Hydrogen Selective Exfoliated Zeolite Membranes

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DE-09FE0001322 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

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DOE/Non-DOE Share: $793,775/ $199,997

Period of Performance: 10/1/2009 to 9/30/2014

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http://www.cems.umn.edu/research/tsapatsis/

Related Publications

Long-term steam stability of MWW structure zeolites (MCM-22 and ITQ-1)
By: Elyassi, Bahman; Zhang, Xueyi; Tsapatsis, Michael
MICROPOROUS AND MESOPOROUS MATERIALS Volume: 193 Pages: 134-144 Published: JUL 15 2014

Solution-processable exfoliated zeolite nanosheets purified by density gradient centrifugation
By: Agrawal, Kumar Varoon; Topuz, Berna; Jiang, Zheyu; et al.
AICHE JOURNAL Volume: 59 Issue: 9 Pages: 3458-3467 Published: SEP 2013

Melt Compounding of Swollen Titanosilicate JDF-L1 with Polysulfone To Obtain Mixed Matrix Membranes for H-2/CH4 Separation
By: Castarlenas, Sonia; Gorgojo, Patricia; Casado-Coterillo, Clara; et al.
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH Volume: 52 Issue: 5 Pages: 1901-1907 Published: FEB 6 2013

Modeling and Optimization of Membrane Reactors for Carbon Capture in Integrated Gasification Combined Cycle Units
By: Lima, Fernando V.; Daoutidis, Prodromos; Tsapatsis, Michael; et al.
INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH Volume: 51 Issue: 15 Pages: 5480-5489 Published: APR 18 2012

Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane
By: Varoon, Kumar; Zhang, Xueyi; Elyassi, Bahman; et al.
SCIENCE Volume: 334 Issue: 6052 Pages: 72-75 Published: OCT 7 2011

MCM-22/Silica Selective Flake Nanocomposite Membranes for Hydrogen Separations
By: Choi, Jungkyu; Tsapatsis, Michael
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY Volume: 132 Issue: 2 Pages: 448-+ Published: JAN 20 2010

Outline

Introduction: Zeolite Membranes from nanosheets and 2-dimensional zeolites

Techno-economic Evaluation

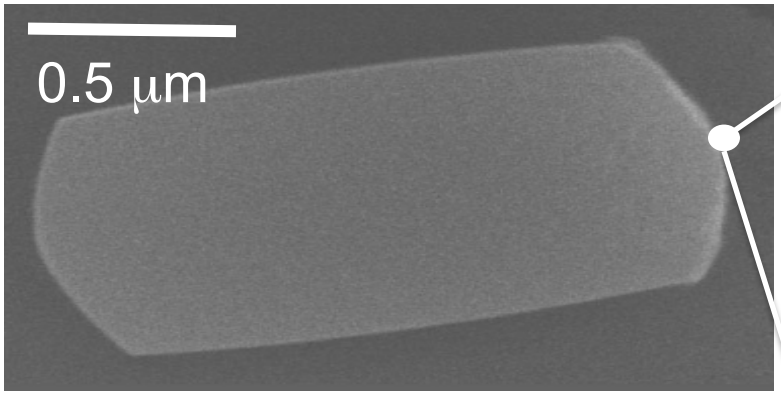
Exfoliation Studies

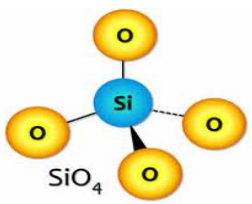
Membrane Preparation Approaches

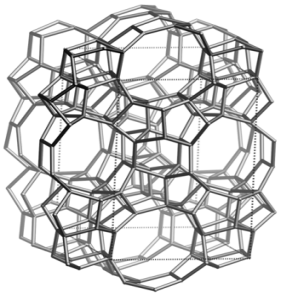
Stability Results

Conclusions and Outlook

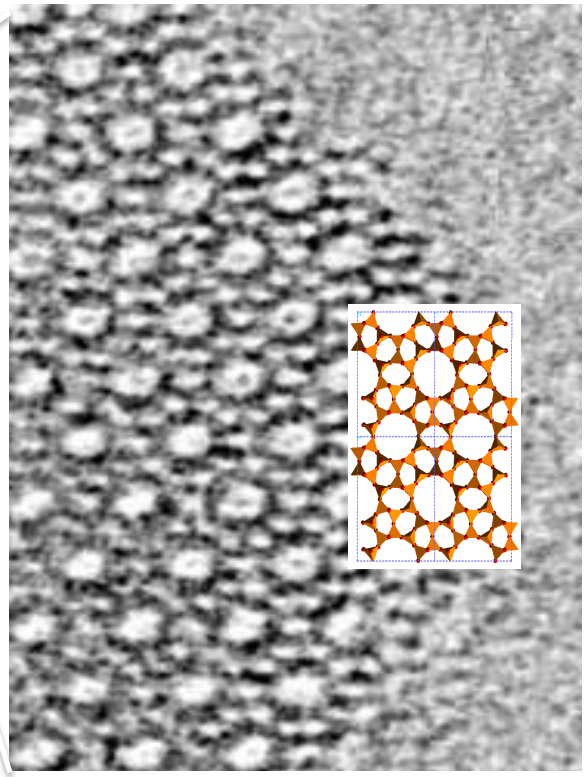
Typical micrometer-sized zeolite crystals







Zeolite ZSM-5 (MFI)



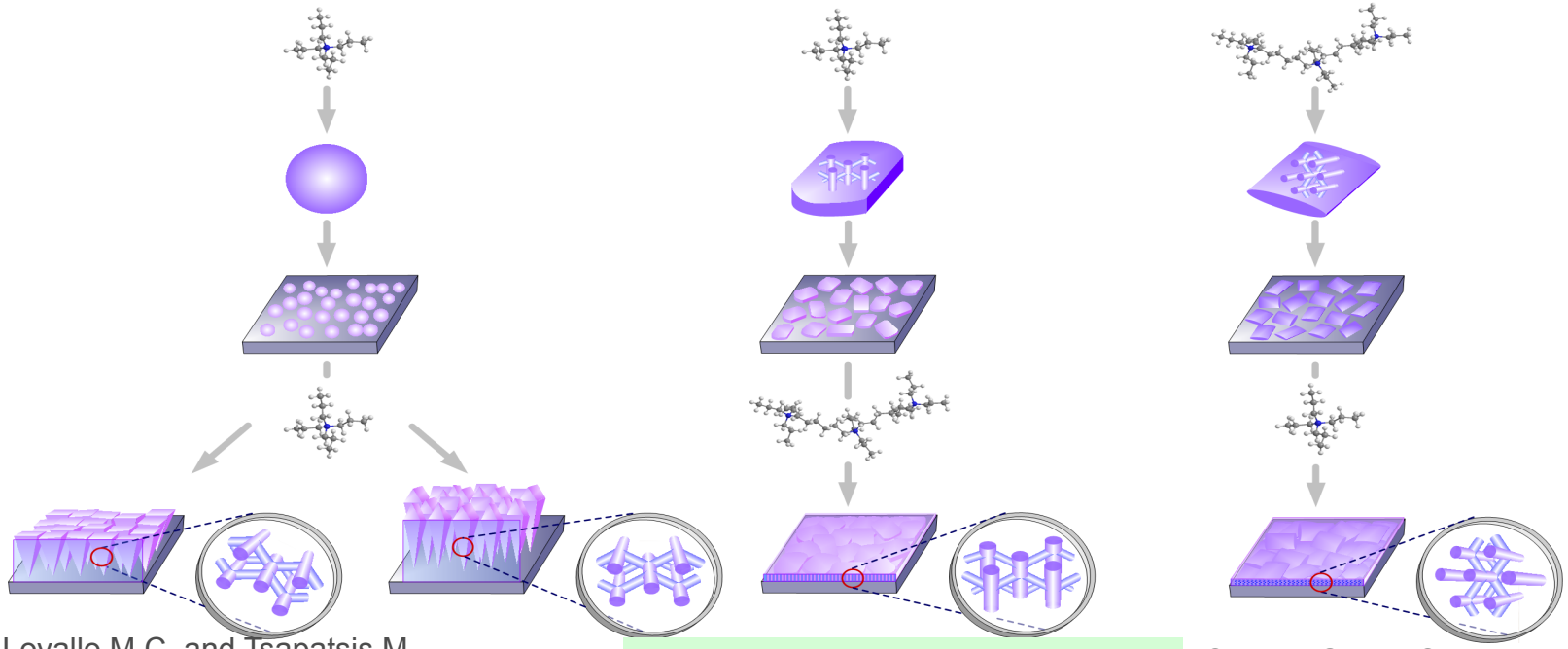
2nm

KOKOTAILO, GT; LAWTON, SL; OLSON, DH; et al. Nature, 272(5652), 437-438 (1978)
FLANIGEN, EM; BENNETT, JM; GROSE, RW; et al. Nature 271(5645), 512-516 (1978)

IZA approved framework structures:

- Framework Type Code (FTC): ABW ACO AEI AEL AEN AET AFG AFI AFN AFO AFR AFS AFT AFX AFY AHT ANA APC APD AST ASV ATN ATO ATS ATT ATV AWO AWW BCT *BEA BEC BIK BOF BOG BPH BRE BSV CAN CAS CDO CFI CGF CGS CHA -CHI -CLO CON CZP DAC DDR DFO DFT DOH DON EAB EDI EMT EON EPI ERI ESV ETR EUO EZT FAR FAU FER FRA GIS GIU GME GON GOO HEU IFR IHW IMF ISV ITE ITH ITR ITW IWR IWS IWV IWW JBW JRY KFI LAU LEV LIO -LIT LOS LOV LTA LTF LTL LTN MAR MAZ MEI MEL MEP MER ***MFI*** MFS MON MOR MOZ *MRE MSE MSO MTF MTN MTT MTW **MWW** NAB NAT NES NON NPO NSI OBW OFF OSI OSO OWE -PAR PAU PHI PON RHO -RON RRO RSN RTE RTH RUT RWR RWY SAO SAS SAT SAV SBE SBN SBS SBT SFE SFF SFG SFH SFN SFO SFS SGT SIV SOD SOF SOS SSF SSY STF STI *STO STT STW -SVR SZR TER THO TOL TON TSC TUN UEI UFI UOS UOZ USI UTL VET VFI VNI VSV WEI -WEN YUG ZON

Control of Preferred Orientation and Grain Boundary Structure



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Boudreau L. and Tsapatsis M. **Chemistry of Materials**, 9(8), 1705-1709 (1997)

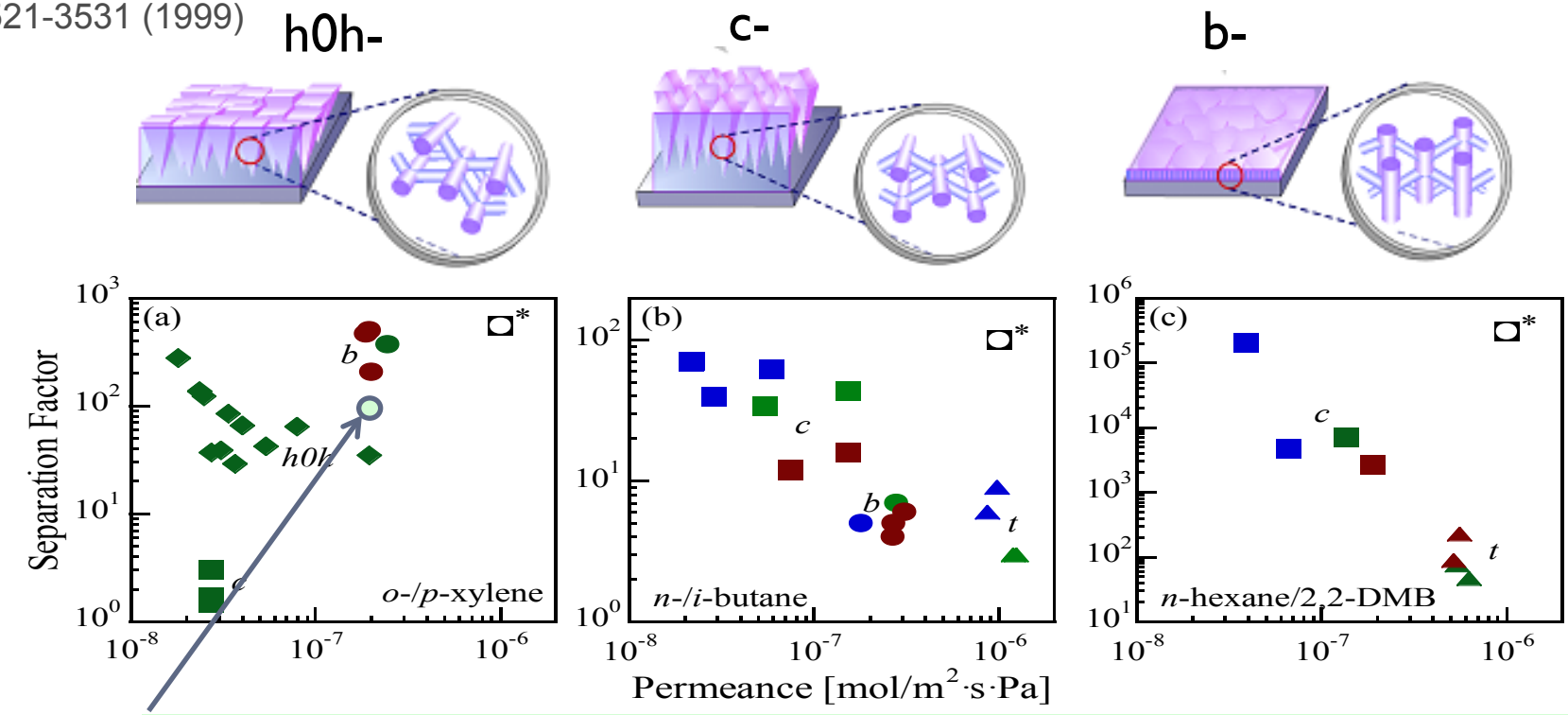
Gouzinis A. and Tsapatsis M. **Chemistry of Materials** 10, 2497-2504 (1998)

