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University of Minnesota

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

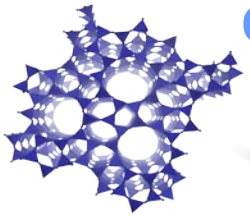
Tsapatsis' Group at the University of Minnesota

July 2010

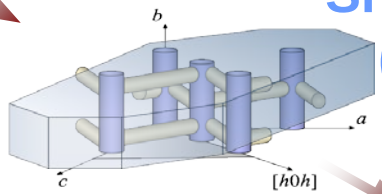
Materials for Separations and Catalysis

Motivation: Hierarchical manufacturing of zeolite films

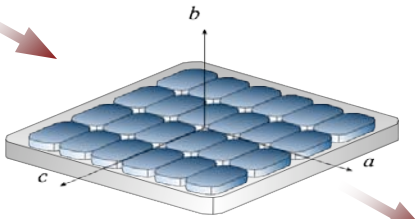
For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. **2007**, *46*, 7560–7573



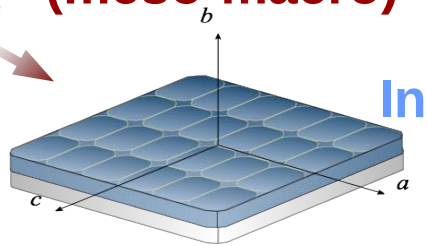
Crystal Structure (nm)



Shaped Crystal (10-100nm)



Oriented Monolayer of Crystals (meso-macro)



Intergrown Film

AIChE Journal, 42(11), 3020-3029 (1996)

Chemistry of Materials 10, 2497-2504 (1998)

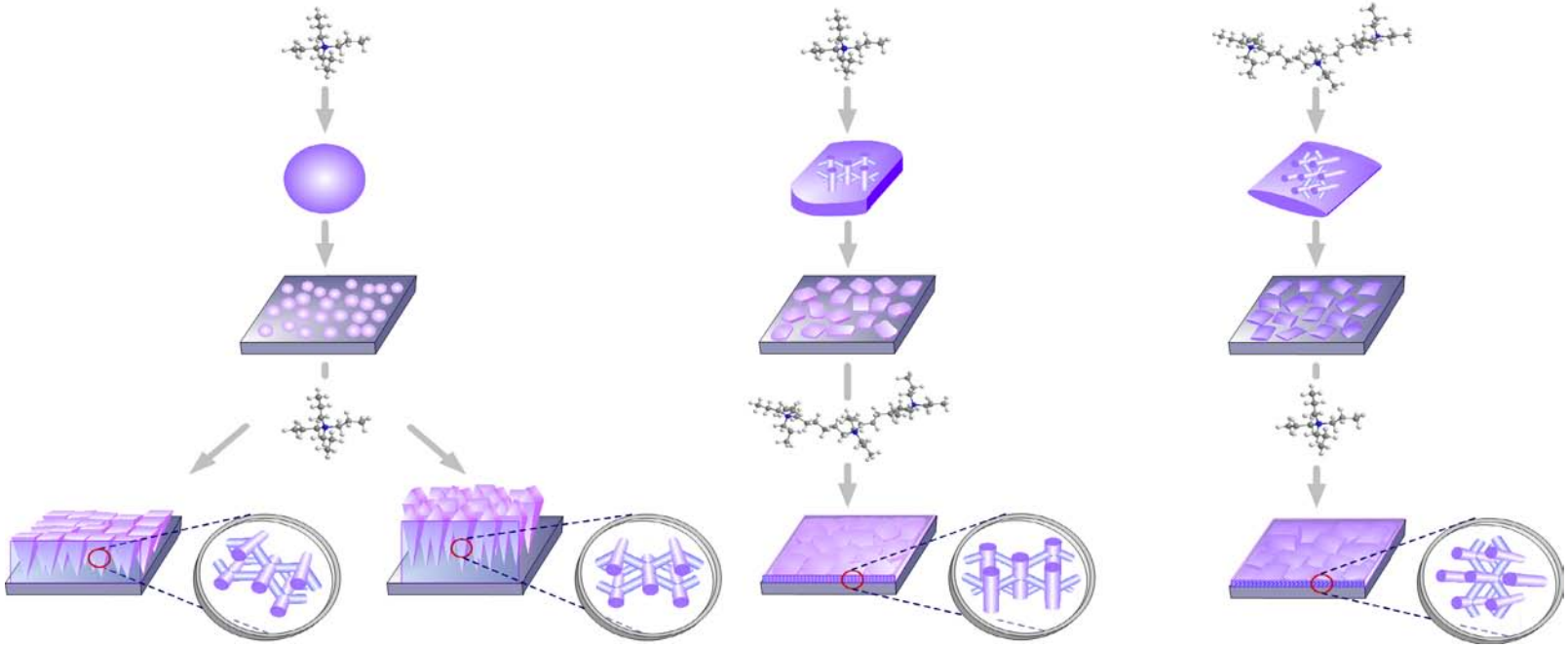
Science 300:(5618), 456-460 (2003)

Angew. Chem. Int. Ed. 45, 1154-1158 (2006)

Nature Materials, 7(12), 984-991(2008)

Science 325 (5940), 590-594 (2009)

Seeded Growth Approach

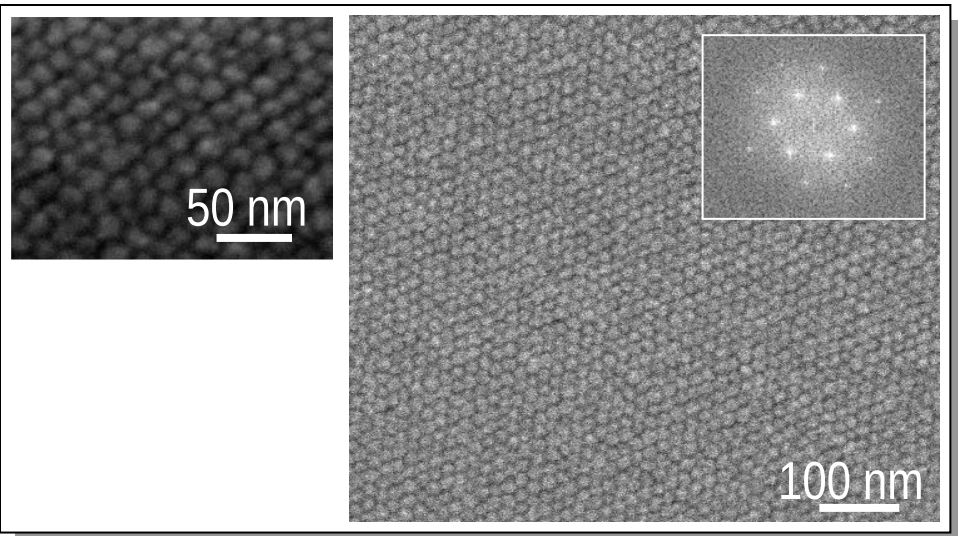


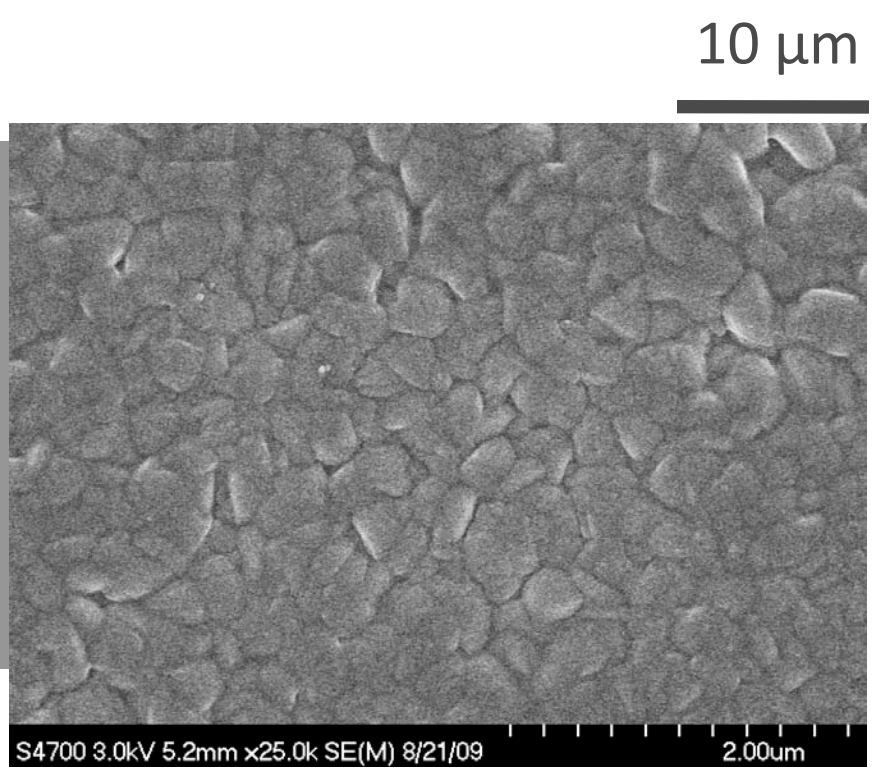
Chemistry of Materials 10, 2497-2504 (1998)

Science 300:(5618), 456-460 (2003)

Angew. Chem. Int. Ed. 45, 1154-1158 (2006)

Example: Nanoparticle films as seeds for zeolite membranes





Angew. Chem. Int. Ed. In Press (2010) *High Performance Randomly Oriented Zeolite Membranes Using Brittle Seeds and Rapid Thermal Processing*

Problems: **High Cost, Scale up not demonstrated, grain boundary defects**

Membranes with flakes for Separation Processes

Journal of Membrane Science, 52 (1990) 275–288
Elsevier Science Publishers B.V., Amsterdam

MEMBRANES CONTAINING SELECTIVE FLAKES*

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Summary

Polymer membranes containing selectively permeable flakes will show selective fluxes. If the flakes are highly selective, the relative fluxes will be proportional to the square root of the inherent selectivity. If the flakes are modestly selective, the relative fluxes may approach this more modest value. Achieving this selectivity requires carefully adjusting the diffusion coefficient in the polymer continuum to the geometric average of the diffusion coefficients in flakes times the aspect ratio of the flakes. These results are compared with other theories of composite membranes.

Introduction

Membranes containing impermeable flakes show much lower permeabilities than membranes without such flakes. For example, a polycarbonate film containing twenty percent mica flakes shows a steady state carbon dioxide flux one hundred times less than that across a pure polycarbonate film of equal thickness [1]. The lag time to reach this steady state is eighty times longer than that for the film without flakes [2]. As a result, flake-filled membranes are candidates for a variety of packaging materials.

In studies of such materials, I have wondered about a membrane with selectively permeable flakes. Such a membrane could be used to separate chemical mixtures even when the flake materials were difficult to fabricate as membranes. For example, zeolite 5A adsorbs linear alkanes but largely rejects branched alkanes [3]. A membrane containing flakes of zeolite 5A might be substantially more permeable to linear alkanes than to branched alkanes. The resulting flake-filled composite might be more effective than a flawed membrane of zeolite alone [4].

In this paper, I estimate the properties expected for such flake-filled membranes. In so doing, I build on earlier studies of membranes with impermeable flakes [1,2]. These earlier studies made substantial approximations which were

*Paper presented at the Third Ravello Symposium on Advanced Membrane Science and Technology, Ravello, Italy, October 2–7, 1988.

0376-7388/90/$03.50 © 1990 — Elsevier Science Publishers B.V.

justified by later experiments. I will use these approximations again in the analysis presented here. The results show what successes and what limitations we can expect from membranes with selective flakes.

Theory

Past models of flake-filled membranes have idealized the flakes as regularly spaced bricks, like those shown in Fig. 1 [1,5–7]. Such an idealization involves three implicit assumptions. The first, that the flakes exist within regular lamellae, has not been completely investigated and is probably the most severe [8,9]. The second, that the flakes are regularly spaced, is probably not serious, for analyses based on random flakes give equivalent results [1]. The third, that the flakes are very long, is not that serious either, because diffusion will always select the shortest route around the flakes, and hence be less influenced by the flakes' longer dimensions.

