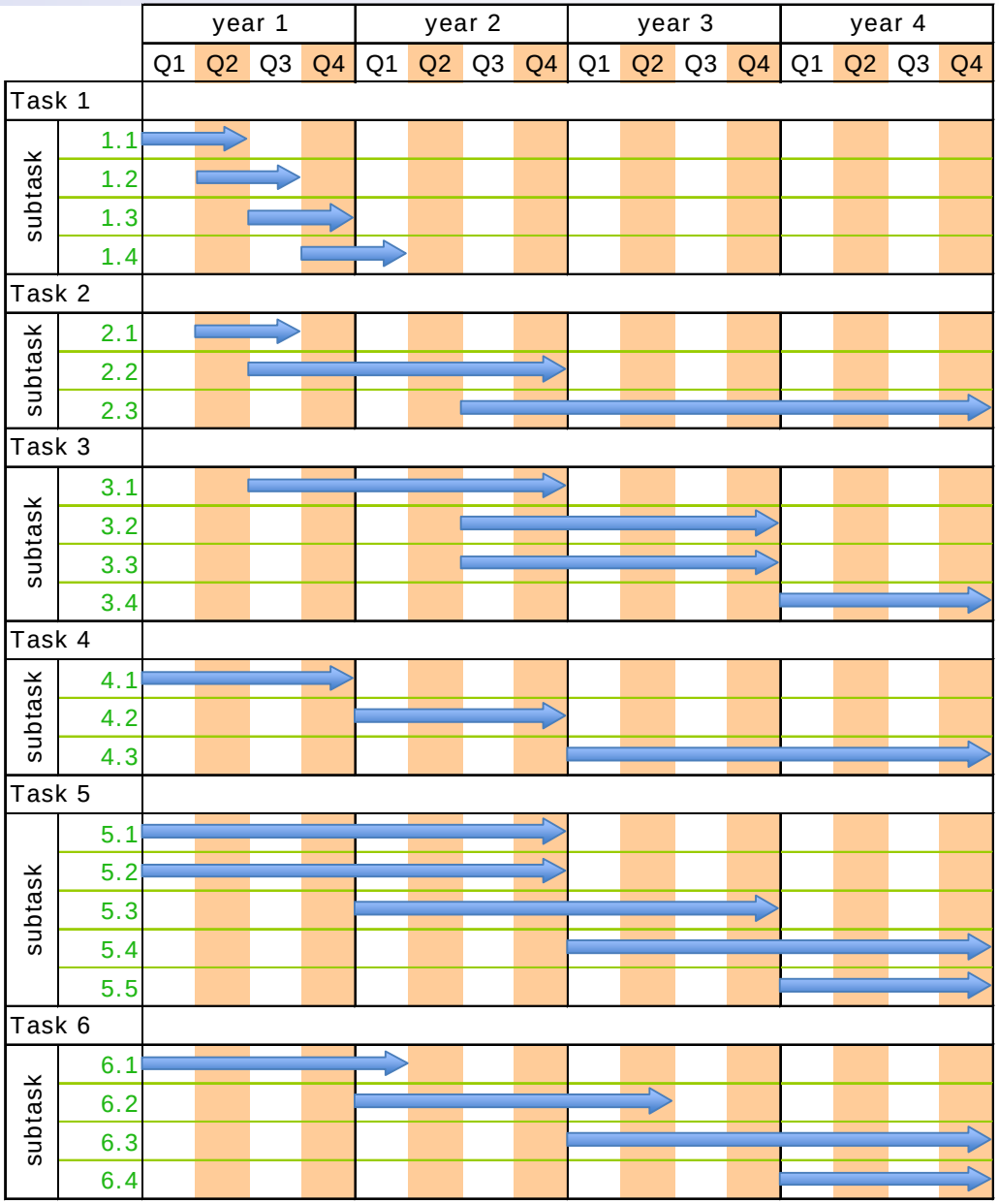
- **Reactor boundary conditions, size: consistent with IGCC process specifications**
- **Step 1: Systems level model of entire process (gasifier, membrane reactor, heat exchangers, air separation, turbines) in MATLAB**
- **Assumptions: few basic components, lumped compartments in gasifier/turbines, static heat exchanger models, etc.**
- **Benchmarking of overall steady state performance figures/targets**
- **Step 2: Incorporate membrane model in ASPEN simulation of IGCC**

6.3 – Technoeconomic analysis and optimization

- **Optimization of process conditions to achieve desired carbon recovery and electricity demand**
- **Energetic and economic evaluation**
- **Heat integration alternatives and impact**
- **Preliminary optimization using MATLAB model**
- **Optimization using detailed ASPEN model**
- **Comparison with conventional options (additional reactor cost vs. cost of downstream separations)**

6.4 – Operability and control analysis

- **Use of systems level transient model to assess operability of IGCC process**
- **Study effect of integration on controllability**
- **Develop control strategies for the membrane reactor and the entire integrated process**
- **Evaluate performance for changes in power demand, feed conditions, membrane characteristics etc.**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