Lai Z., Bonilla G., Diaz I., Nery J.G., Sujaoti K., Amat M., Kokkoli E., Terasaki O., Thompson R. Tsapatsis M. and Vlachos D.G. **Science** 300:(5618), 456-460 (2003)
Lai Z., Nikolich J.P., Tsapatsis M. **Advanced Functional Materials** 14:(7), 716-729 (2004)

Choi J., Ghosh S., Lai Z. Tsapatsis M. **Angew. Chem. Int. Ed.** 45, 1154-1158 (2006)

Separation performance depends strongly on microstructure: Grain orientation and Grain Boundaries

Xomeritakis G., Gouzinis A., Nair S., He M., Overnay R., Okubo T., Tsapatsis M. **Chemical Engineering Science** 54, 3521-3531 (1999)



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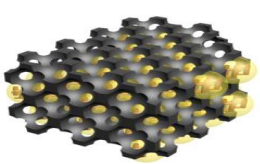
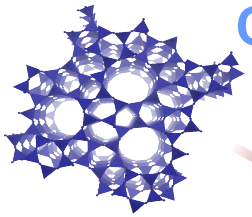


Choi J., Jeong H.K., Snyder M.A., Stoeger J.A, Masel R.I., Tsapatsis M. **Science** 325(5940), 590-594 (2009)

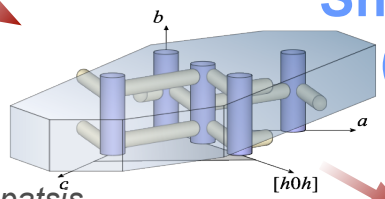
W. Fan, M.A. Snyder, S. Kumar, PS Lee, W. C. Yoo, A. V. McCormick, R. L. Penn, A. Stein and M. Tsapatsis, **Nature Materials**, 7(12), 984-991(2008)

Lee P.-S., Zhang X., Stoeger J.A., Malek A., Wei F., Sandeep K., Yoo W.C., Al Hashimi S., Penn R.L. Stein A. Tsapatsis M. **Journal of the American Chemical Society** 133(3), 493-502 (2011)

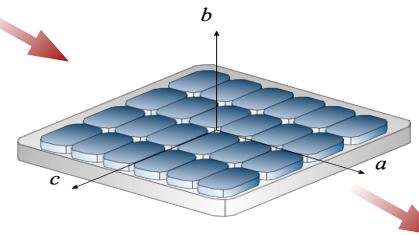
Hierarchical manufacturing of zeolite films



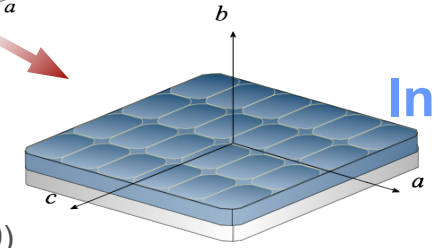
Crystal Structure (nm)



Shaped Crystal (10-100nm)



Oriented Monolayer of Crystals



Intergrown Film

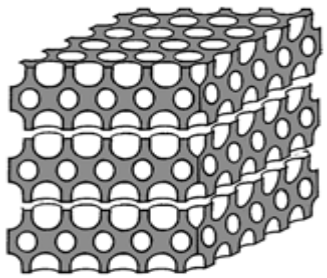
For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. **2007**, *46*, 7560–7573

For extension to MOFs:
Ranjan and Tsapatsis
Chemistry of Materials
21(20), 4920-4924 (2009)

Yoo, Yeonshick; **Lai, Zhiping; Jeong, Hae-Kwon**
MICROPOROUS AND MESOPOROUS MATERIALS 123, 1-3, 100-106 (2009)

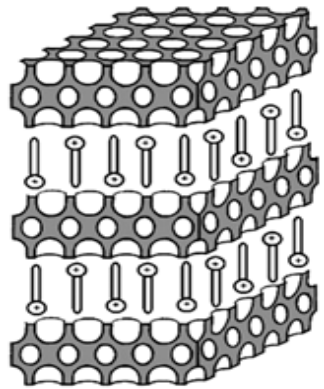
And ZIFs
Pan, Yichang; Li, Tao; Lestari, Gabriella; **Lai, Zhiping** JOURNAL OF MEMBRANE SCIENCE, 390, 93-98 (2012)
Andrew J. Brown, Dr. J. R. Johnson, Megan E. Lydon, William J. Koros, Christopher W. Jones, **Sankar Nair** ANGEWANDTE CHEMIE-INTERNATIONAL EDITION, 51, 10615-10618 (2012)

Layered zeolites:
first introduced by Mobil in 1990's for pillared MWW



Swelling

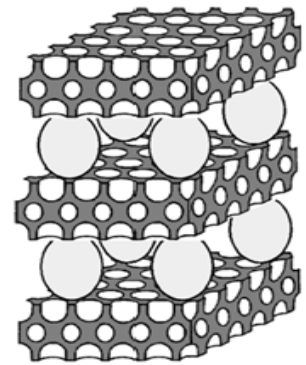
C_{16}TMAOH

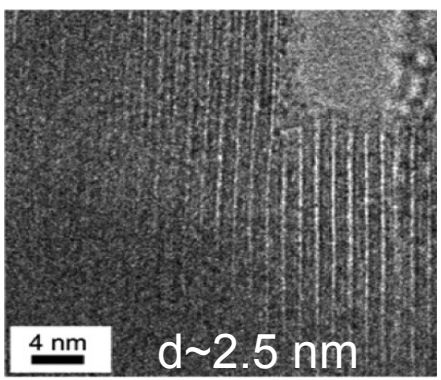


MCM-22 (P)
(swelled)

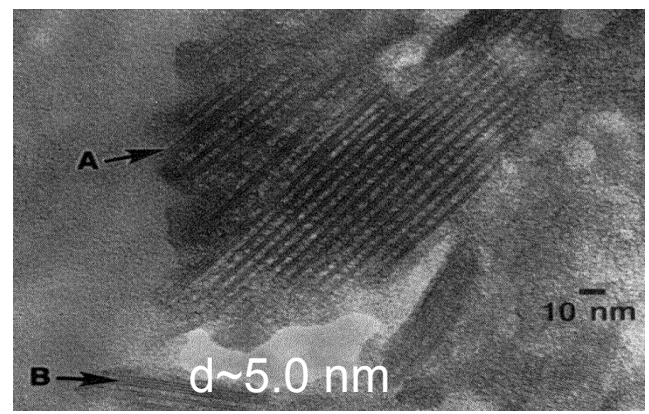
Pillaring
and
Calcination

TEOS





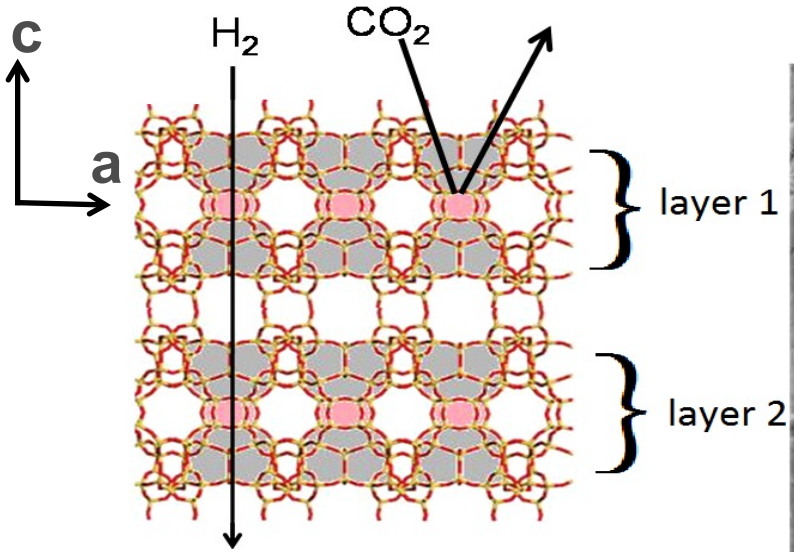
MCM-22 (P)



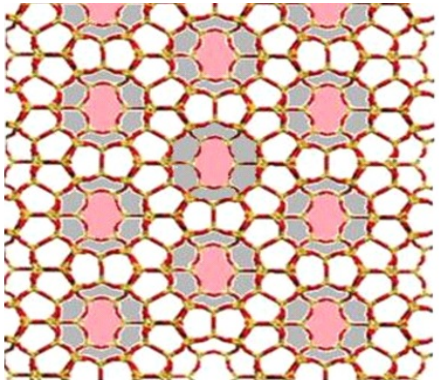
MCM-36

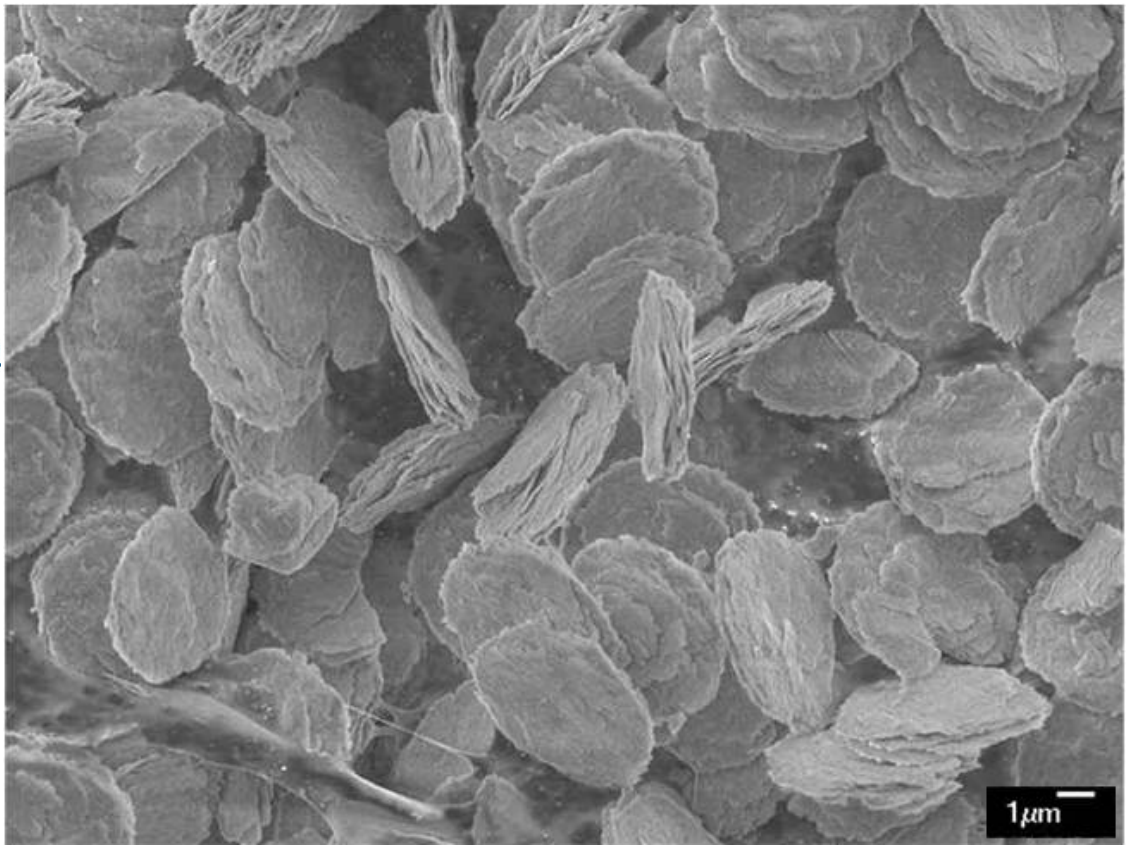
W. J. Roth, C. T. Kresge, J. C. Vartuli, M. E. Leonowicz, A. S. Fung, S. B. McCullen, in *Stud. Surf. Sci. Catal., Vol. 94* (Eds.: H. K. Beyer, H. G. Karge, I. Kiricsi, J. B. Nagy), Elsevier, Amsterdam, **1995**, pp. 301-308.