We begin our analysis by approximating the membrane filled with semipermeable flakes in a similar way. We idealize the membrane as lamellae. Each lamella contains two layers: one of polymer and one containing polymer and flakes. Diffusion first occurs through the layer of only polymer. It then occurs

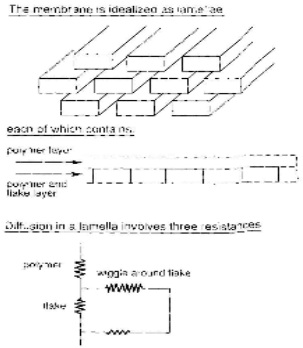
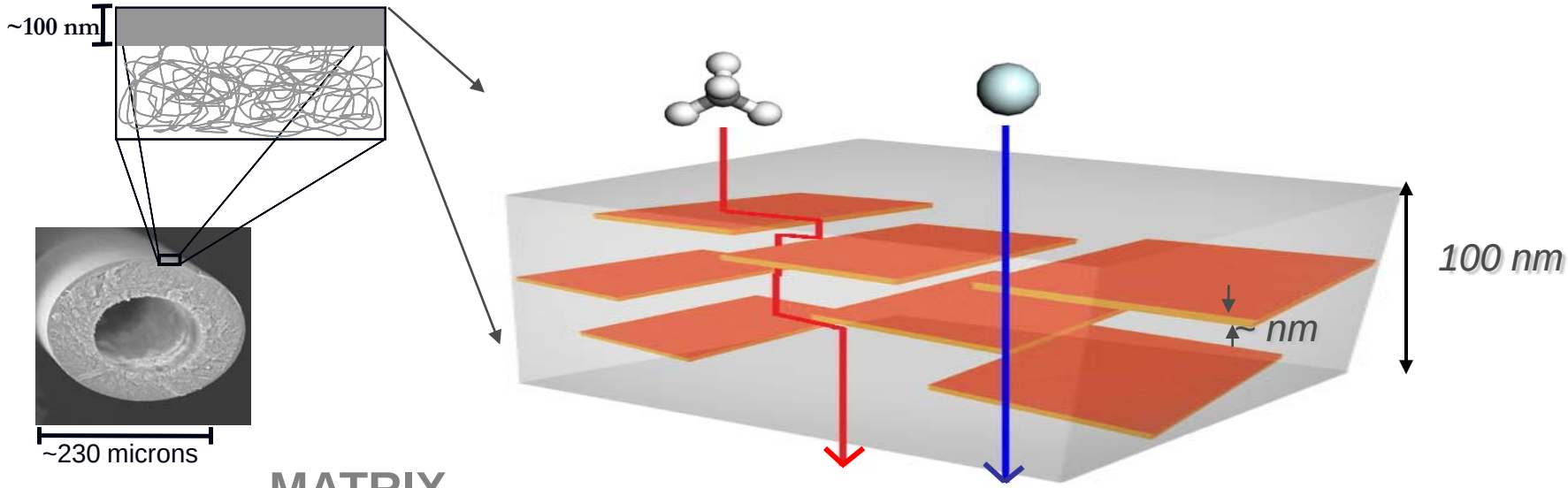


Fig. 1. Idealization of the membrane. These approximations echo those for membranes with impermeable flakes.

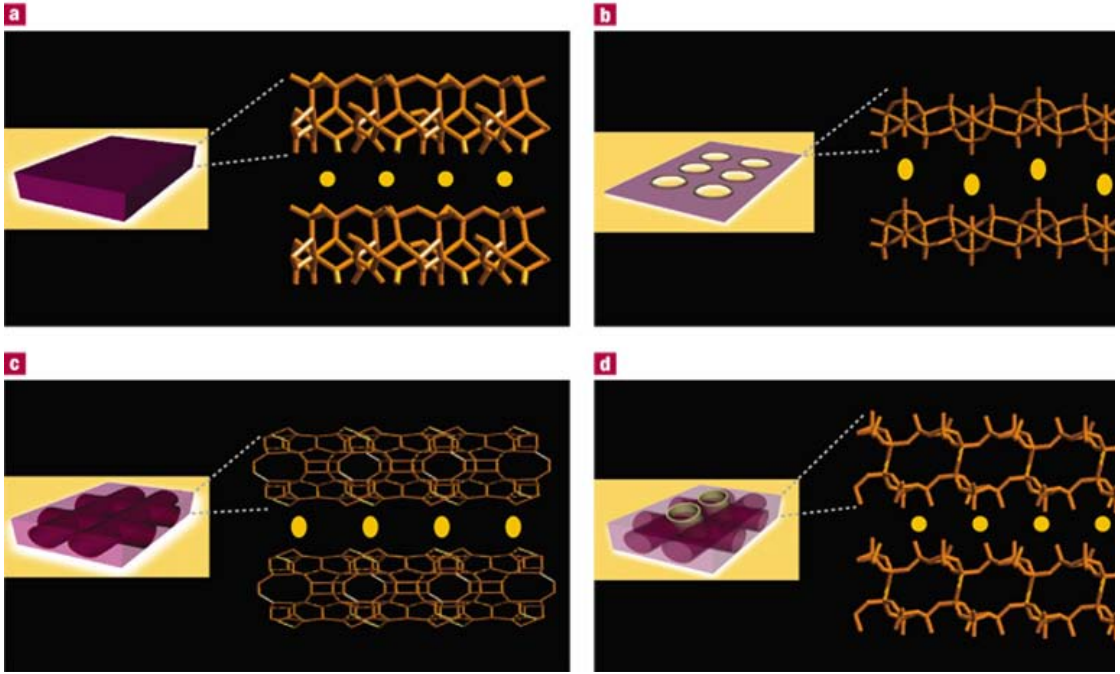
Films of Anisotropic Porous Particles (Selective Flakes)



MATRIX
processability

NANOPOROUS LAYERS
molecular sieving

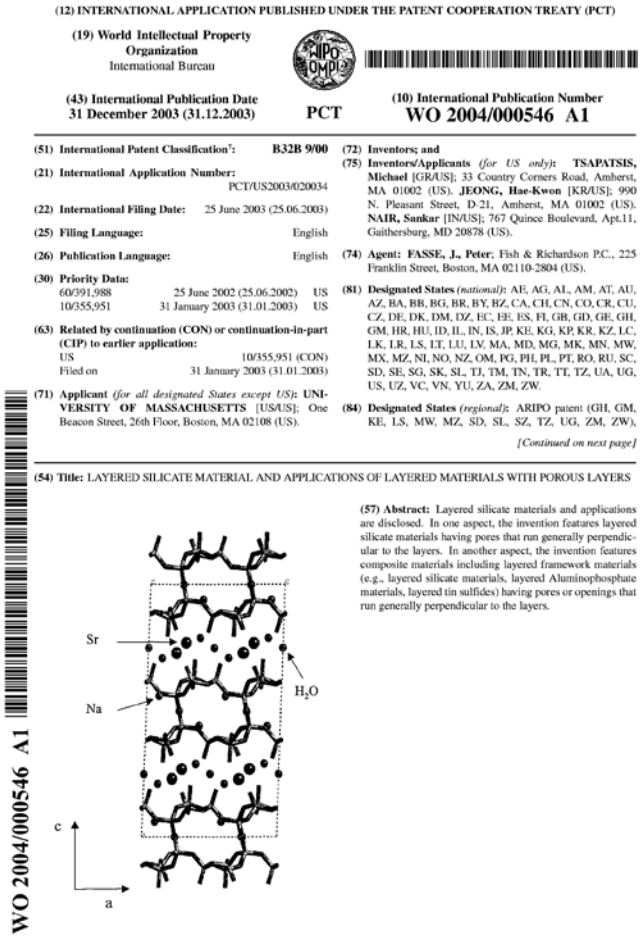
Layered Precursors to Zeolites as Selective Flakes



AlPO: Gao et al., **J. Solid State Chem** 129, 37 (1997)

MCM-22: Corma et al., **Nature** 396, 353-356 (1998)
Leonowicz et al.**Science** 264, 1910-1913 (1994)

AMH-3: Jeong et al., **Nature Materials** 2:(1), 53-58 (2003)



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(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

[Continued on next page]

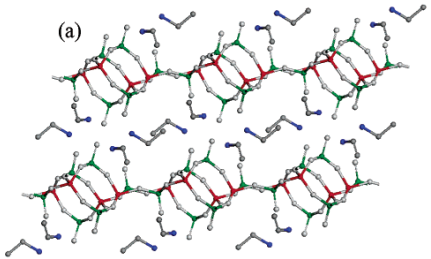
(54) Title: LAYERED SILICATE MATERIAL AND APPLICATIONS OF LAYERED MATERIALS WITH POROUS LAYERS

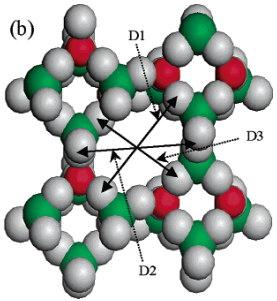
(57) Abstract: Layered silicate materials and applications are disclosed. In one aspect, the invention features layered silicate materials having pores that run generally perpendicular to the layers. In another aspect, the invention features composite materials including layered framework materials (e.g., layered silicate materials, layered Aluminophosphate materials, layered tin sulfides) having pores or openings that run generally perpendicular to the layers.

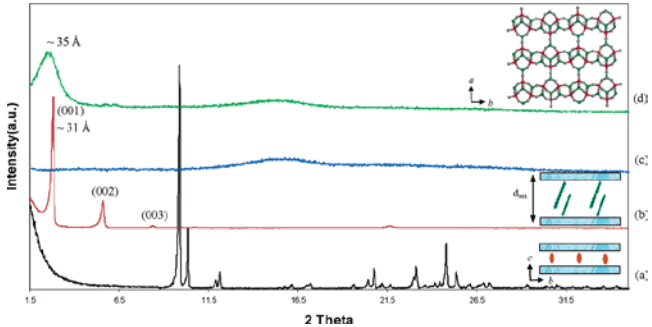
Sr
Na
H_2O
c
a

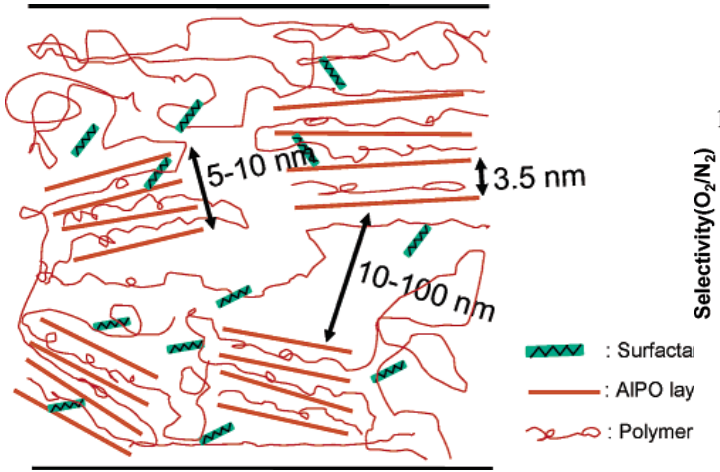
WO 2004/000546 A1

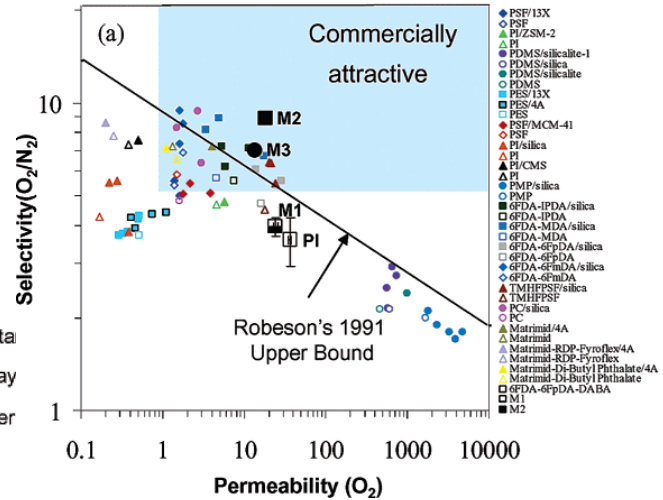
Early results using layered AlPOs *(Chem. Mater., Vol. 16, No. 20, 2004)*