Layered zeolites with 6-MR pores

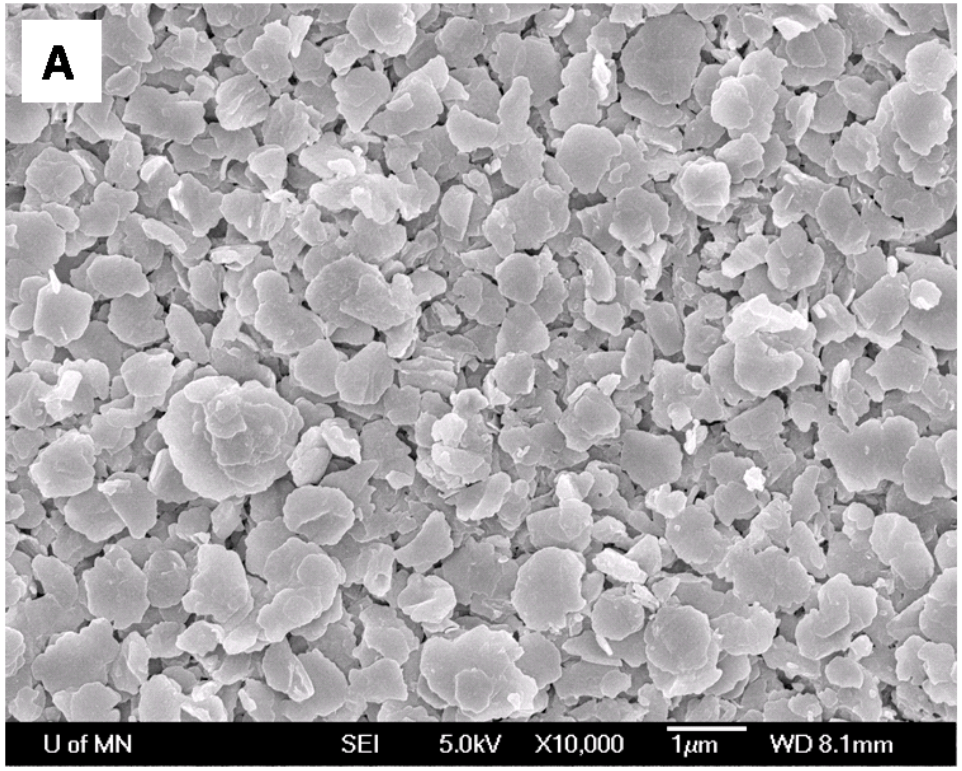


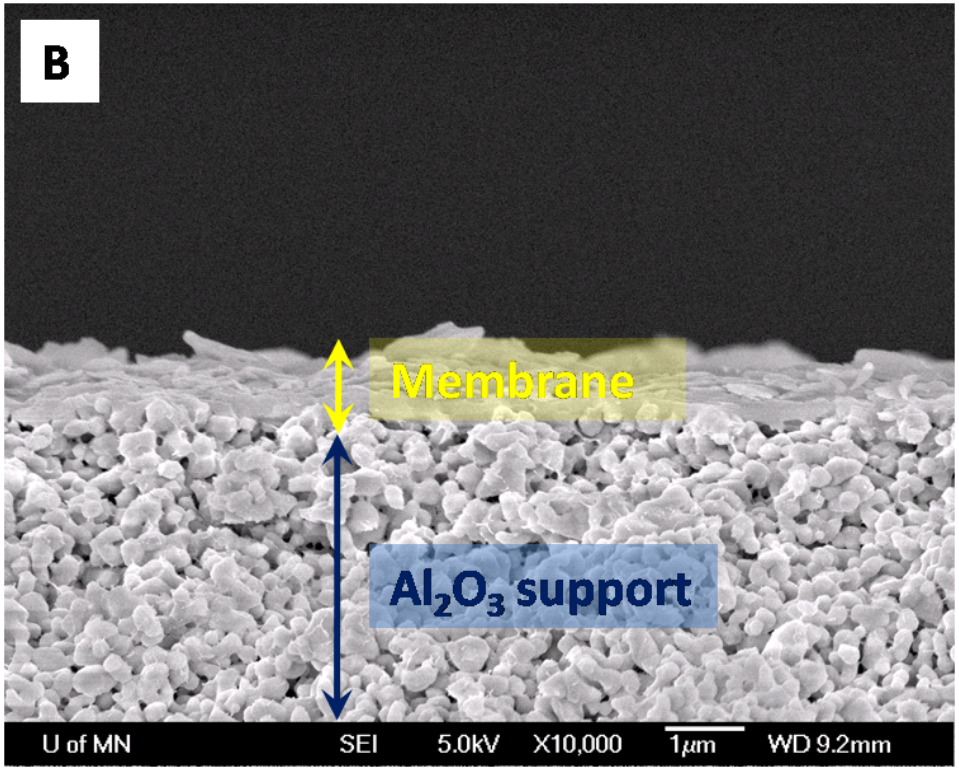
[001]

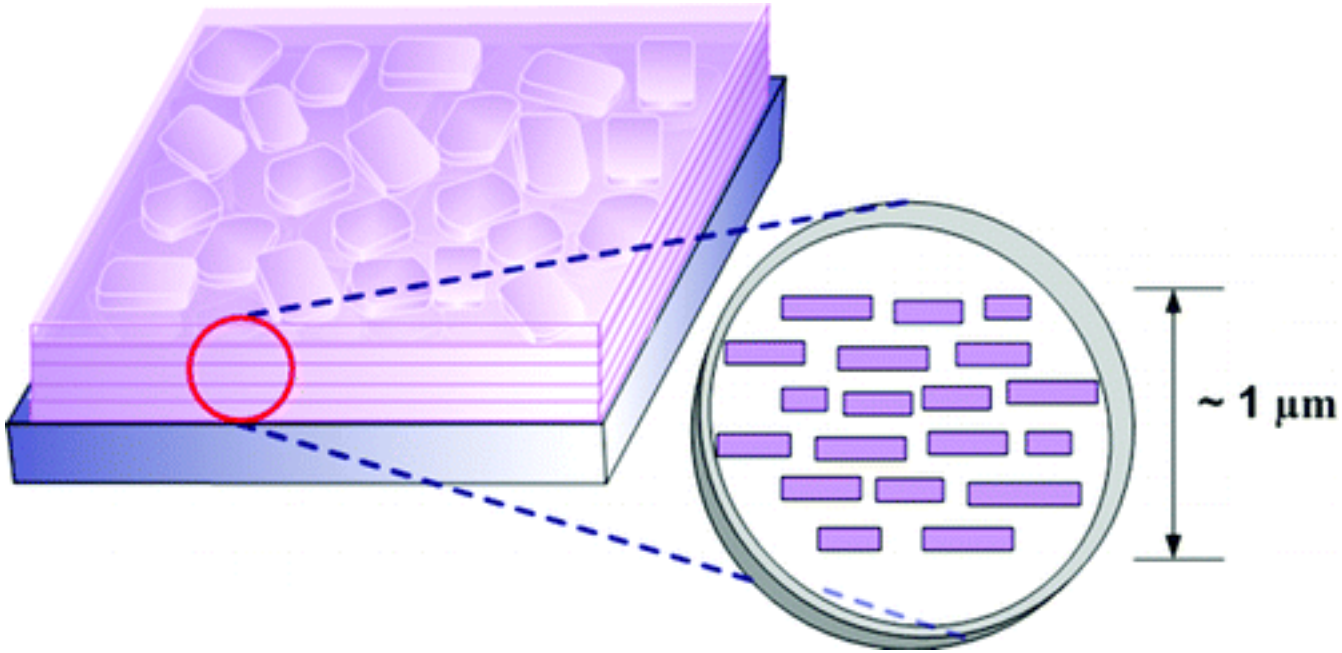




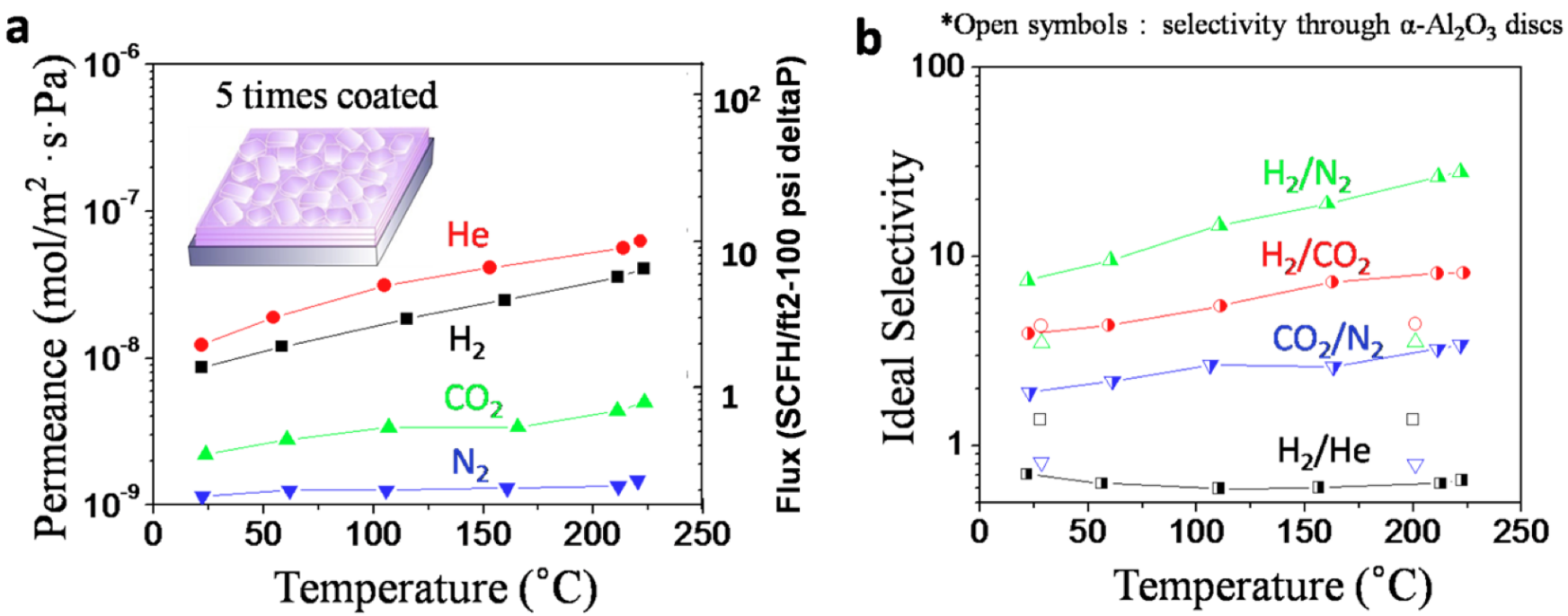
MWW Nanosheet/Mesoporous Silica Composite Membranes



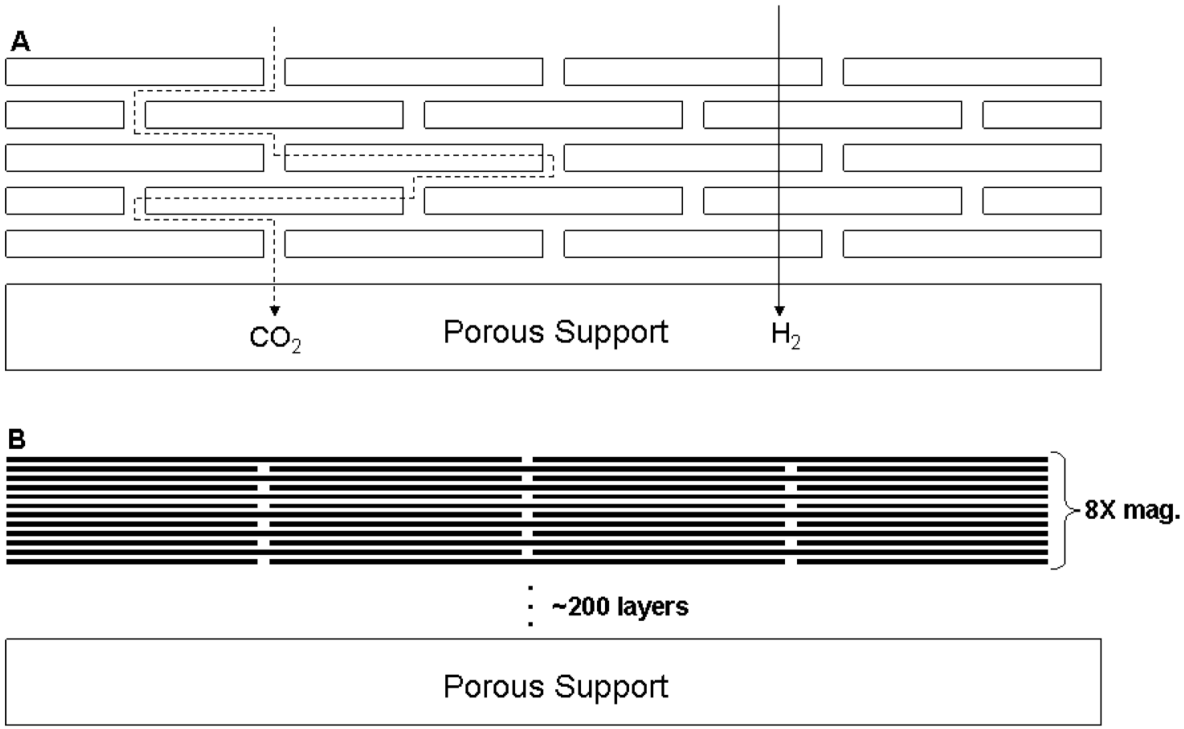



~ 1 µm

Selective membrane demonstrated (from 2008 proposal)



Proposed concept (2008)



Outline

Introduction: Zeolite Membranes from Nanosheets and 2-dimensional zeolites

Techno-economic Evaluation

Exfoliation Studies

Membrane Preparation Approaches

Permeation and Stability Results

Conclusions and Outlook

Systems Modeling: Objectives and Approach

Develop a WGS membrane reactor (MR) model

Integrate MR model into IGCC system model

Analyze effect of reactor design and membrane characteristics on integrated plant performance

- **achieve DOE R&D target goal of 90% CO_2 capture [(1),(2)]**
- **satisfy stream constraints for CO_2 capture and gas turbine fuel (H_2 rich)[(3)]**
- **quantify power generation**

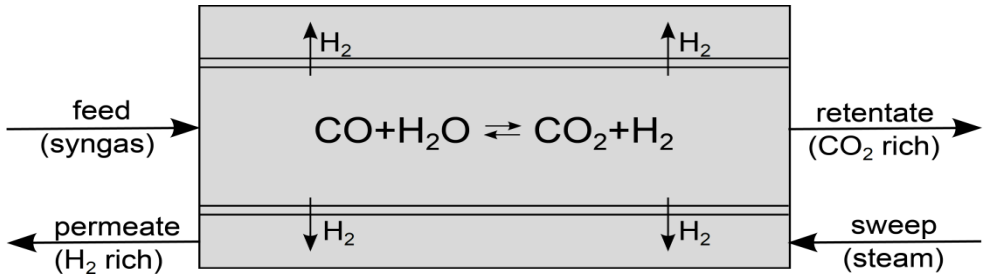
Perform optimization studies and techno-economic analysis for integrated plant

Received input from DOE/NETL personnel (John Marano and Jared Ciferno)