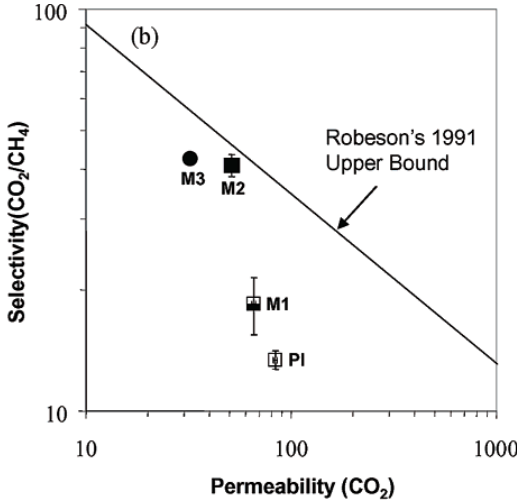






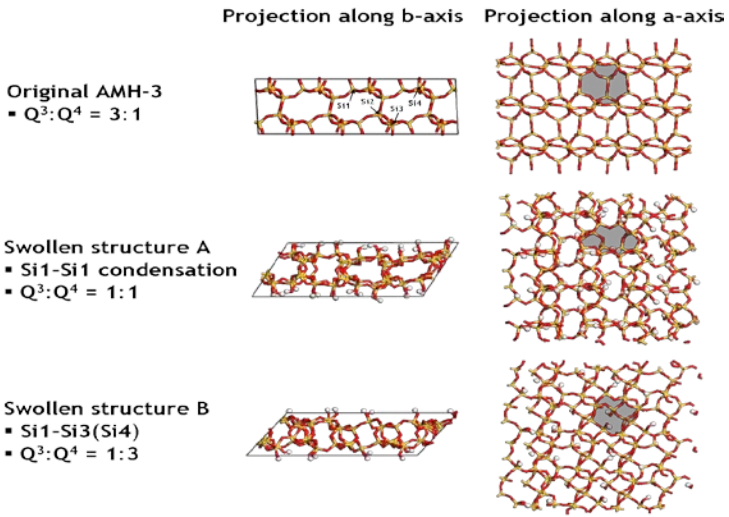


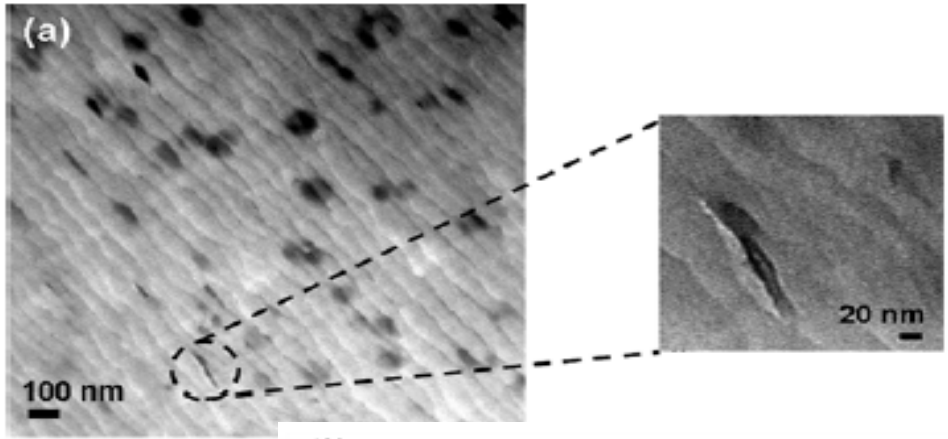


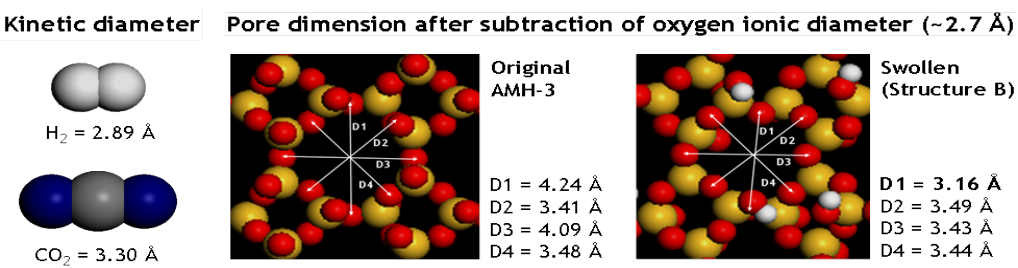


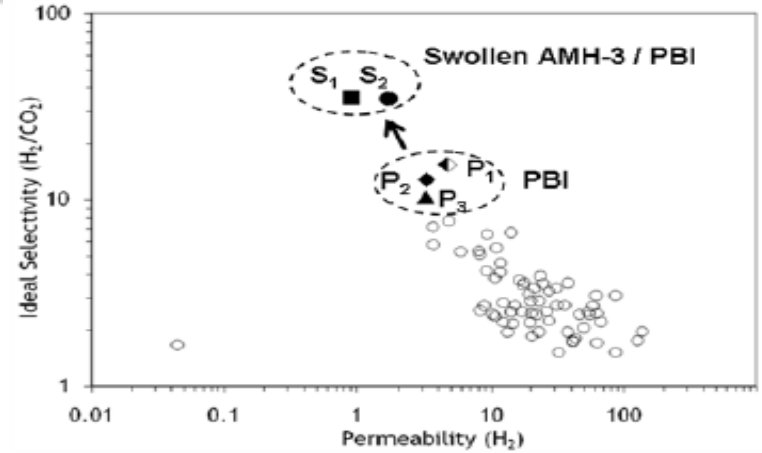
Layered structure not preserved; Exfoliation not achieved; However, Selectivity enhancement demonstrated for the first time

Swelling of AMH-3 *results in altered layer structure*





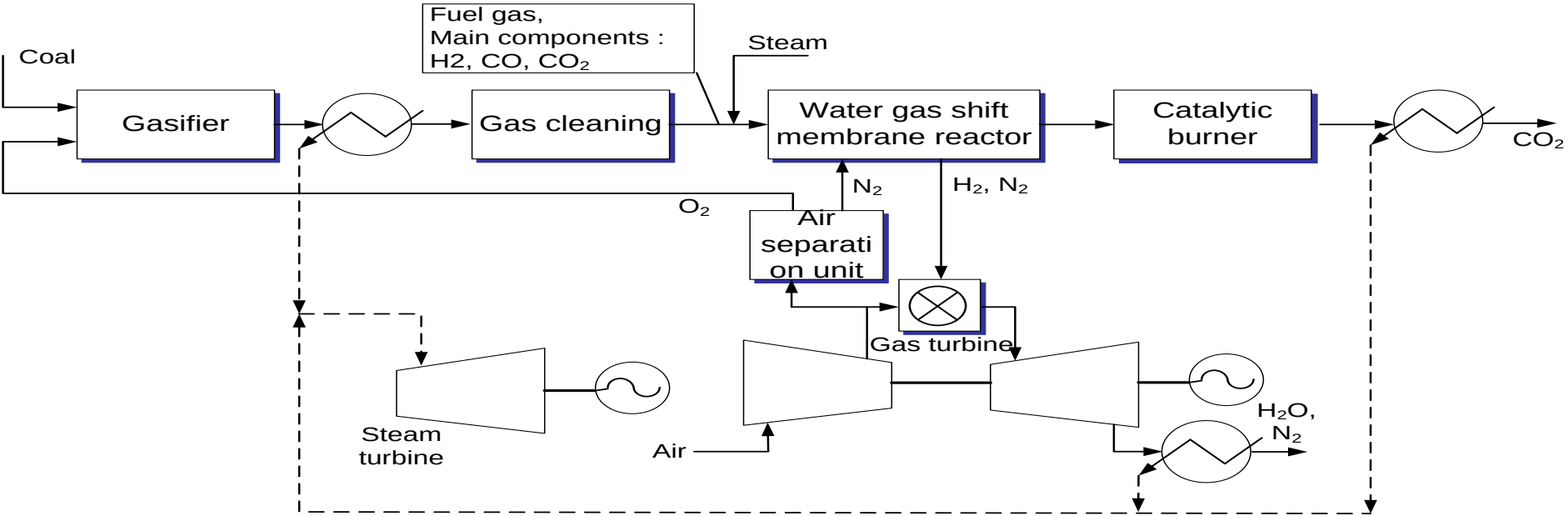




Selectivity enhancement demonstrated

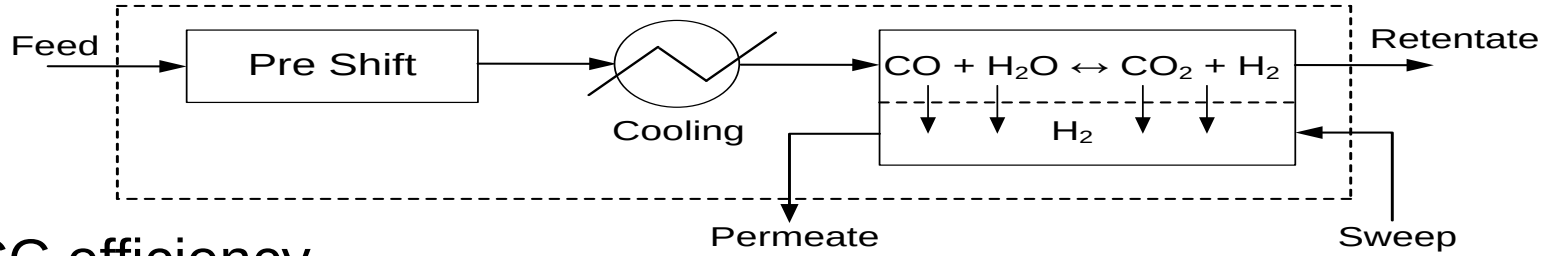
Angew. Chem. Int. Ed. 47(3), 552-555 (2008)

Example of Application: Hydrogen Selective Membranes



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

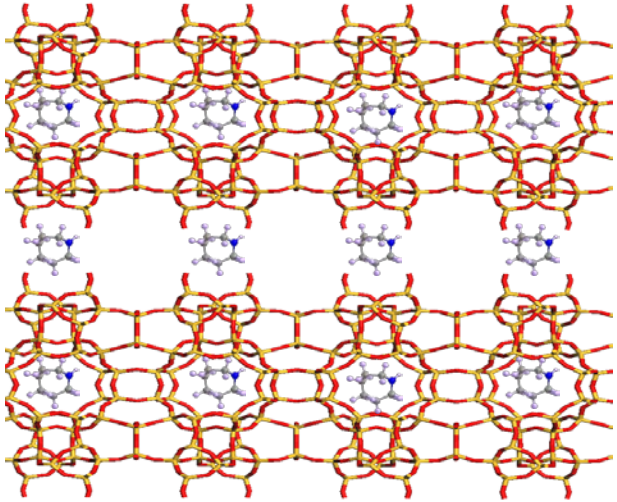
hydrogen/carbon dioxide selectivity = 15

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)

MWW Layers as hydrogen selective flakes

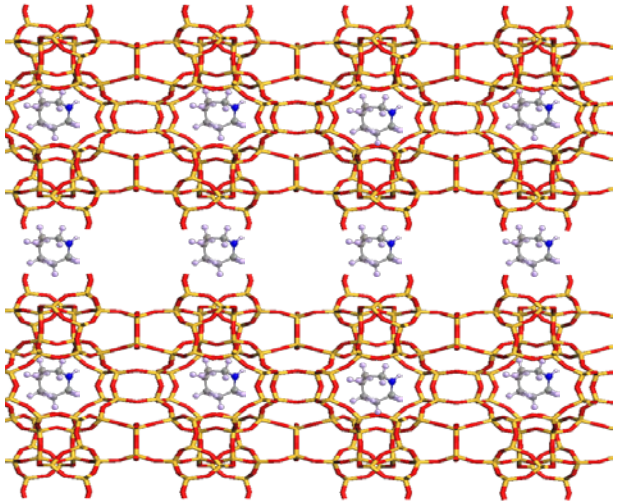


MCM-22(P)

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

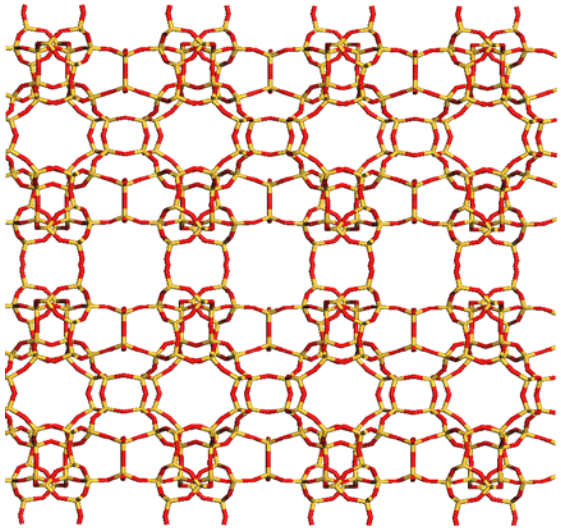
[1]*Rubin and Chu, US Patent 4954325,* ***1990***

MWW Layers as hydrogen selective flakes



MCM-22(P)

Calcination
540 °C

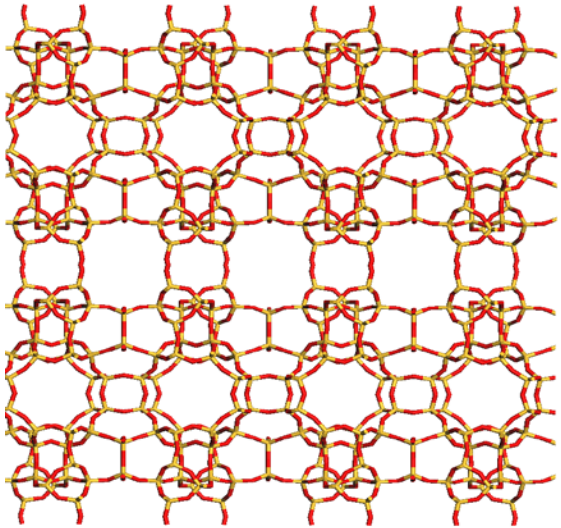


MCM-22

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

MWW Layers as hydrogen selective flakes

- High thermal stability
- Large sorption capacity
- Important for catalysis



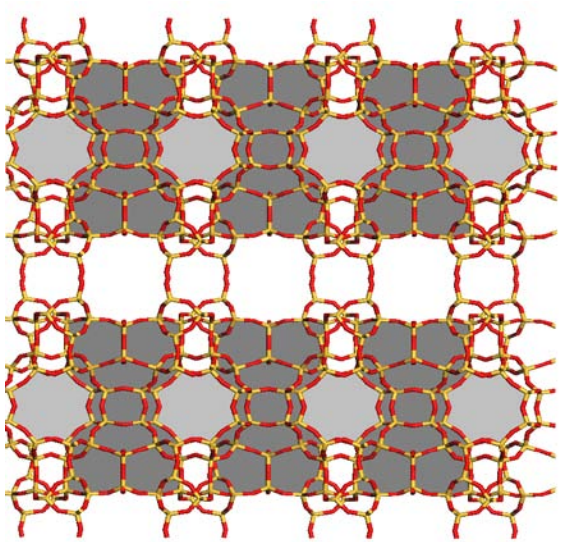
MCM-22

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

MWW Layers as hydrogen selective flakes

Unique and unusual pore structure

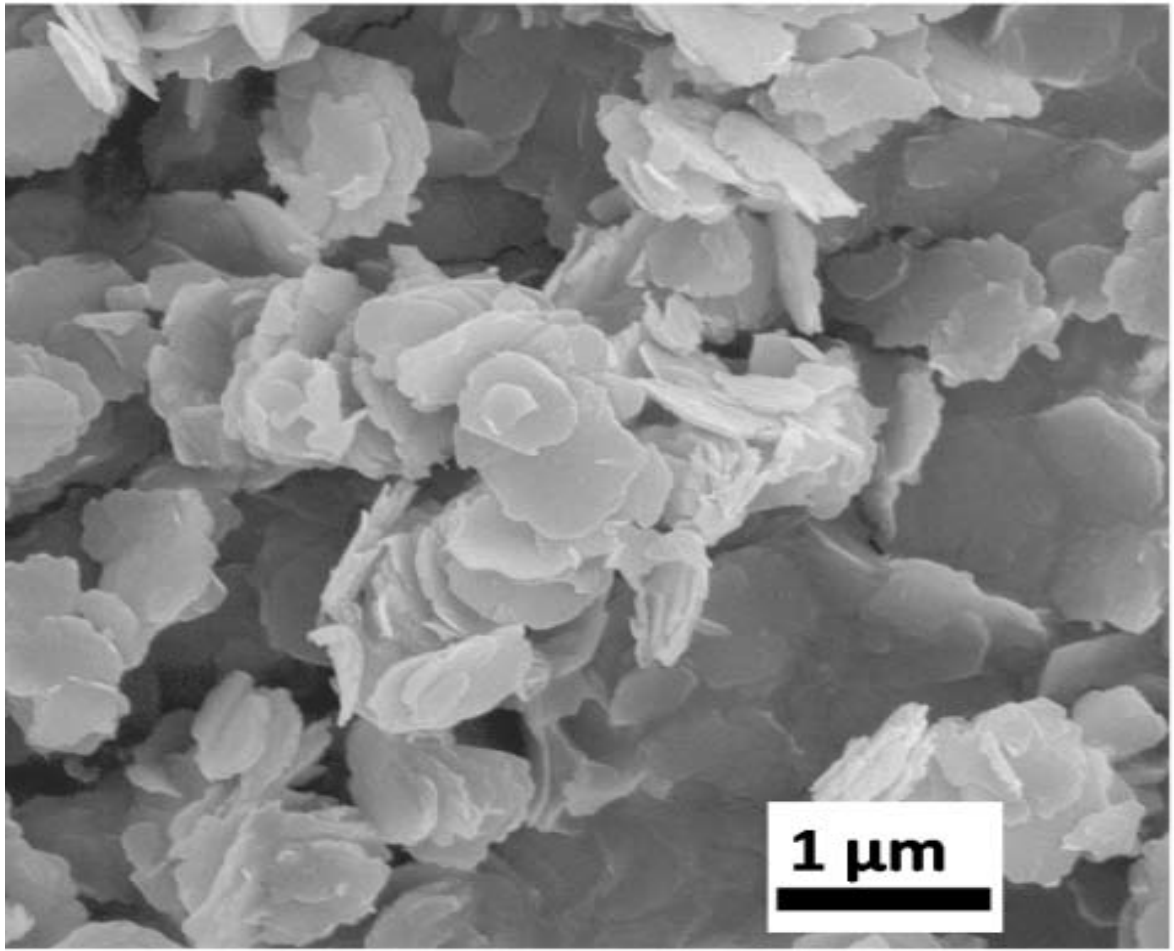
- 12-ring 6-ring cups

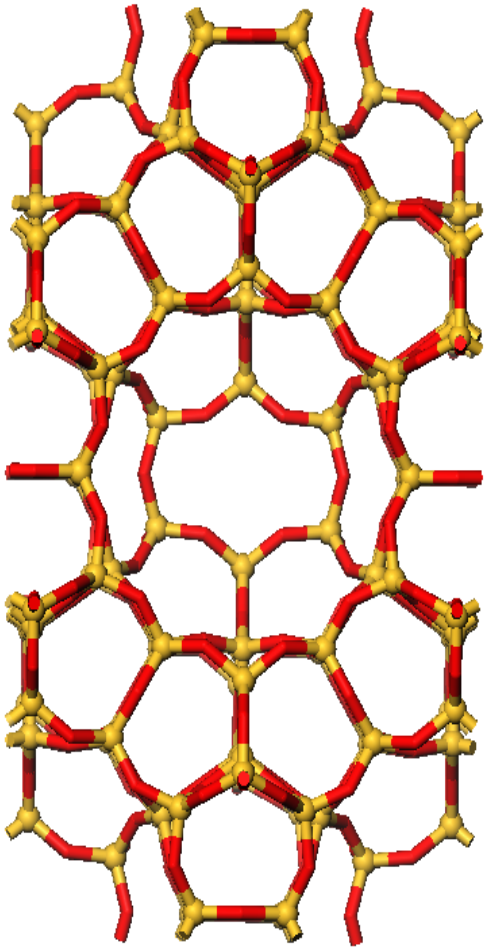


MCM-22

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

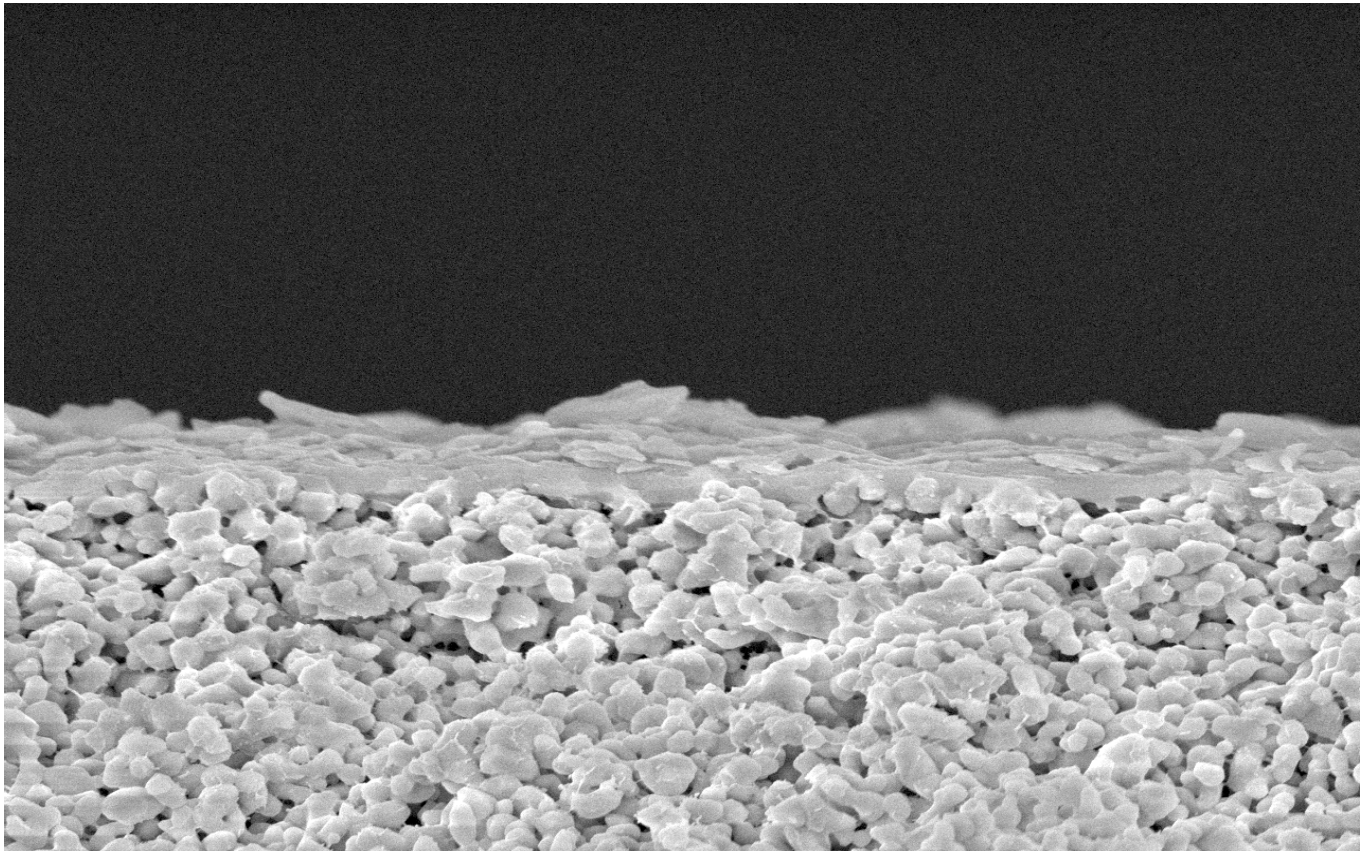
MWW Crystals





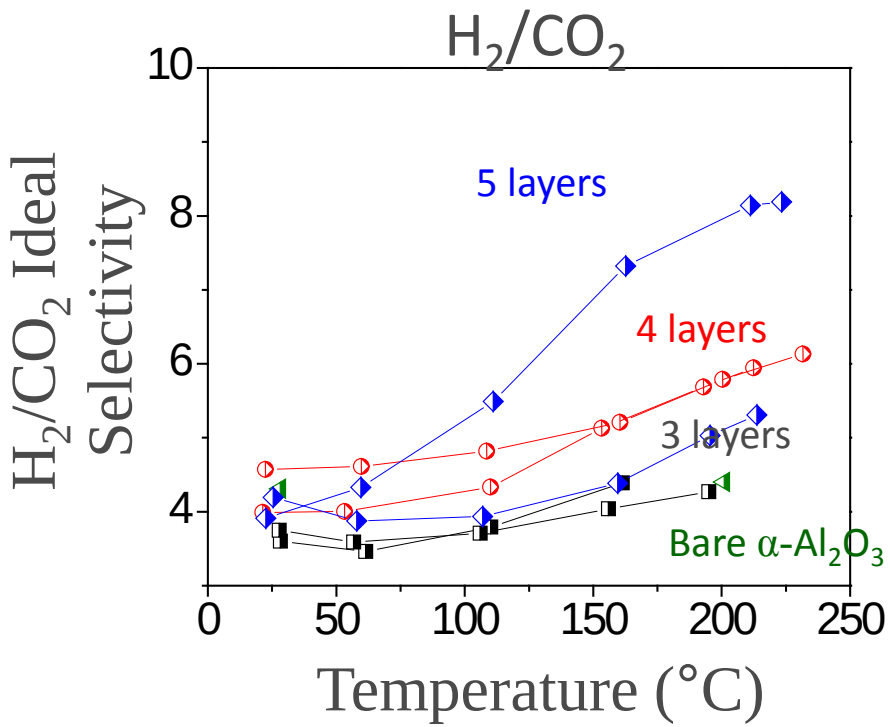
Layer by layer deposition (**JACS** 132(2), 448-449 (2010))

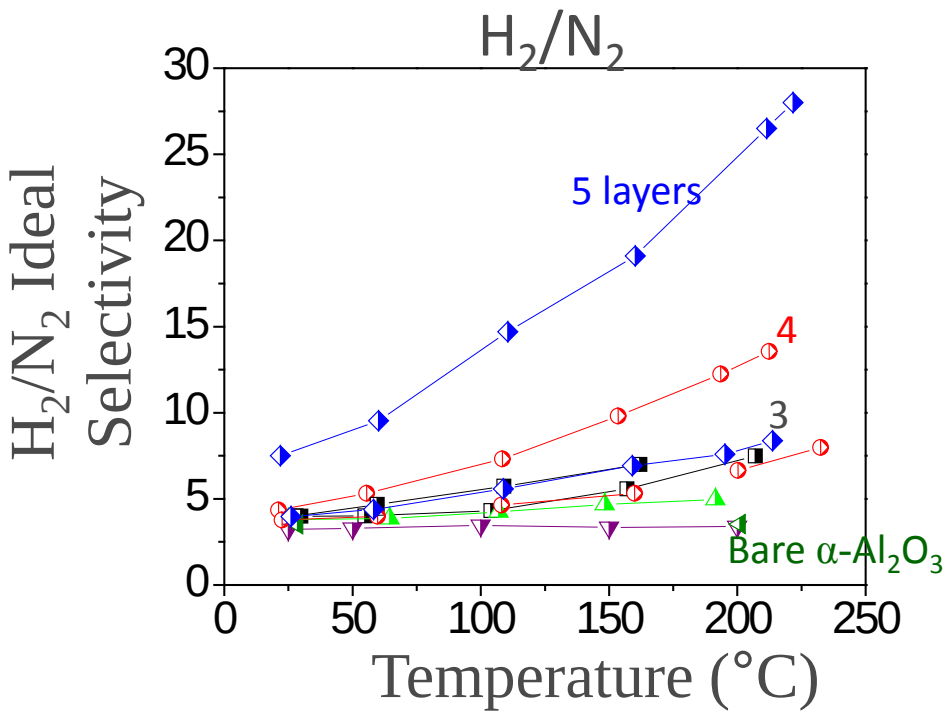
5 layers of MCM-22/surfactant-templated-mesoporous-silica on porous alumina