(1) Marano, **Report to DOE/NETL** (2010)
(2) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)
(3) Lima et al., **Ind. Eng. Chem. Res.** 51, 5480-5489 (2012)

MR Modeling Assumptions and Simulation Set Up

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

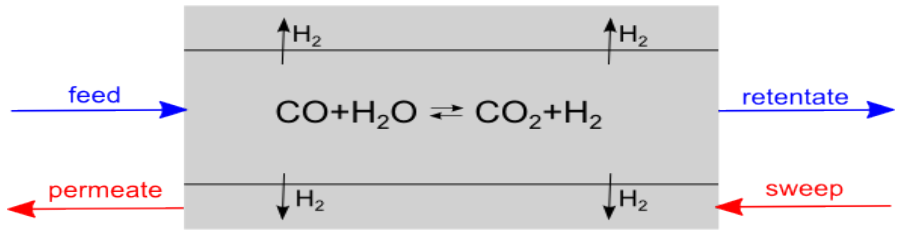


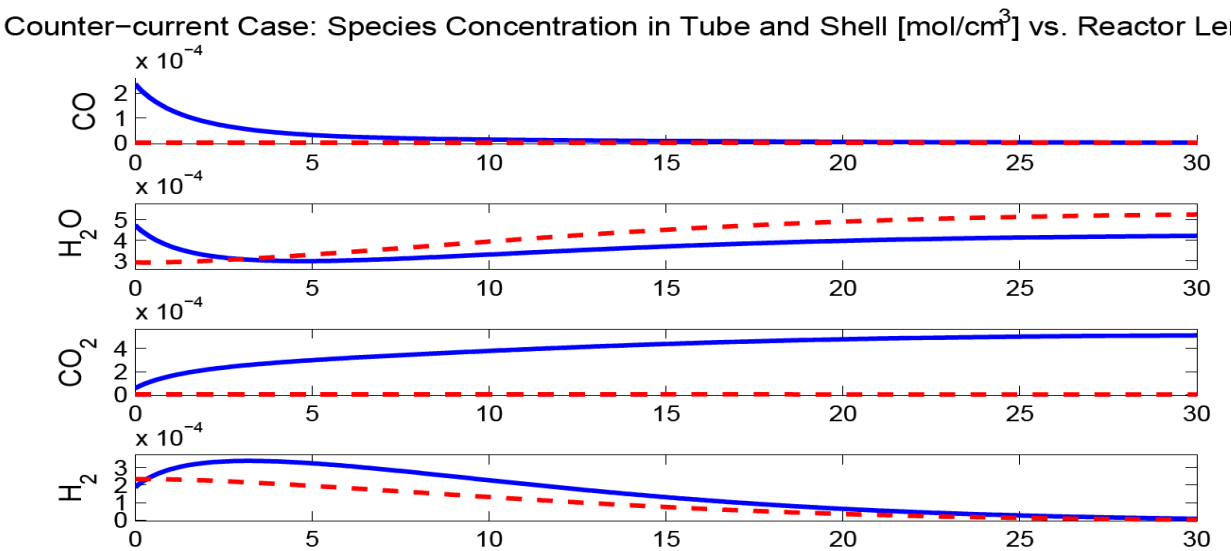
- **Assumptions**
  - **1-dimensional shell and tube reactor**
  - **catalyst packed in tube side**
  - **thin membrane layer placed on surface of tube wall**
  - **sweep gas flows in shell side**
  - **plug-flow operation**
  - **constant temperature and pressure**
  - **steady-state operation**
  -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

- **Flow configurations**
  - **co-current**
  - **counter-current**
- **Simulation conditions**
  - **catalyst type and reaction rate [2]**
  - **reactor dimensions (lab)**
  - **consistent with IGCC specifications**
- **Model used to perform simulation and optimization studies [3]**

(1) Marano, **Report to DOE/NETL** (2010)
(2) Choi and Stenger, **J. Power Sources** 124, 432-439 (2003)
(3) Lima et al., **Ind. Eng. Chem. Res.** 51, 5480-5489 (2012)

Counter-current Simulation Results: Concentration Profiles

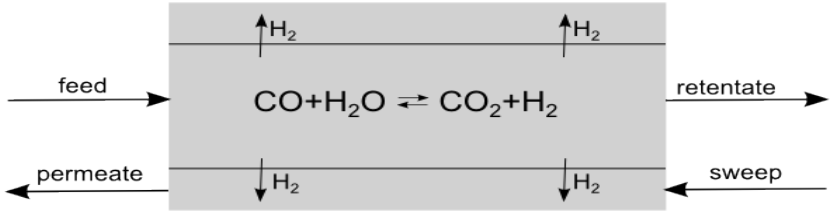




Simulation conditions

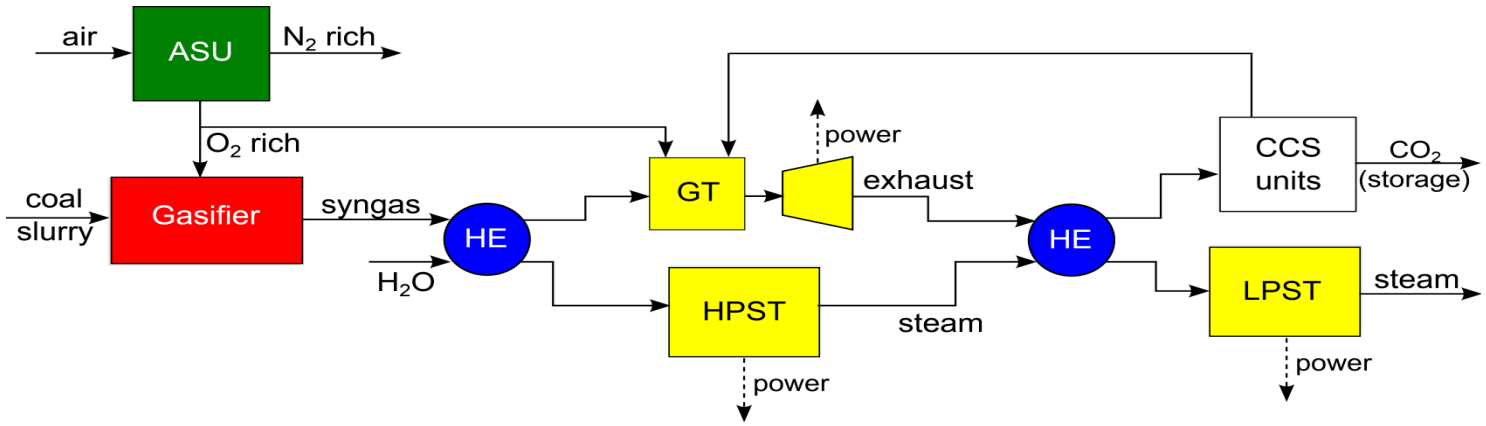
- **MR length of 30 cm**
- **Q_{H2} = 0.1 mol/(s.m^2.atm)**
- **$S_{H2/all}$ = 1000**
- **steam as sweep gas**

Counter-current Simulation Results: Changing Membrane Selectivity



Membrane Reactor Parameter	Value [%] ($S_{H2/all}$ = 1000)	Value [%] ($S_{H2/all}$ = 100)	Value [%] ($S_{H2/all}$ = 10)	Target [%]
$X_{CO} = \frac{\text{CO converted}}{\text{CO in feed}}$	99.84	99.34	**95.02**	**98**
$R_{H_2} = \frac{H_2 \text{ in permeate}}{(H_2+CO) \text{ in feed}}$	99.06	99.00	97.21	**95**
$C_{CO_2} = \frac{(CO+CO_2) \text{ in retentate}}{(CO+CO_2) \text{ in feed}}$	98.97	90.15	**29.07**	**90**
$P_{(CO_2+H_2O),R} = \frac{(CO_2+H_2O) \text{ in retentate}}{\text{total in retentate}}$	96.31	96.62	98.30	**95**
$P_{H_2,P} = \frac{H_2 \text{ in permeate}}{\text{total in permeate}}$	44.27	**43.14**	**34.05**	**44**
$y_{H_2,R} = \frac{H_2 \text{ in retentate}}{\text{total in retentate}}$	0.66	0.51	0.01	**(≤)2**

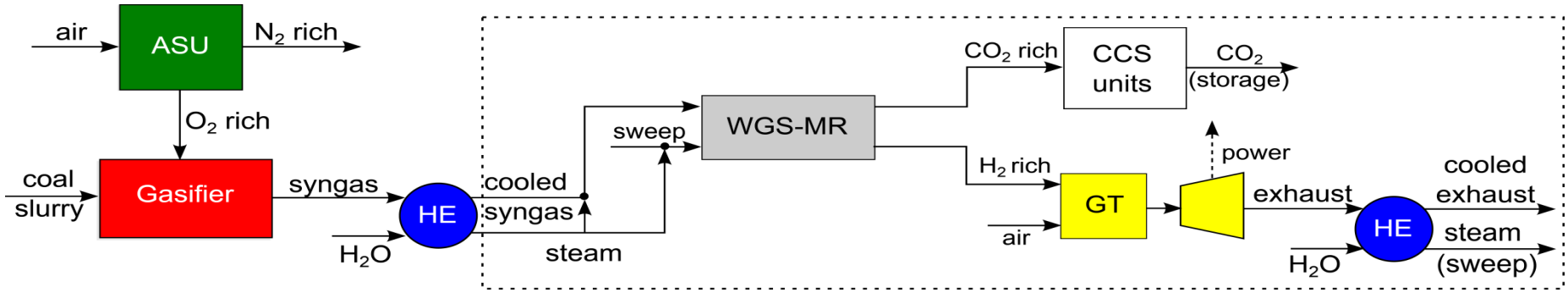
IGCC Plant Modeling Assumptions (MATLAB)



- **Simplified systems-level model of entire process (ASU, gasifier, turbines, and heat exchangers) in MATLAB**
- **Assumptions: few basic components, lumped compartments in gasifier/ turbines, static heat exchanger models (1)**
- **Developed model validated using published simulation data (1)**

(1) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)

Integration of MR into IGCC Plant (MATLAB)

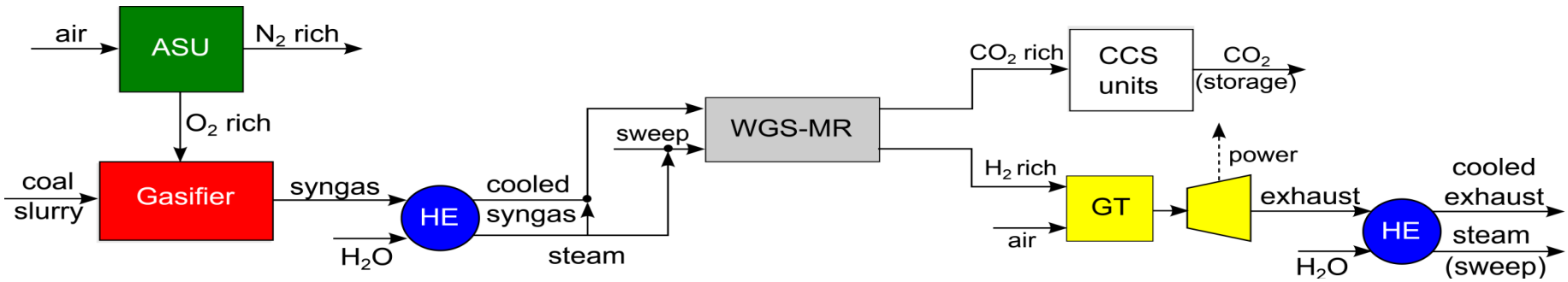


- **Scale up MR model at steady state**
- **MR integration downstream of gasifier** [(1),(2)]
- **Effect on turbines/heat exchangers**
- **Steam integration for MR utilization**

- **Simulation studies performed** [(3)]
- **Novel optimization problem formulated** [(3)]
  - **minimize cost of membrane as function of surface area**
  - **determine optimal operating point that satisfies all constraints**

(1) Marano and Ciferno, **Energy Procedia** 1, 361-368 (2009)
(2) Bracht et al., **Energy Convers. Mgmt** 38, S159-164 (1997)
(3) Lima et al., **Submitted for Publication** (2014)

Integration of MR into IGCC Plant: Simulation Results



- **Process simulation conditions** [1],[2],[3]
  - **$P_t \approx 53$ atm, $P_s \approx 26$ atm**
  - **$T_t \approx 390°C$, $T_s \approx 390°C$**
  - **$S_{H2/all} = 1000$, $Q_{H2} = 0.2$ mol/(s.m^2.atm)**
  - **$A_m = 6800$ m^2**

- **Performance variables** [2]
  - **carbon capture**

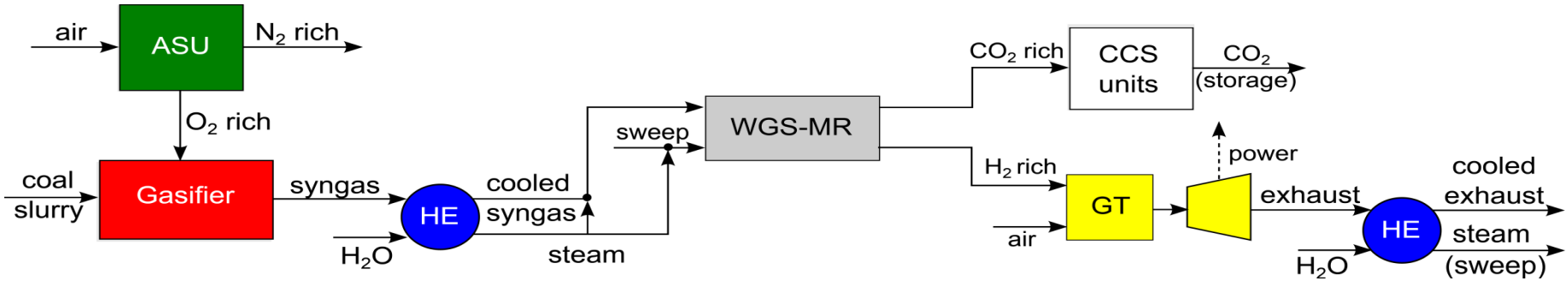
$$C_{CO_2} = \frac{\text{carbon captured}}{\text{carbon in feed}} = 98.54\%$$