1μm

Comparison of Ideal Selectivity

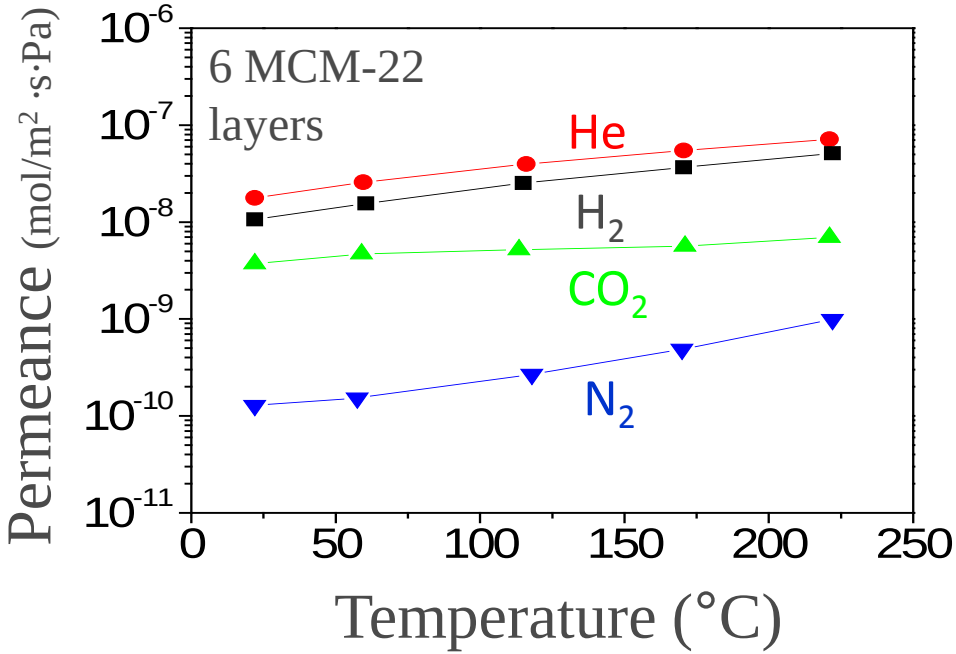


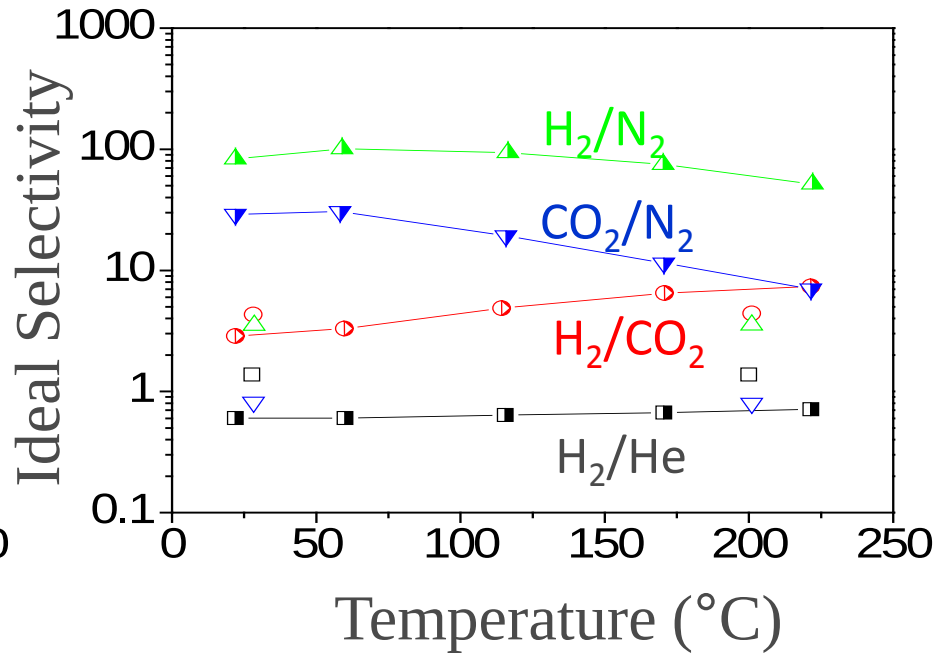


The ideal selectivity (H_2/CO_2 and H_2/N_2) increased monotonically with temperature and improved with the number of deposition cycles.

MCM-22/Silica Membranes for Hydrogen Separations

*Open symbols : selectivity through α-Al_2O_3 discs

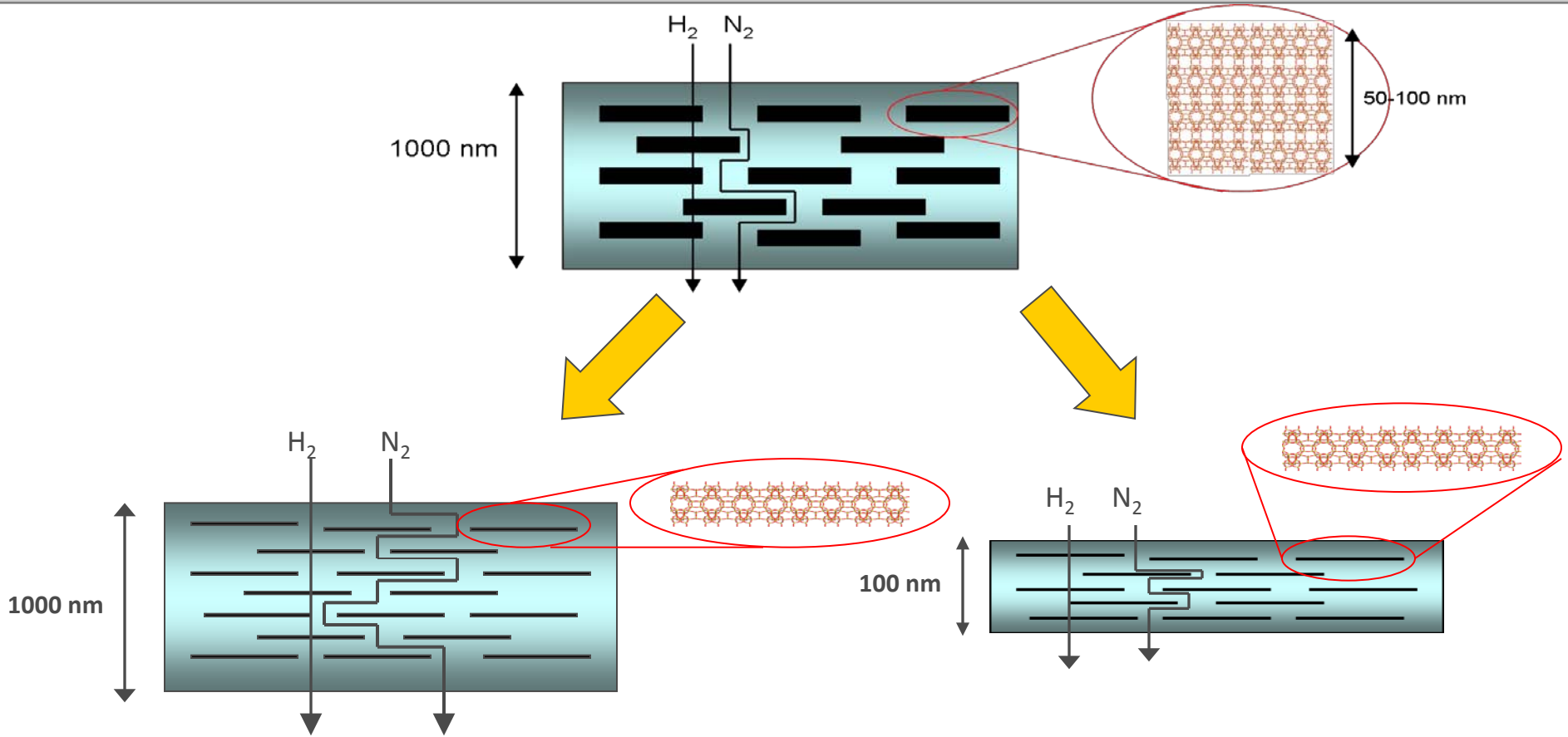




Choi J. and Tsapatsis M. **Journal of the American Chemical Society** 132(2), 448-449 (2010)

Experimental Demonstration of Selective Flake Composite Concept

Advantages by reduction in flake thickness

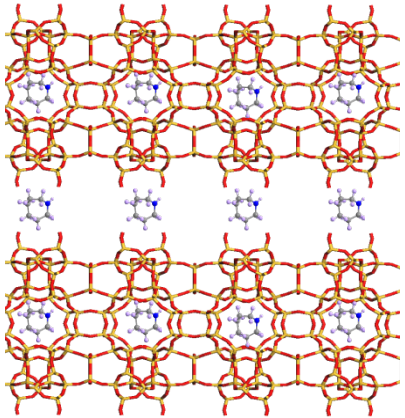


Increase selectivity without decreasing throughput

Increase throughput without decreasing selectivity

Challenge: Methods to exfoliate the zeolitic layers while preserving framework connectivity (pore structure)

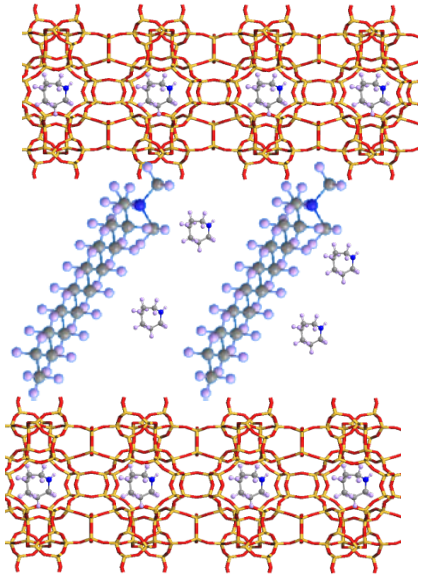
XRD, TEM and TGA results are consistent with the following picture:



MCM-22(P)