  - **power generation**

$$W = 614.07 \text{ MW}$$

(1) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)
(2) Haslbeck et al., **Baseline Report to DOE/NETL** (2010)
(3) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)

IGCC-MR Simulation Results: Changing Membrane Characteristics

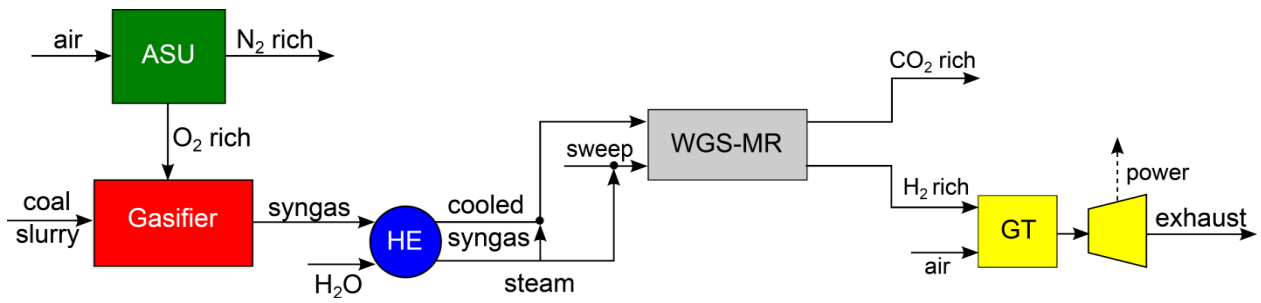


IGCC Performance Variable	Nominal ($S_{H2/all}$ = 1000, Q_{H2} = 0.2)	Case I ($S_{H2/all}$ = 100, Q_{H2} = 0.2)	Case II ($S_{H2/all}$ = 1000, Q_{H2} = 0.1)
$C_{CO_2} = \frac{\text{carbon captured}}{\text{carbon in feed}}$ [%]	98.54	**85.97**	99.35
W = power generated [MW]	614.07	622.95	**550.07**

Q_{H2} = mol/(s.m^2.atm)

IGCC-MR Differential Cost Analysis

- **Cost comparison between IGCC with and without MR**
- **Same amount of coal and power generation (≈ 615 MW)**
- **Cost differences**
  - **larger ASU (IGCC) (1): ≈ $290 million/30 years**
  - **steam and gas turbines differences (IGCC) (1): ≈ $40 million/30 years; ≈ $117 million/30 years (with oxy-combustion corrections);**
  - **extra heat exchangers (IGCC-MR) (2): $3.78 million/30 years**
  - **added MR with A_m ≈ 5000 m^2 (IGCC-MR nominal): ≈ $5-50 million/lifetime**



(1) Haslbeck et al., **Baseline Report to DOE/NETL** (2010)
(2) Turton et al., **Analysis, Synthesis and Design of Chemical Processes** (2012)

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  - added MR with A_m ≈ 5000 m^2 (IGCC-MR nominal): ≈ $5-50 million/lifetime
- **Calculate MR cost to break even in a 30 year period**
- **Results based on present value of annuity calculation [3] – nominal case**

Lifetime [year]	Cost [$/m^2]	Cost Corrected [$/m^2]
1	5,840	7,210
2	11,680	14,420
3	17,520	21,630

(1) Haslbeck et al., **Baseline Report to DOE/NETL** (2010)
(2) Turton et al., **Analysis, Synthesis and Design of Chemical Processes** (2012)
(3) Lima et al., **Submitted for Publication** (2014)

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  - **extra heat exchangers (IGCC-MR) (2): $3.78 million/30 years**
  - **added MR with A_m ≈ 4700 m^2 (IGCC-MR Case I): ≈ $4.7-47 million/lifetime**
- **Calculate MR cost to break even in a 30 year period**
- **Results based on present value of annuity calculation (3) – Case I**

Lifetime [year]	Cost [$/m^2]	Cost Corrected [$/m^2]
1	6,170	7,620
2	12,340	15,240
3	18,510	22,860

(1) Haslbeck et al., **Baseline Report to DOE/NETL** (2010)
(2) Turton et al., **Analysis, Synthesis and Design of Chemical Processes** (2012)
(3) Lima et al., **Submitted for Publication** (2014)

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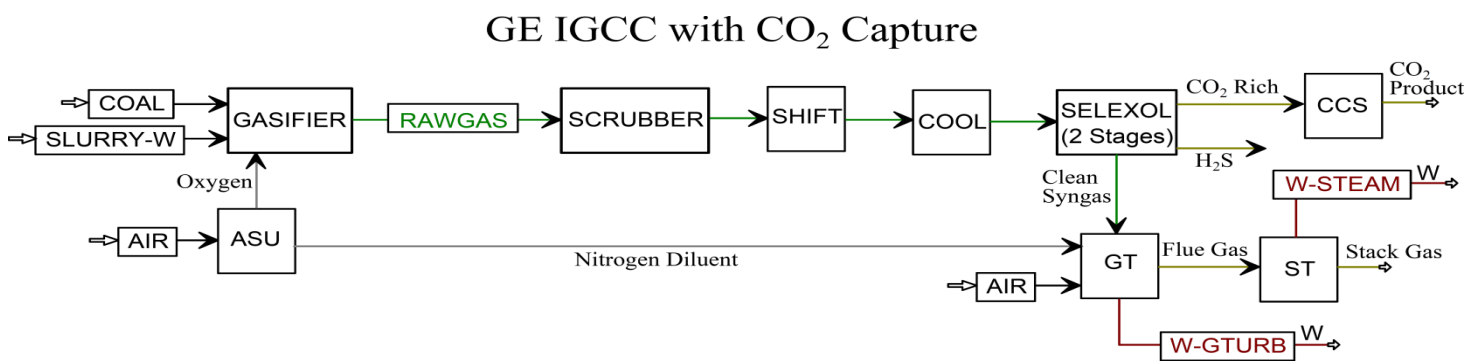
  - extra heat exchangers (IGCC-MR) [2]: $3.78 million/30 years
  - added MR with A_m ≈ 7300 m^2 (IGCC-MR Case II): ≈ $7.3-73 million/lifetime
- **Calculate MR cost to break even in a 30 year period**
- **Results based on present value of annuity calculation [3] – Case II**

Lifetime [year]	Cost [$/m^2]	Cost Corrected [$/m^2]
1	3,910	4,860
2	7,820	9,720
3	11,730	14,580

(1) Haslbeck et al., **Baseline Report to DOE/NETL** (2010)
(2) Turton et al., **Analysis, Synthesis and Design of Chemical Processes** (2012)
(3) Lima et al., **Submitted for Publication** (2014)

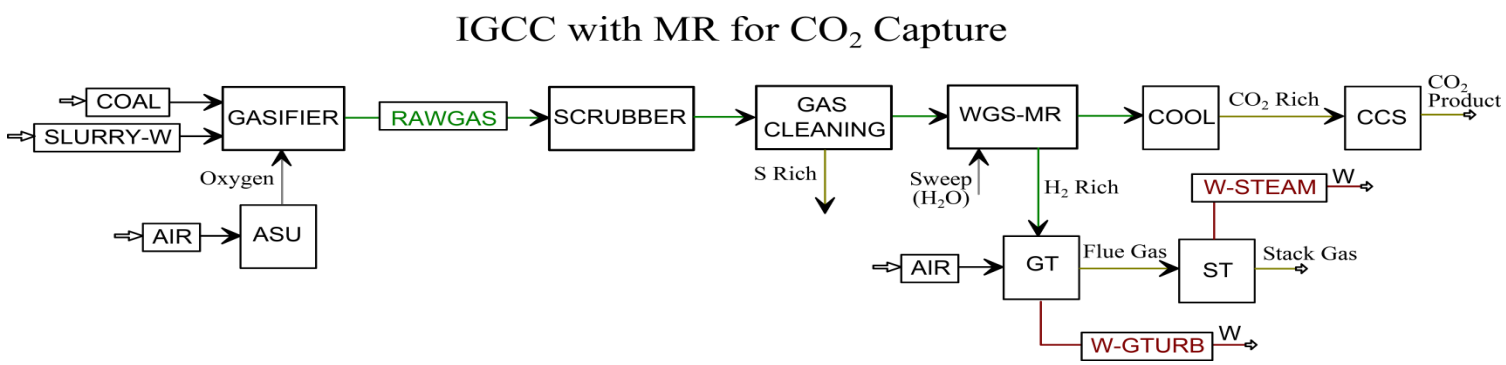
Integration of MR into IGCC Flowsheet (Aspen)



- **MR integration into Aspen flowsheet**
  - **used available baseline IGCC model (MITEI) [1]**
  - **MR model implemented in Aspen Custom Modeler**
  - **model incorporated into IGCC baseline model**
- **Simulation & techno-economic analysis (Ongoing)**
  - **feasibility of replacing current technology (CO shift followed by physical absorption) for CO_2 capture**
  - **achieve DOE target goal for CO_2 capture and satisfy stream constraints**

(1) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)

Integration of MR into IGCC Flowsheet (Aspen)



- **MR integration into Aspen flowsheet**
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(1) Field and Brasington, **Ind. Eng. Chem. Res.** 50, 11306-11312 (2011)

Modeling Conclusions

- **Conclusions**
  - **MR model developed and integrated into IGCC process model in MATLAB**
  - **Simulation and optimization studies for IGCC-MR plant performed**
    - **simulation results indicated successful nominal case**
    - **novel constrained optimization problem formulated and solved**
  - **Techno-economic assessment of IGCC-MR process completed (MATLAB)**
  - **MR cost analysis showed break even costs within feasible range**
- **Ongoing work (Aspen)**
  - **IGCC-MR base case flowsheet developed**
  - **Preliminary simulation studies and techno-economic analysis indicated MR costs within the feasible range**

Outline

Introduction: Zeolite Membranes from nanosheets and 2-dimensional zeolites

Techno-economic Evaluation

Exfoliation Studies (Key issue: exfoliation with structure preservation)

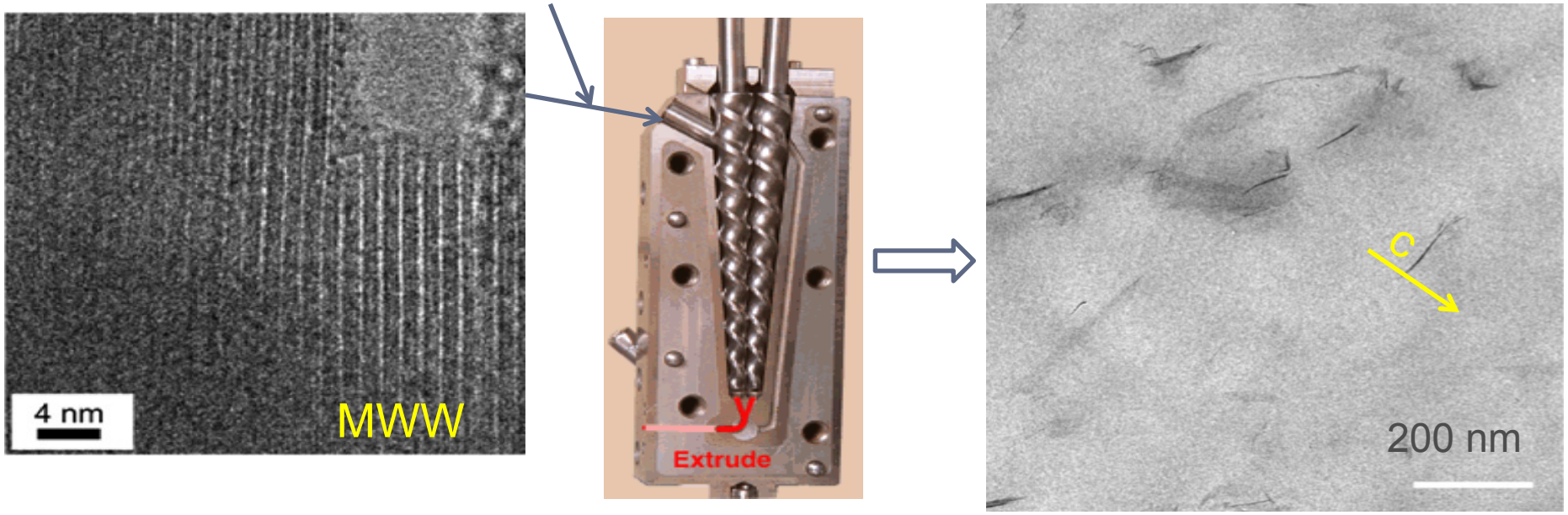
Membrane Preparation Approaches

Permeation and Stability Results

Conclusions and Outlook

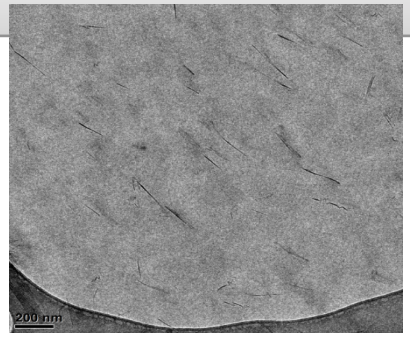
Exfoliated zeolite nanosheets by “melt-blending”

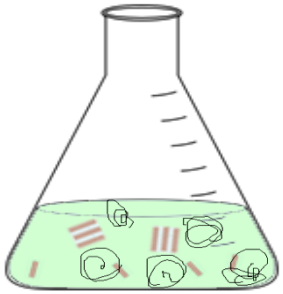
Layered zeolite & Polymer



S. Maheshwari, E. Jordan, S. Kumar, F. S. Bates, R. L. Penn, D. F. Shantz, M. Tsapatsis, **J. Am. Chem. Soc.** 2008, *130*, 1507-1516;
“Layered Zeolite materials and Methods Related Thereto” Tsapatsis M., Maheshwari S., Koros W. and Bates F.S., US Patent 8,501,068 B2 (2013)