Swelling

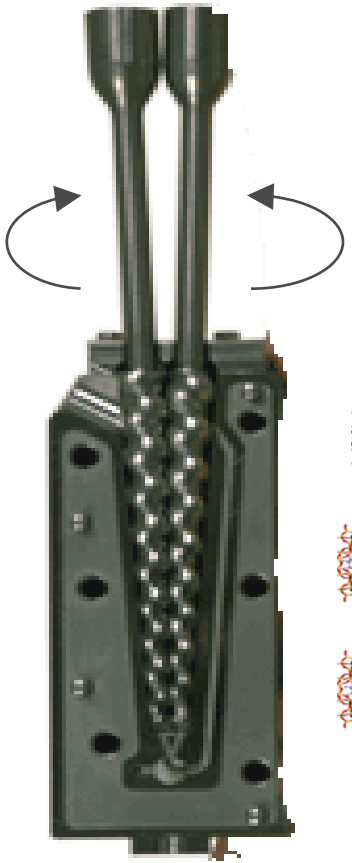
Acidification



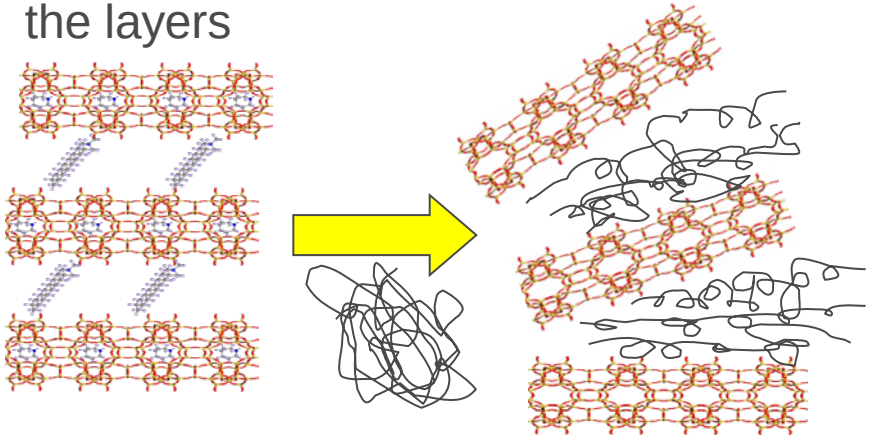
Swollen Structure

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

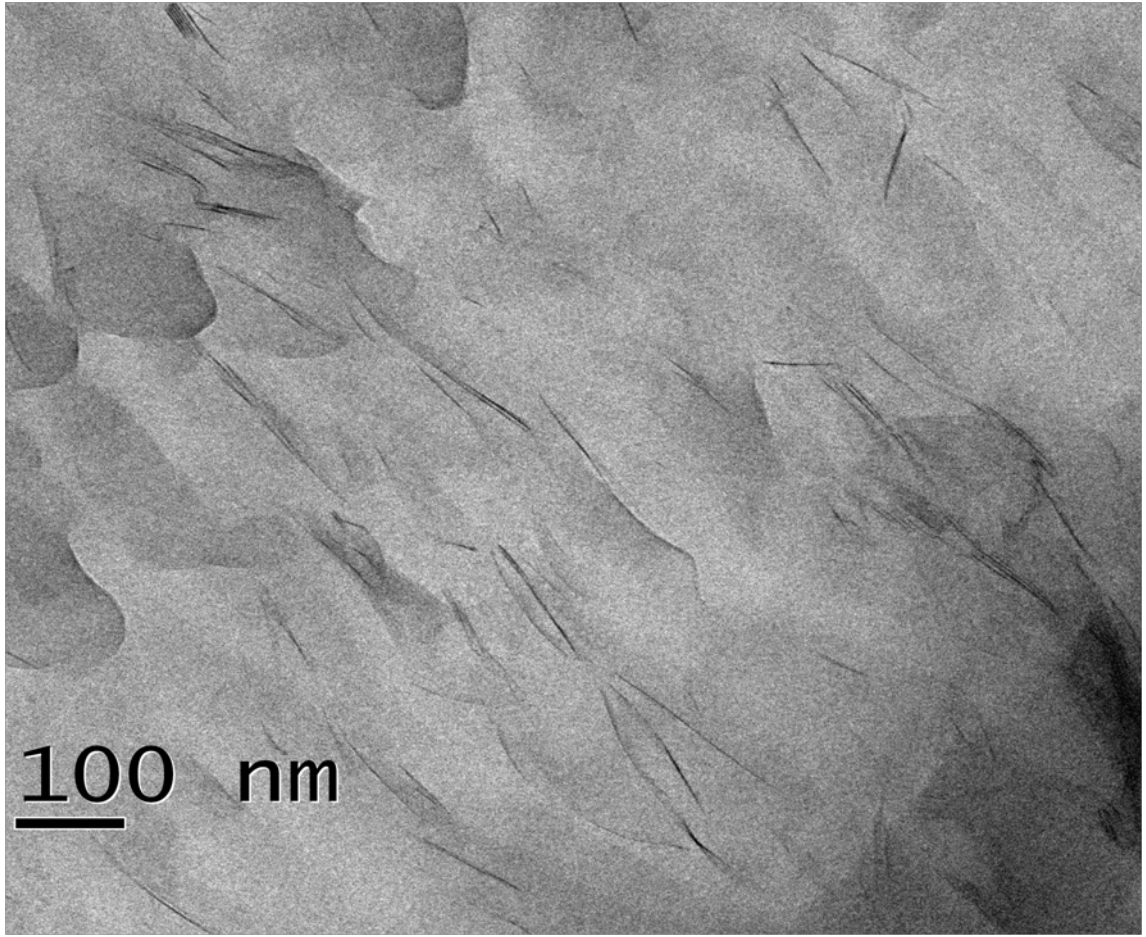
Polystyrene nanocomposite by melt compounding



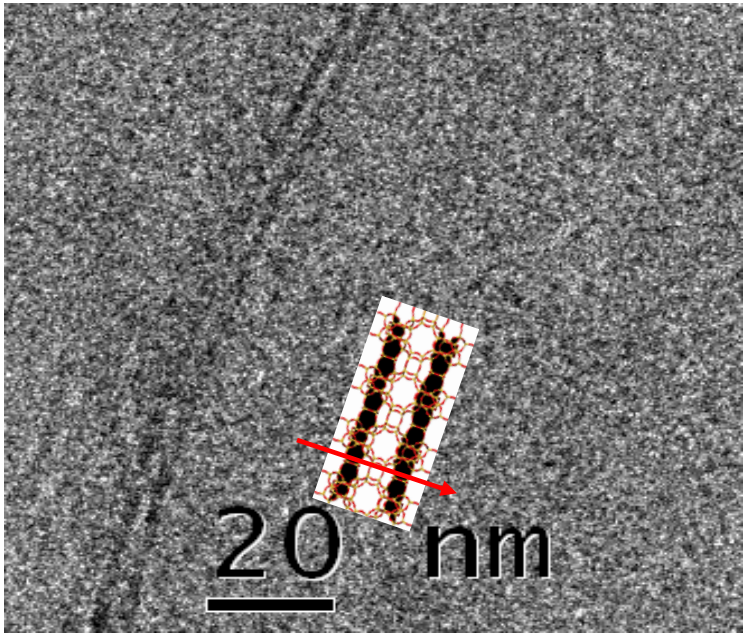
- Mixing of molten polymer and swollen zeolite layers
- Separation of layers by combined effect of shear forces and polymer diffusion between the layers



Polymer nanocomposite by melt compounding



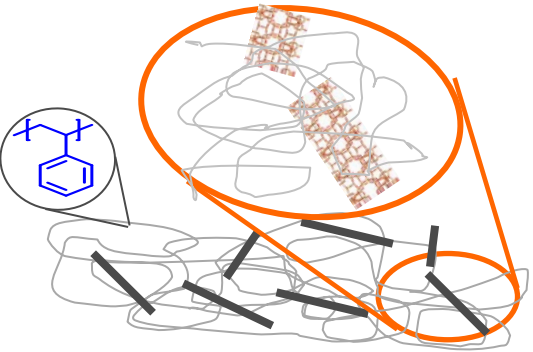
Preservation of pore structure of layers after exfoliation



Recovery of zeolite layers by depolymerization

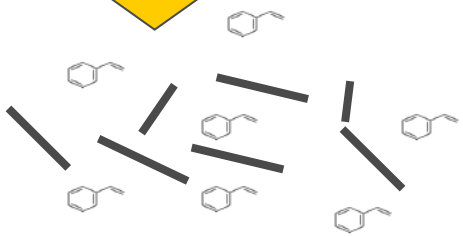
"Layered Zeolite materials and Methods Related Thereto" Tsapatsis, M., Maheshwari S., Koros W. and Bates F.S.

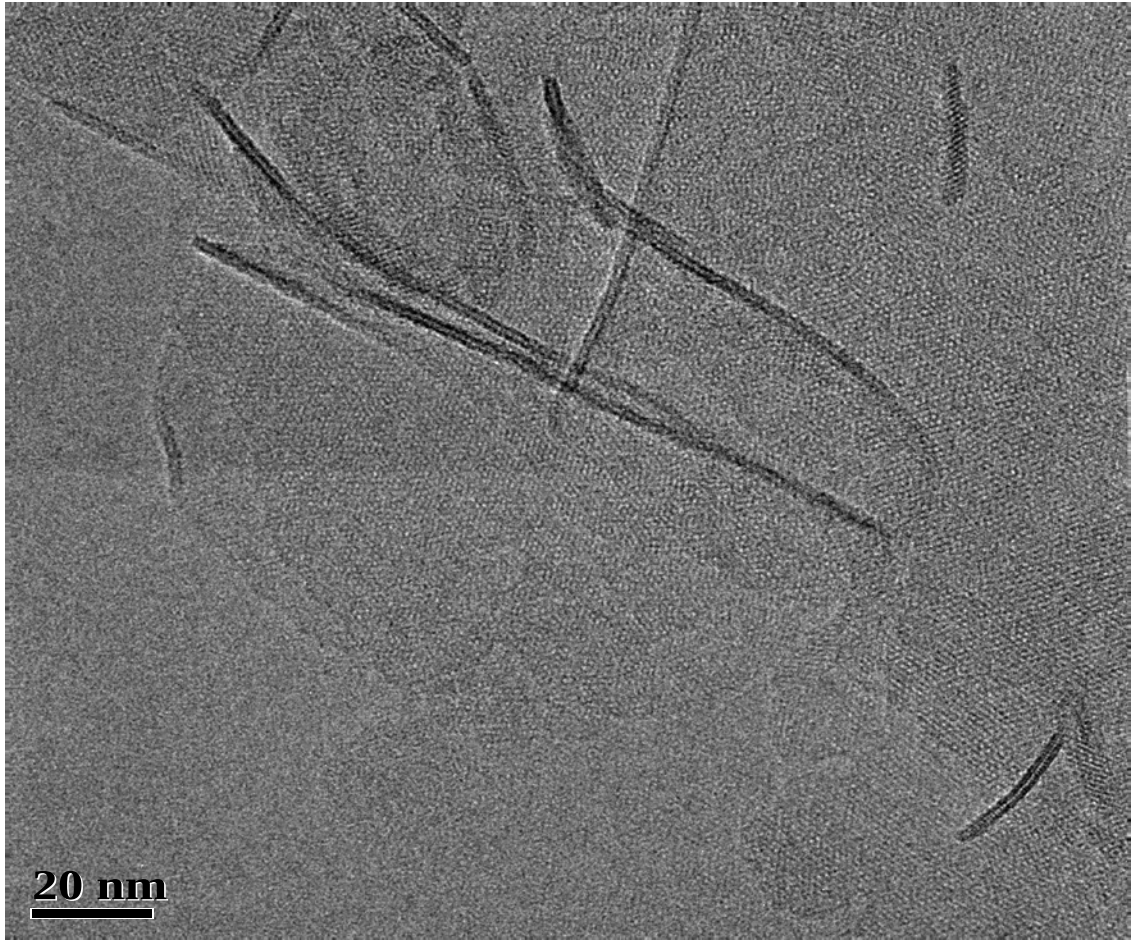
PCT/US2008/012455; WO2009108166



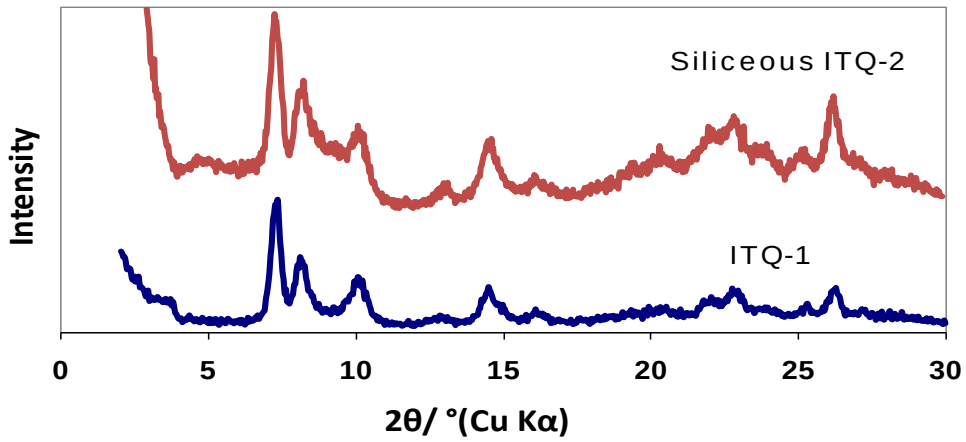
Polymer Nanocomposite

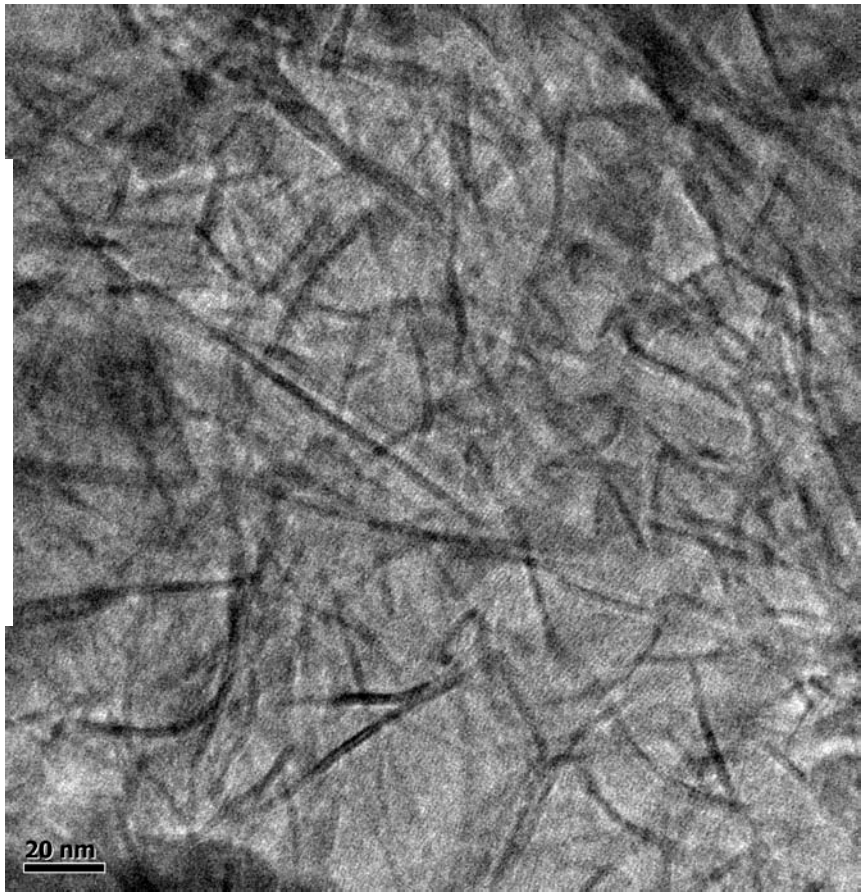
depolymerization



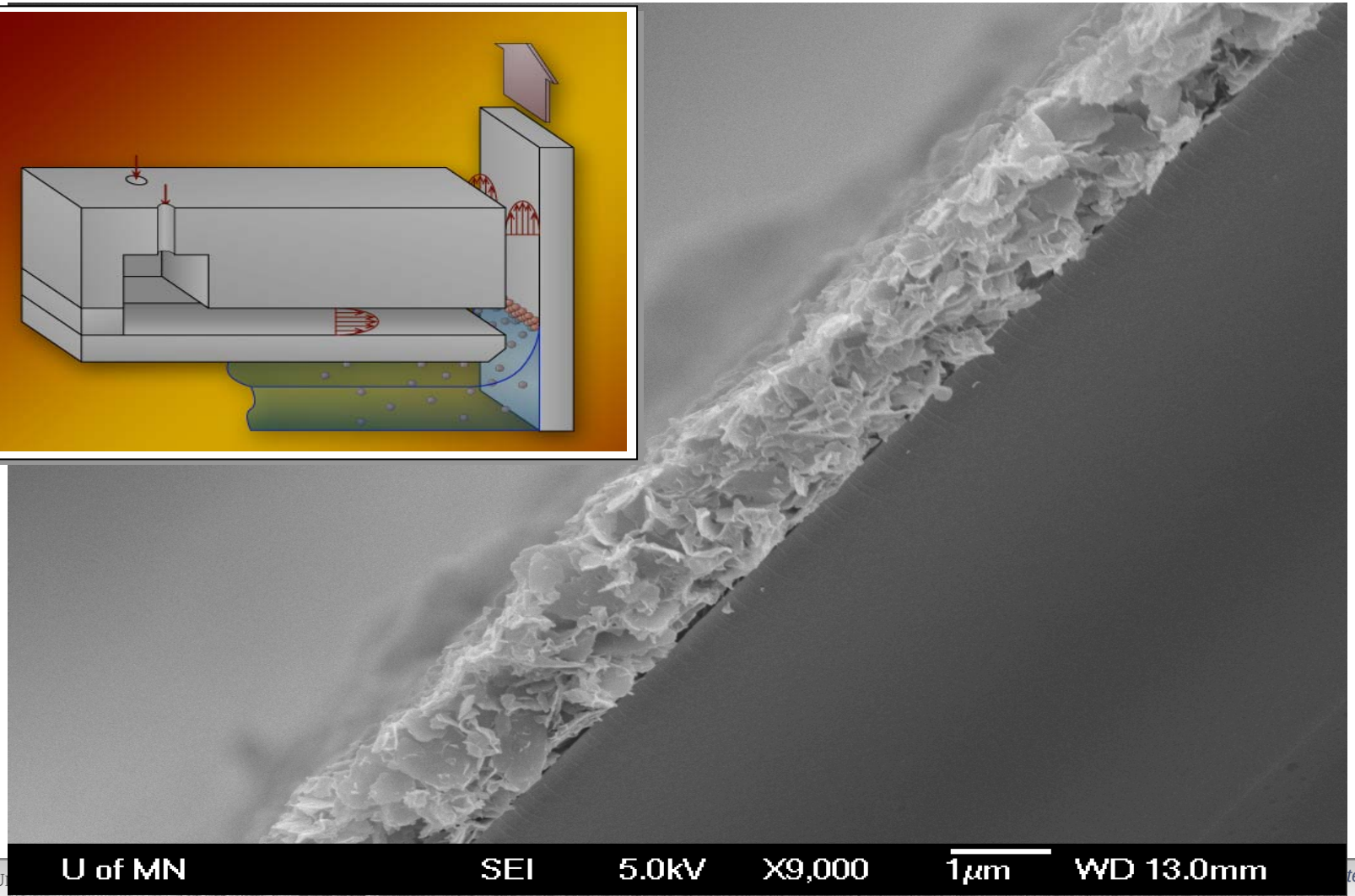


Exfoliation of siliceous MCM-22(P) in gram quantity

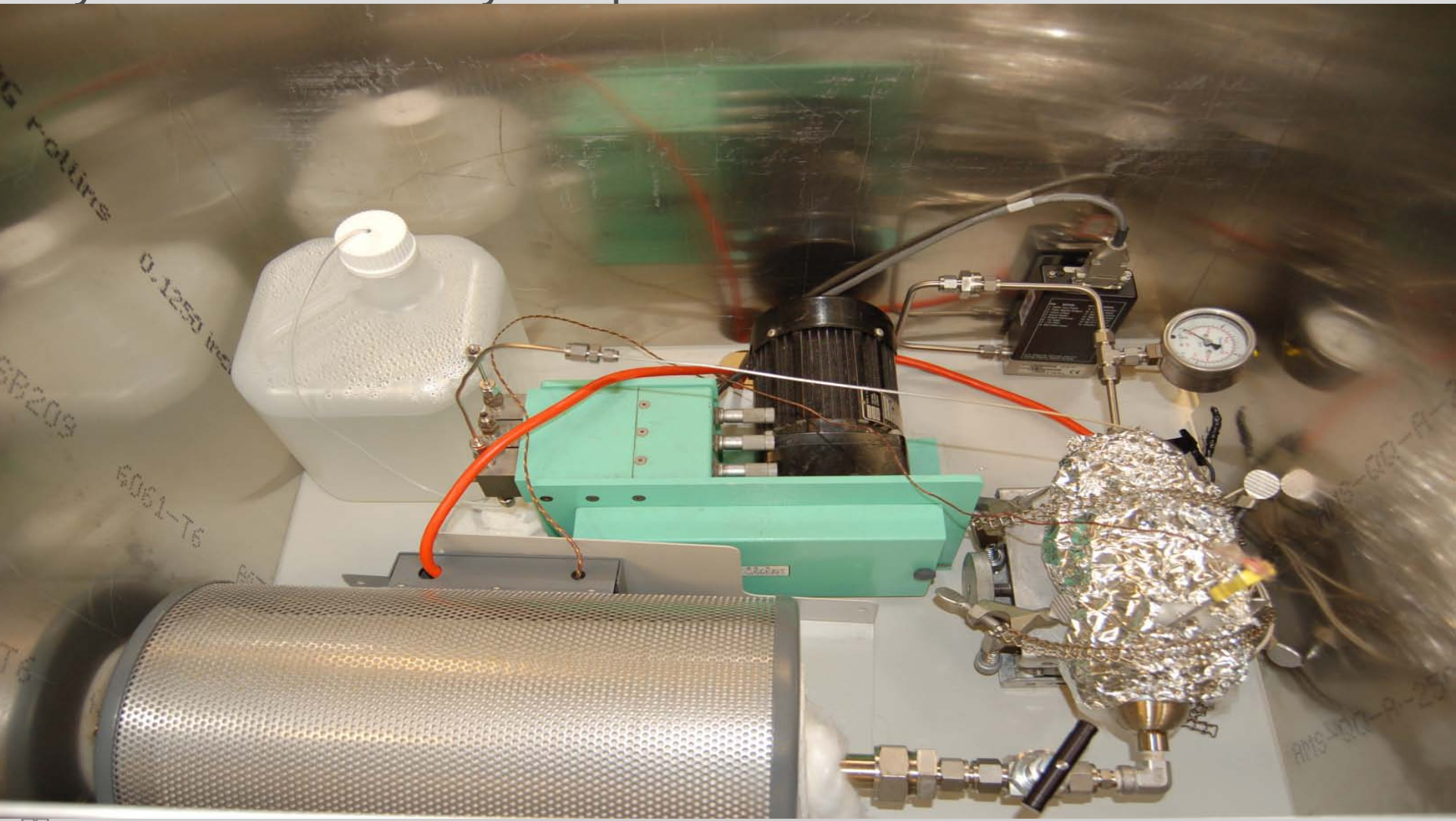




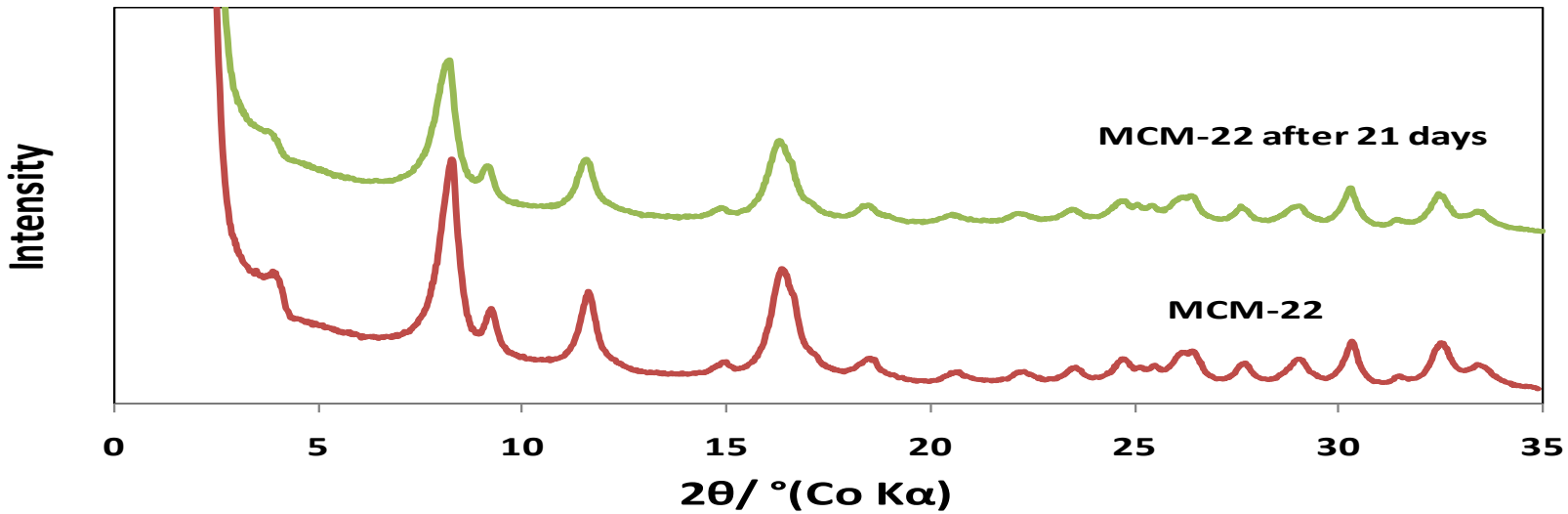
Evaporation Induced Convective Assembly of MWW layers on Si wafer



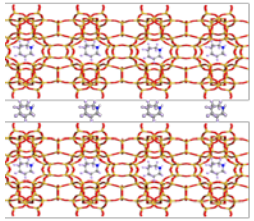
Hydrothermal stability setup



Hydrothermal treatment of MWW (~90% steam in nitrogen) at 500°C, 10 bar



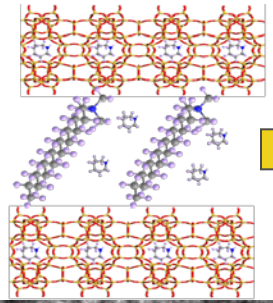
Summary and Future Work

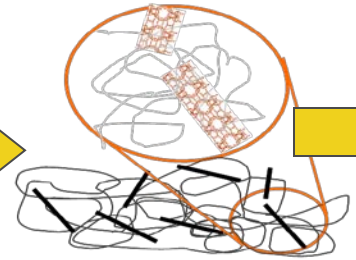


MCM-22(P)