Density Gradient Centrifugation DGC





Dissolution in toluene

Dissolved nanocomposite (ρ=0.87)

Cholorobenzene (ρ = 1.10)

40000g

(ρ = 0.82)

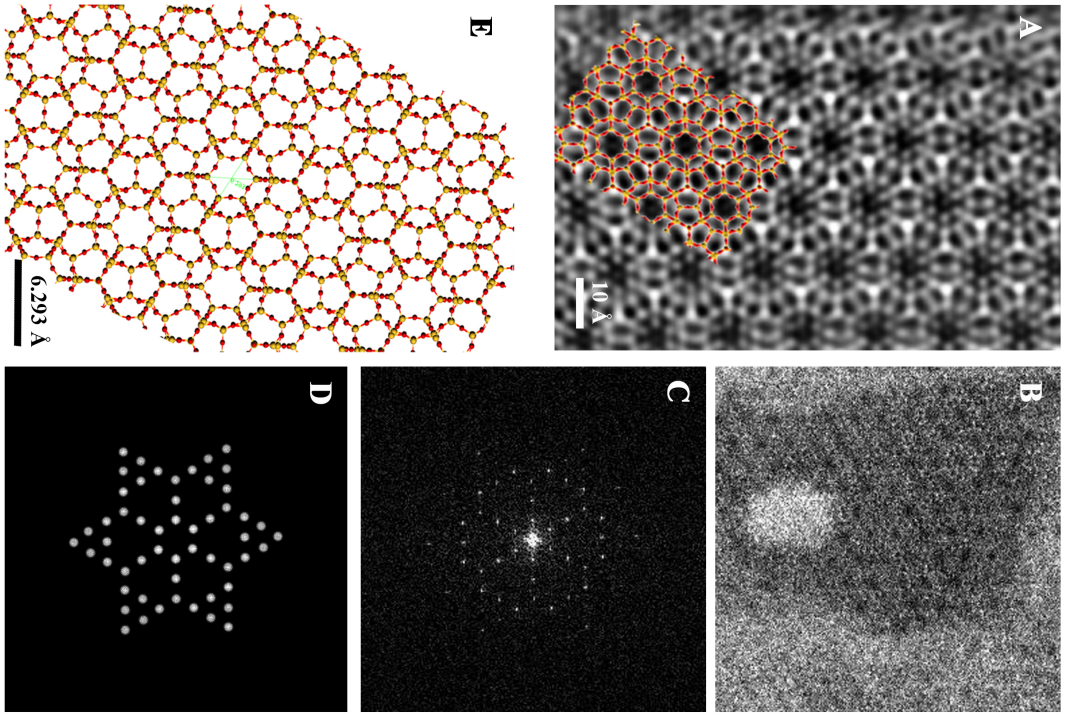
(ρ = 1.10)

(ρ = 1.33)

(ρ = 1.48)

12000g

2-dimensional MWW obtained by MB followed by DGC

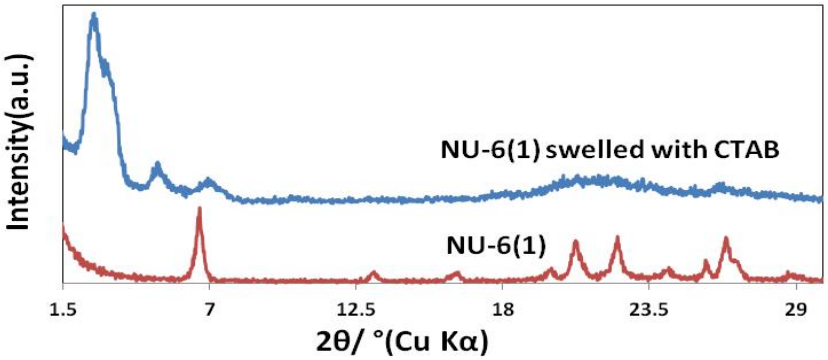


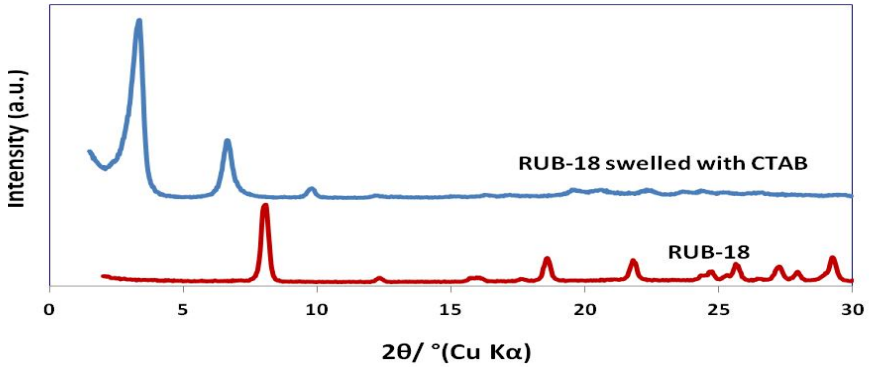
K. Varoon (Agrawal), X. Zhang, B. Elyassi, D. D. Brewer, M. Gettel, S. Kumar, J. A. Lee, S. Maheshwari, A. Mittal, C.-Y. Sung, M. Cococcioni, L. F. Francis, A. V. McCormick, K. A. Mkhoyan, and M. Tsapatsis. **Science** 2011, 334, 72.

Kumar Varoon Agrawal, Topuz B., Navarro M., Nguenkam K., Elyassi B., Francis L.F., Tsapatsis M. **AIChE Journal** 59(9), 3459-3467 (2013)

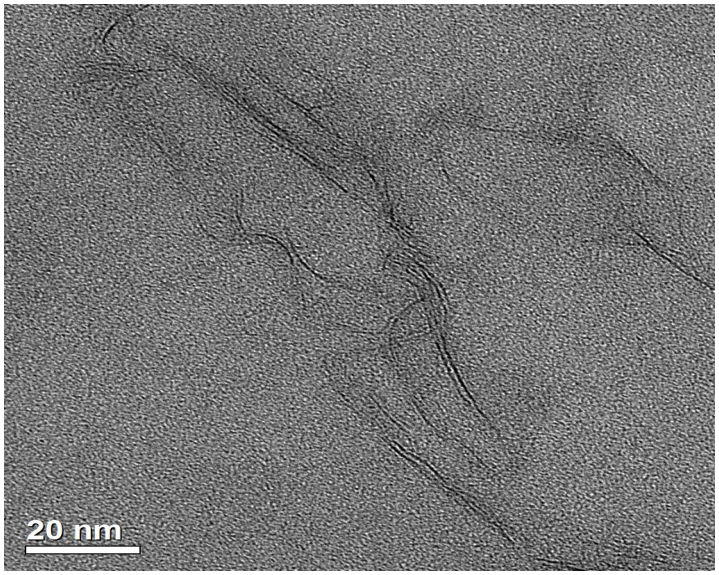
Exfoliation of Nu-6(1) and RUB-18 by melt compounding

XRD patterns

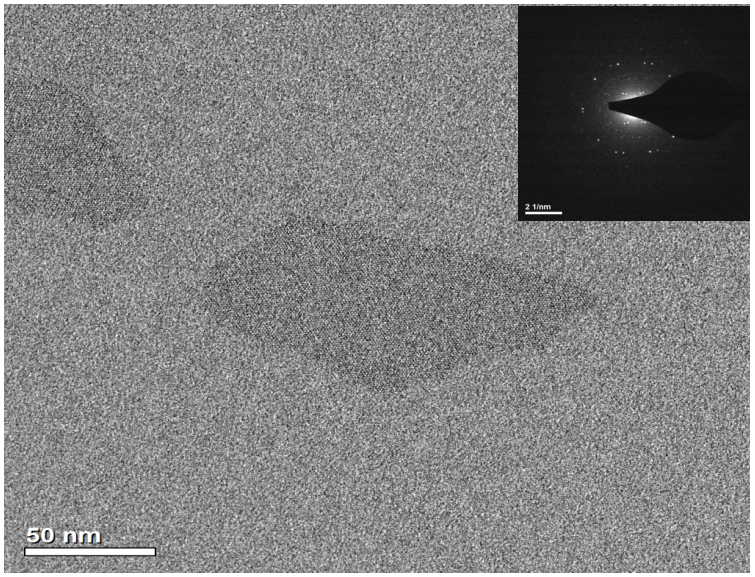




TEM imaging



Exfoliated NU-6(1)



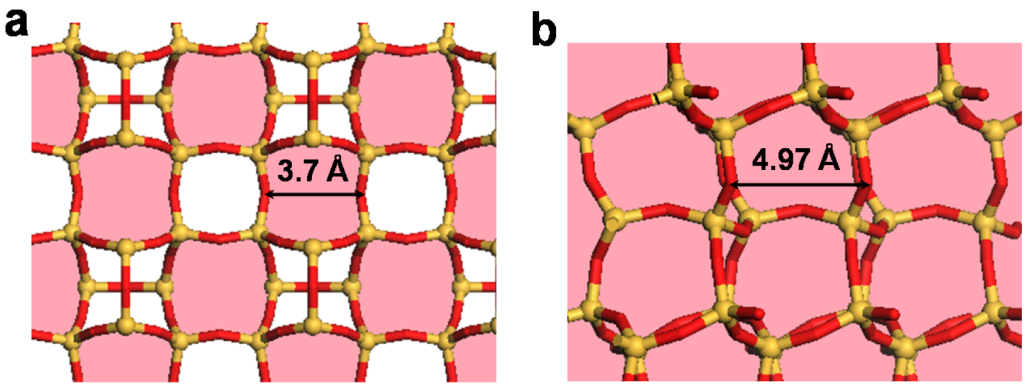
RUB-18

MB&DGC vs. other exfoliation approaches

Other exfoliation approaches explored:
Ball milling, solution-based exfoliation with ultrasonication, gallery functionalization and rapid thermal processing