Swelling

Acidification



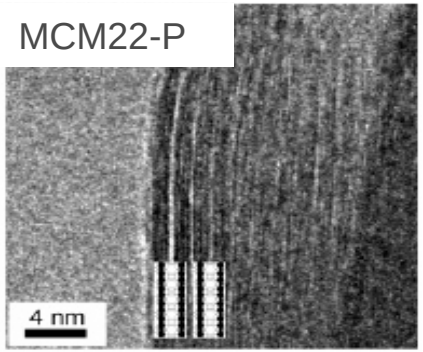


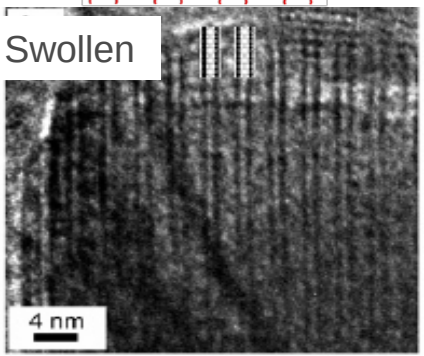
Polymer Nanocomposite

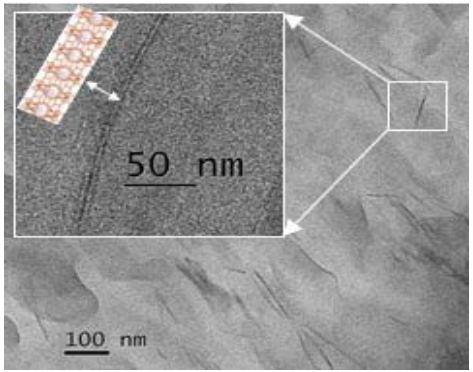
Exfoliated Layers

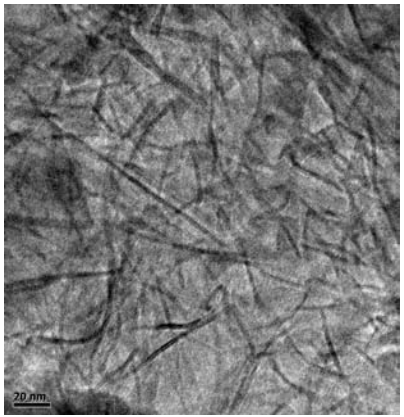
and

Films



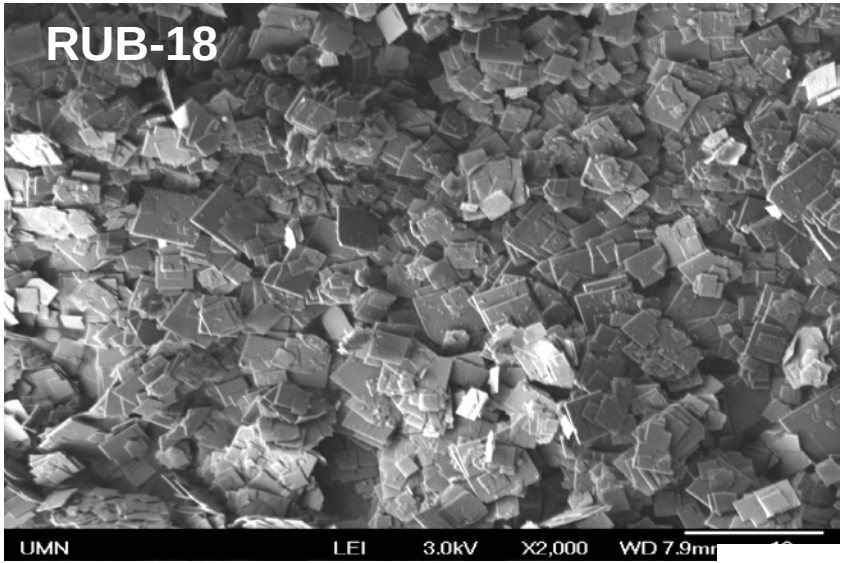


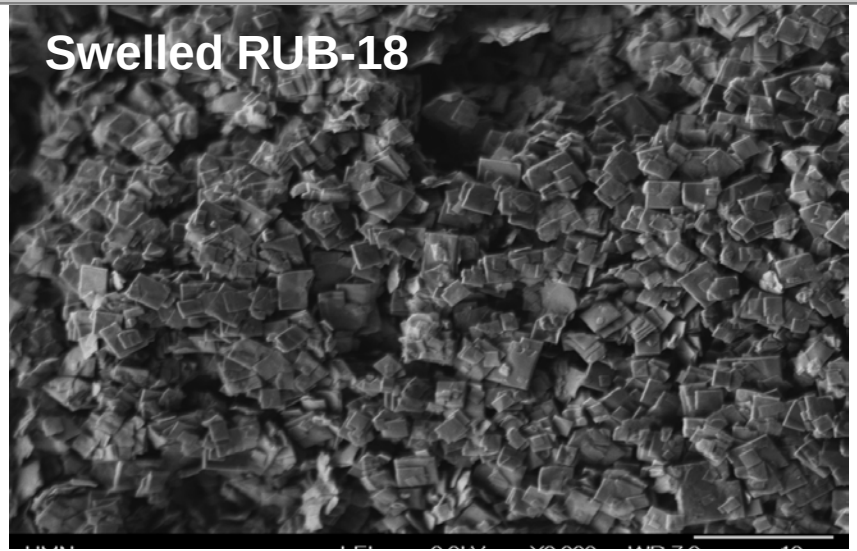


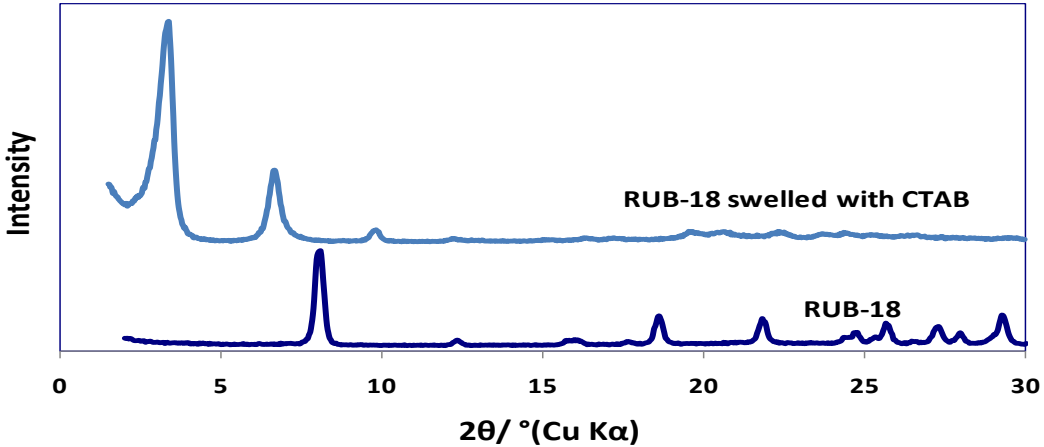


Membrane Performance and Stability Testing continues as planned

Other Materials: Synthesis and swelling of RUB-18







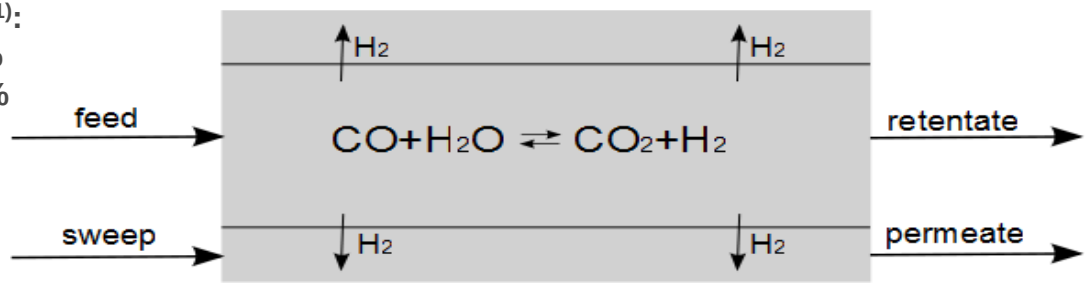
Membrane Reactor Modeling: Objectives and Approach

- **Develop a membrane reactor (MR) model**
  - **integrate model in IGCC**
  - **Study the effect of reactor design on performance**
- **Determine the membrane characteristics necessary to**
  - **achieve DOE target goal of 90 % of CO_2 capture [(1),(2)]**
  - **obtain desired H_2 recovery value of 95 % [(1)]**
- **Satisfy transportation safety constraints of CO_2 capture stream [(1)]**
  - **low CO concentration obtained by reaching desired CO conversion value of 98 %**
  - **H_2 molar fraction below flammability limit of 2 %**
- **Minimize membrane cost as a function of surface area**
- **Advised by Dr. John Marano (NETL consultant)**

(1) Marano, **Report to DOE/NETL** (2010)
(2) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)

MR Modeling Assumptions and Simulation Set Up

Composition [1]:
CO = 24.43 %
H_2O = 48.86 %
CO_2 = 5.68 %
H_2 = 19.33 %

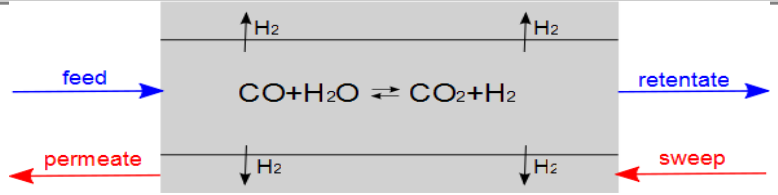


- **Assumptions**
  - **1-dimensional shell and tube reactor**
  - **catalyst packed in the tube side**
  - **thin membrane layer placed in inner side of tube**
  - **sweep gas flows in the shell side**
  - **plug-flow operation for both shell and tube**
  - **constant temperature and pressure**
  - **steady-state operation**
  - **ideal gas law**

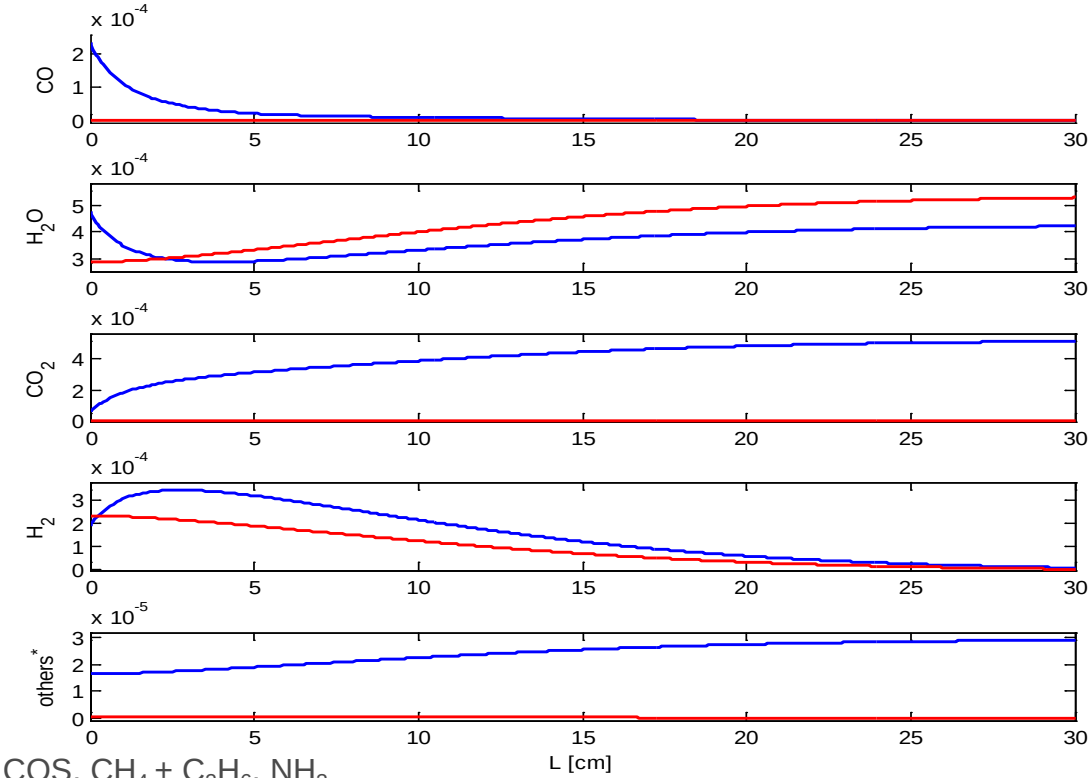
- **Flow configurations**
  - **co-current**
  - **counter-current**
- **Simulation conditions from literature**
  - **catalyst type and reaction rate [2]**
  - **reactor dimensions [3]**
  - **membrane characteristics [4]**
  - **conditions consistent with IGCC specifications**
- **Developed model validated using published simulation data [2]**

(1) Marano, **Report to DOE/NETL** (2010)
(2) Boutikos and Nikolakis, **J. Membr. Sci.** 350, 378-386 (2010)
(3) Amelio et al., **Energy Convers. Mgmt** 48, 2680-2693 (2007)
(4) Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)

Counter-current Simulation Results: Concentration Profiles

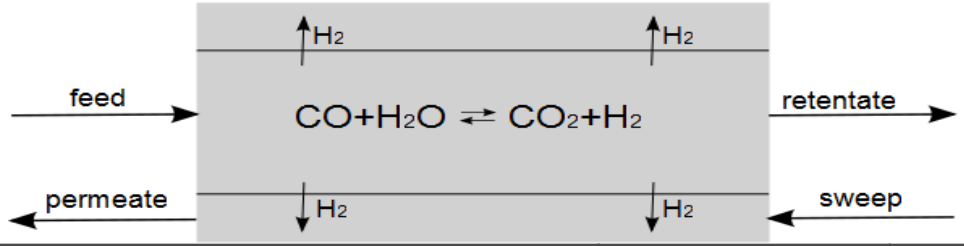


Counter-current Case: Species Concentration in Tube and Shell [mol/cc] vs. Reactor Length



(*) others: N_2 + Ar, H_2S + COS, CH_4 + C_2H_6, NH_3

Counter-current Simulation Results: Changing Membrane Selectivity



(*) $(\% CO_2 + \% H_2O)_R \geq 95\ \%$

Membrane Reactor Parameter	Value [%] ($S_{H2/all}$ = 1000)	Value [%] ($S_{H2/all}$ = 100)	Value [%] ($S_{H2/all}$ = 10)	Target [%]
$X_{CO} = \frac{\text{CO converted}}{\text{CO in feed}}$	99.92	99.95	100.00	98
$R_{H2} = \frac{H_2 \text{ in permeate}}{H_2 + \text{CO in feed}}$	99.16	99.14	97.71	95
$C_{CO2} = \frac{CO + CO_2 \text{ in retentate}}{CO + CO_2 \text{ in feed}}$	98.96	90.07	28.76	90
$P_{CO2,R} = \frac{CO_2 \text{ in retentate}}{\text{total in retentate}}$	52.87*	50.37*	29.68*	95
$P_{H2,P} = \frac{H_2 \text{ in permeate}}{\text{total in permeate}}$	44.29	43.18	34.17	44

Modeling Future Work

- **continue MR model validation using experimental data [1]**
- **analyze different modeling scenarios: 2-dimensional, non-isothermal**
- **perform cost analysis using selected reactor design**
- **integrate MR model in IGCC unit (Matlab and Aspen simulations)**

(1) Tang et al., **J. Membr. Sci.** 354, 114-122 (2010)