MB and DGC remains best method for exfoliation-yield and structure preservation

Other potentially hydrogen-selective layers were exfoliated by this approach



Outline

Introduction: Zeolite Membranes from nanosheets and 2-dimensional zeolites

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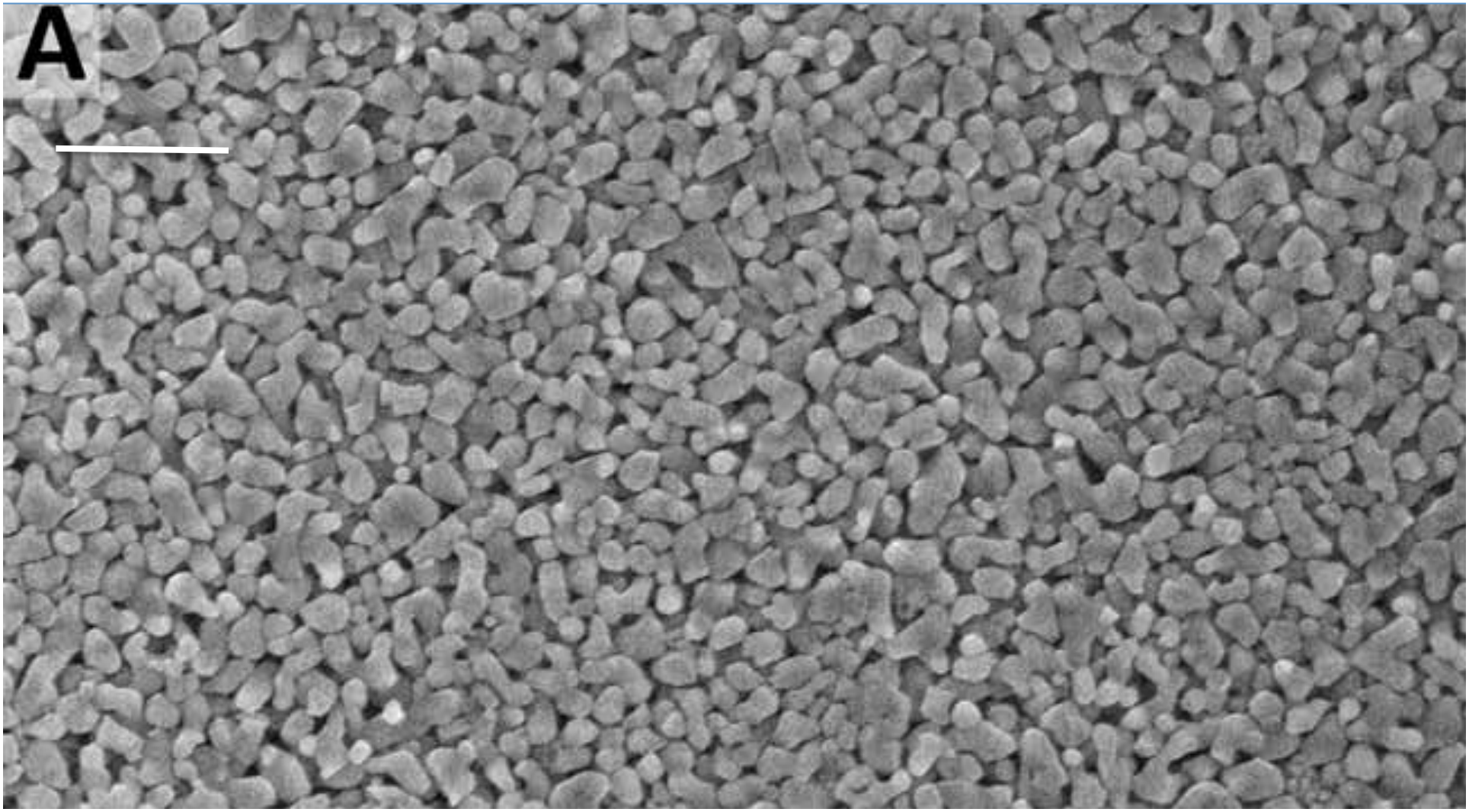
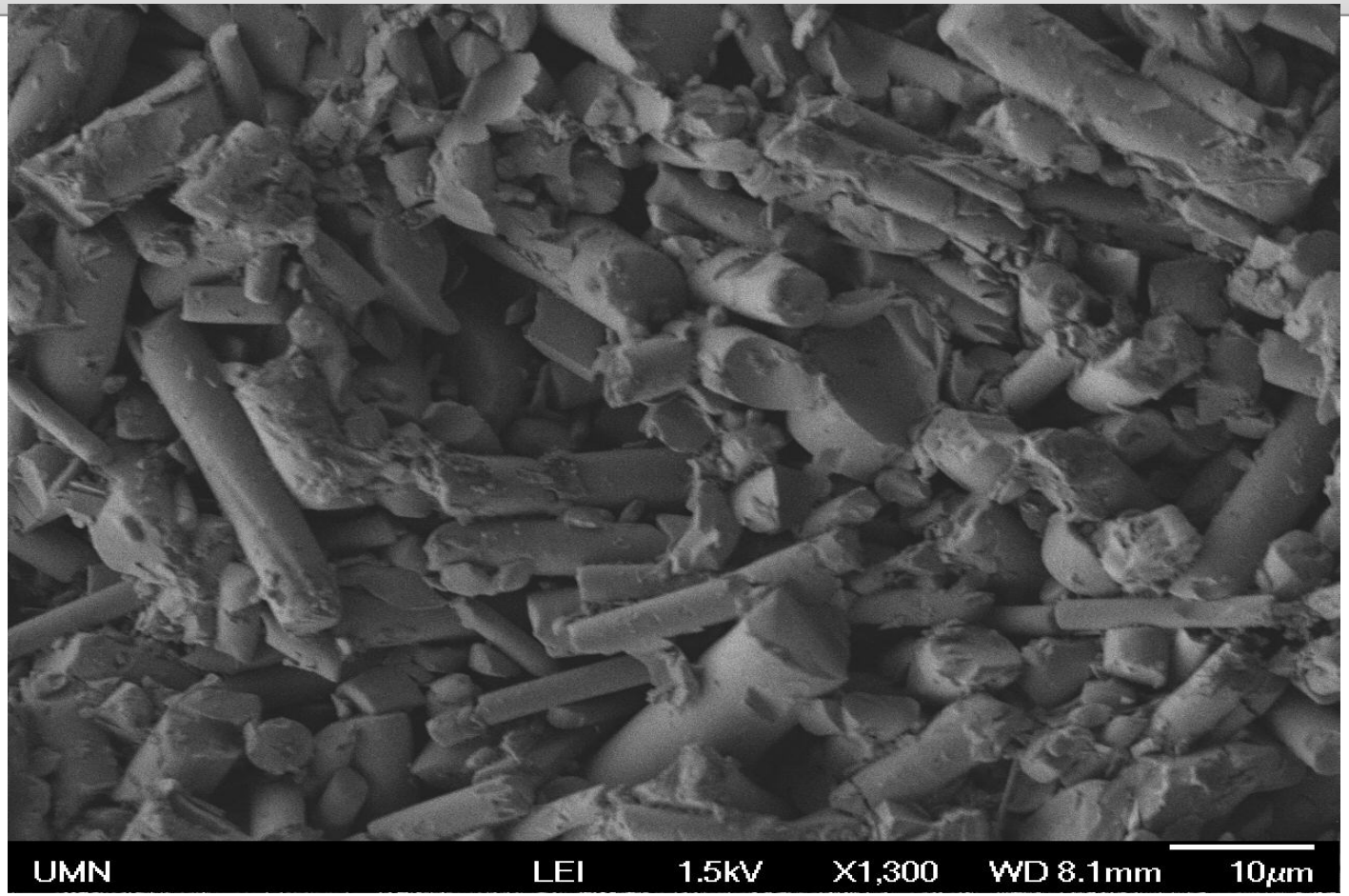
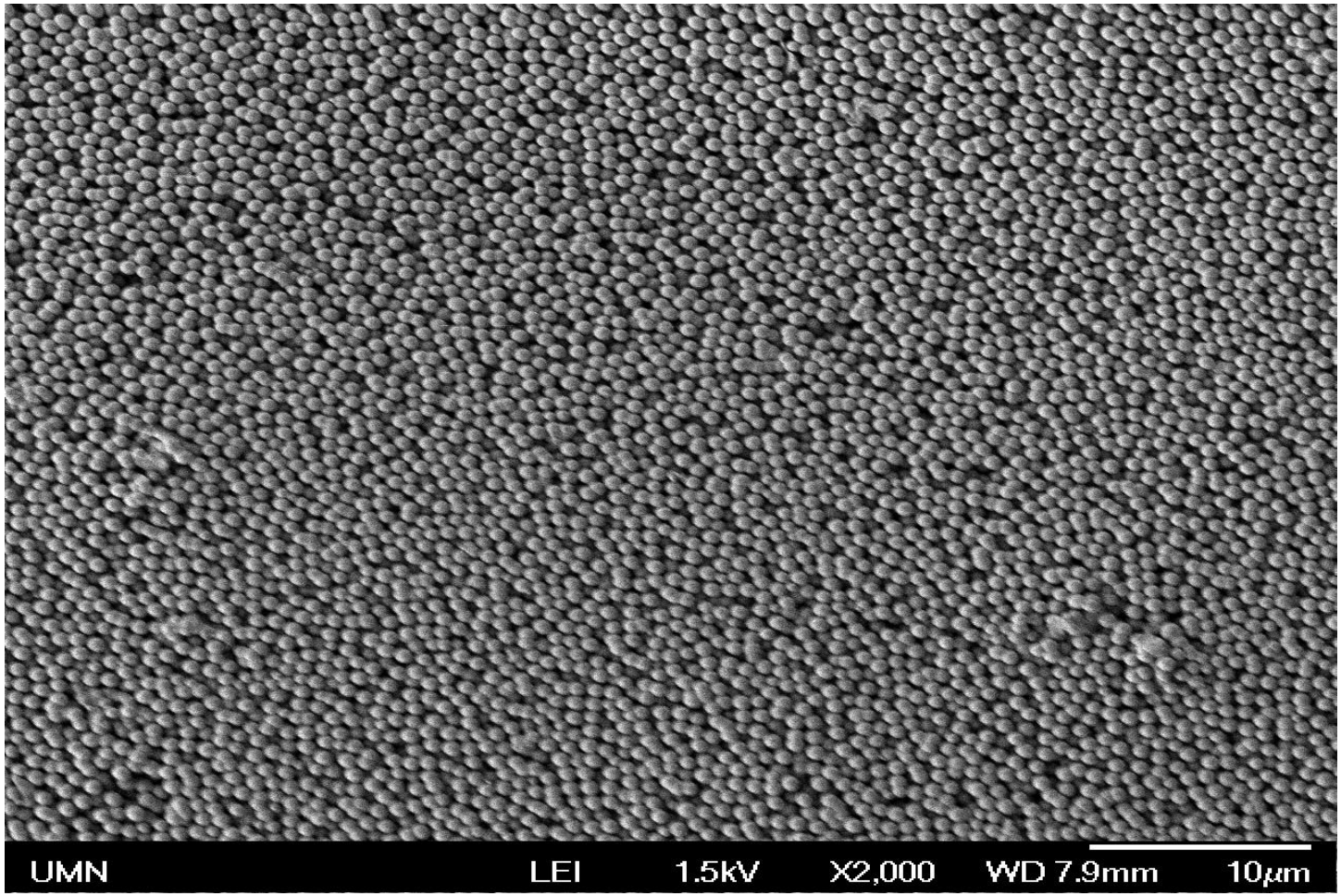
Flat alumina support (smooth surface)



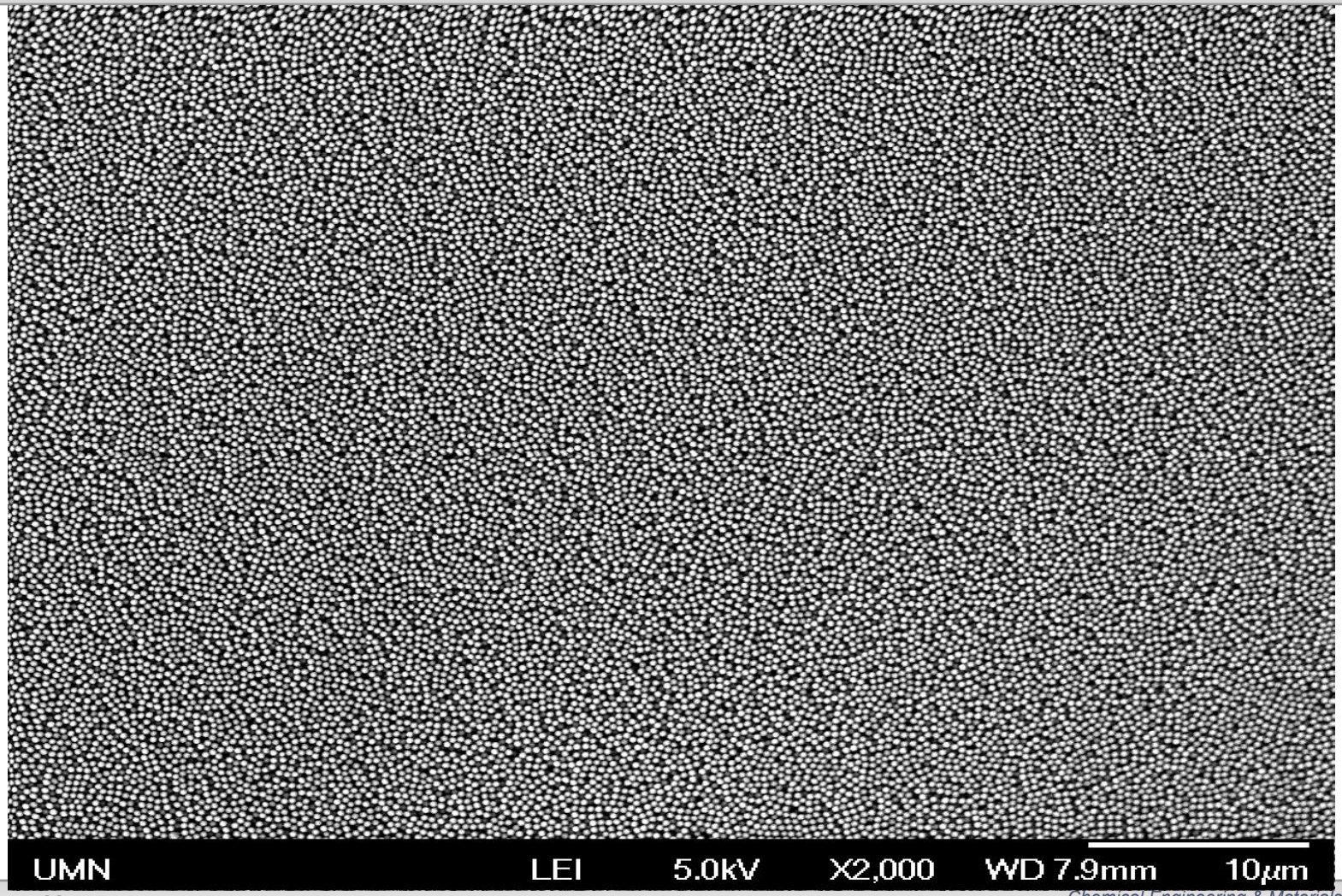
Flat silica supports
(developed under ARPAE support)



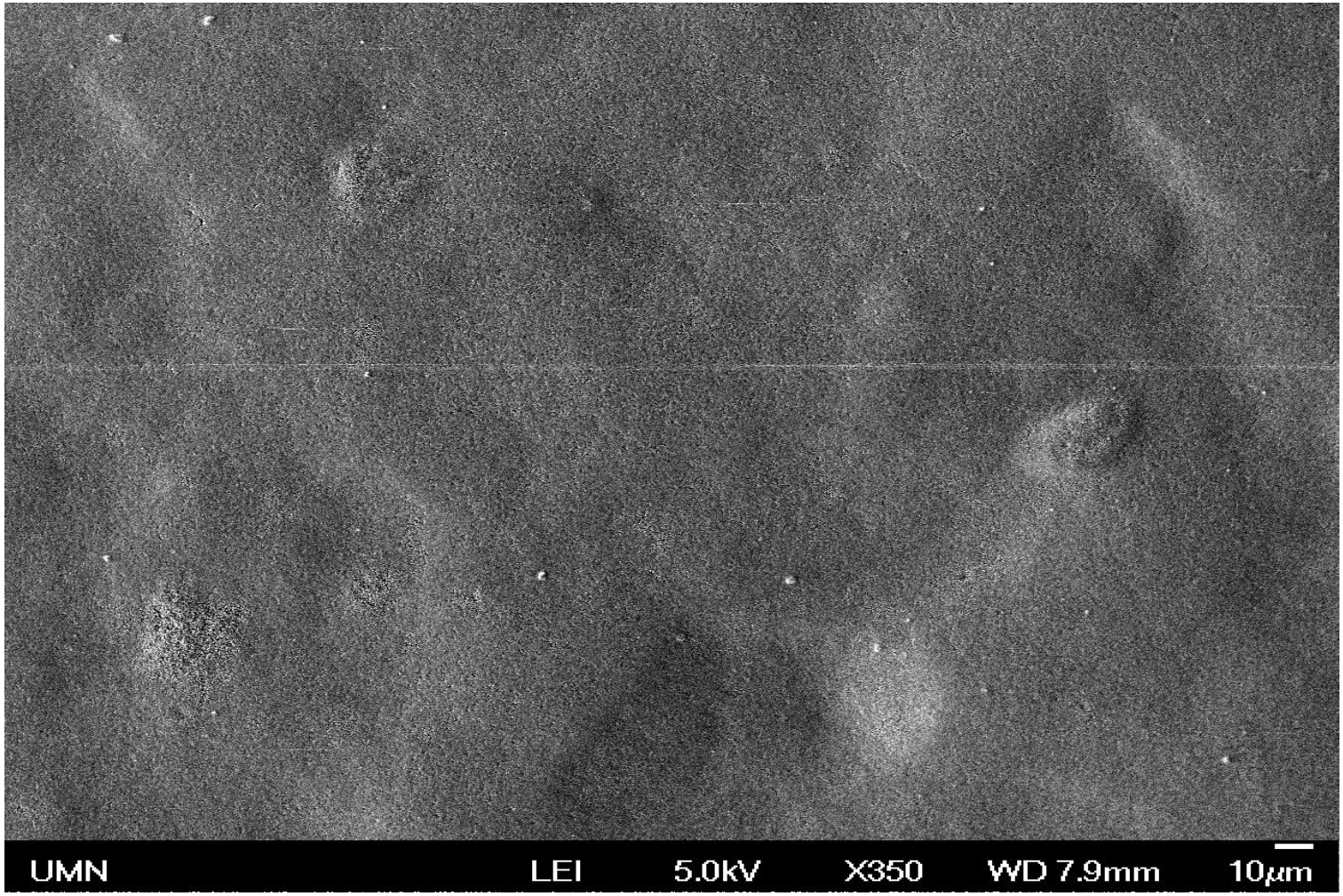
Coating with 1micron Stober 4wt% in ethanol



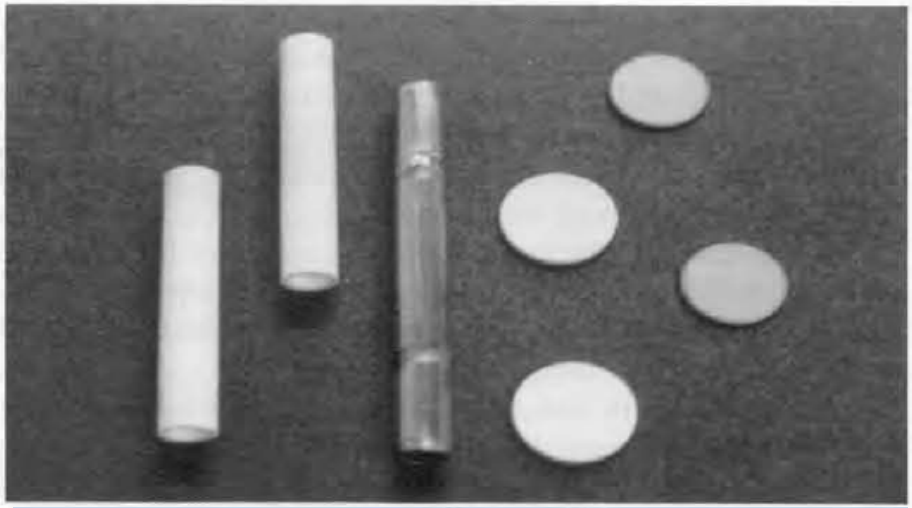
Coat with 350nm Stober 5wt% in ethanol



Coat with 50nm Stober in ethanol



Membrane supports



Morigami, Y; Kondo, M; Abe, J; Kita, H; Okamoto, K
SEPARATION AND PURIFICATION TECHNOLOGY
25, 251-260 (2001)

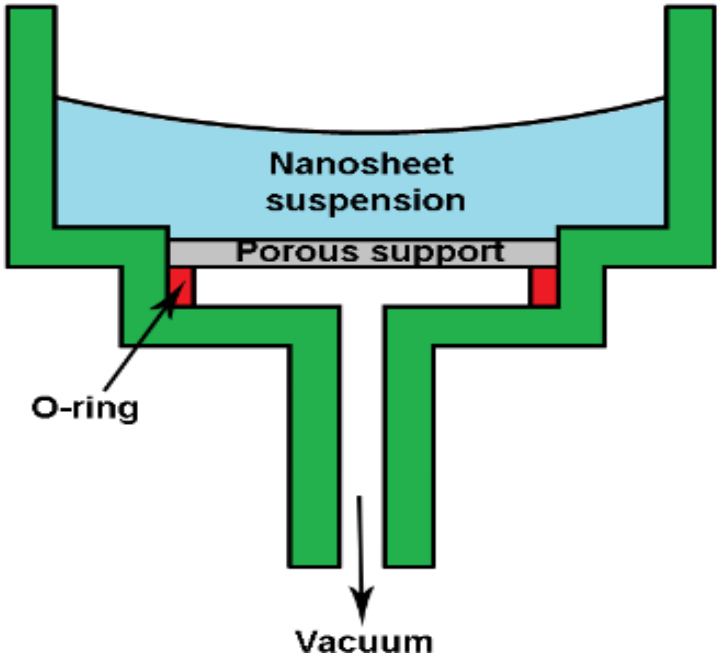
Caro, Juergen; Noack, Manfred
MICROPOROUS AND MESOPOROUS MATERIALS
115, 215-233 (2008)

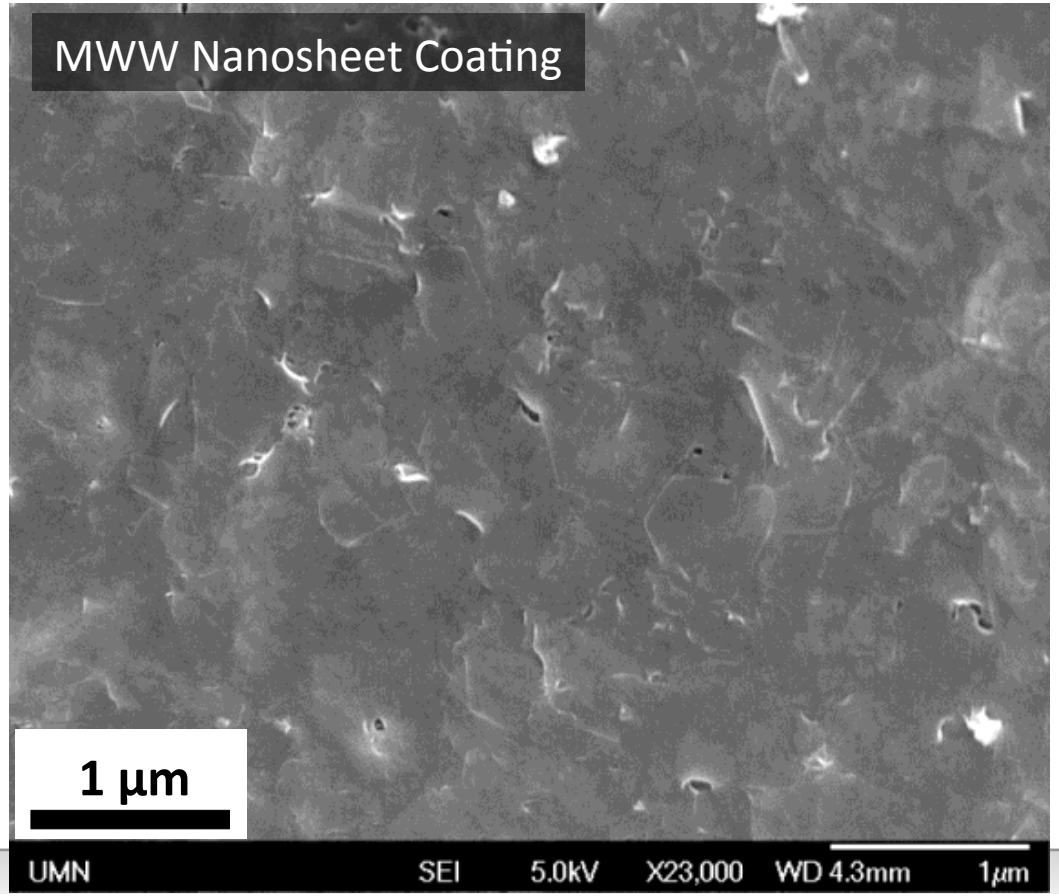
Kanezashi, Masakoto; O'Brien, Jessica; Lin, Y. S.
JOURNAL OF MEMBRANE SCIENCE
286, 213-222 (2006)

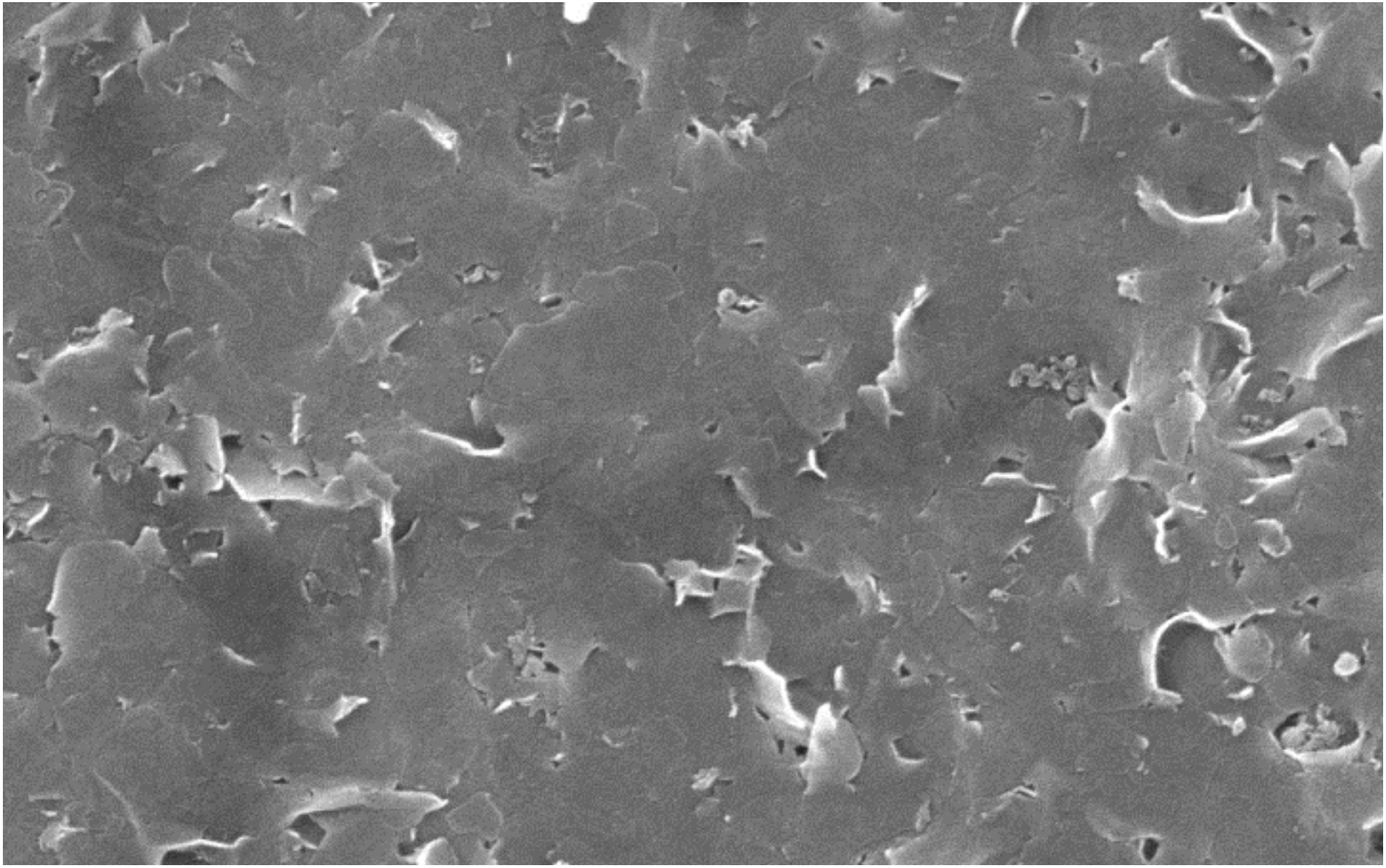
Mahajan, R; Koros, WJ
POLYMER ENGINEERING AND SCIENCE 42
1432-1441 (2002)

Oriented film by simple filtration

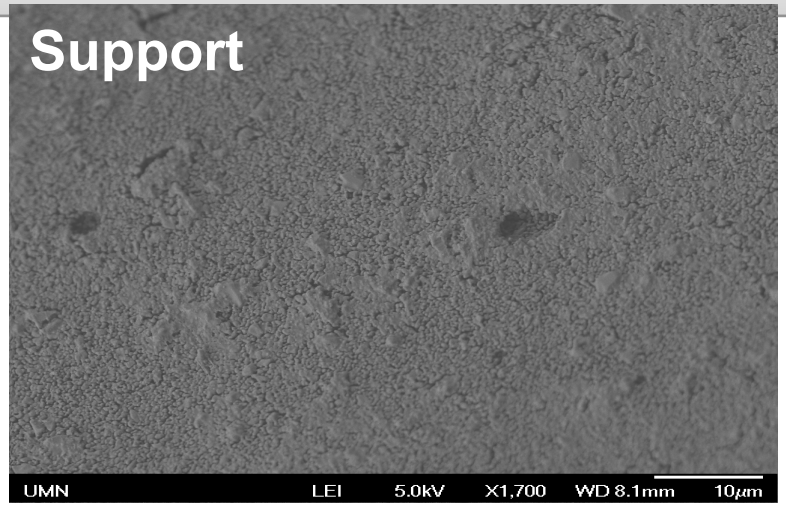
1. Simple filtration of the nanosheet suspension through a porous support.
2. Due to their large lateral size, nanosheet film does not penetrate the 200-nm wide pores of the support.

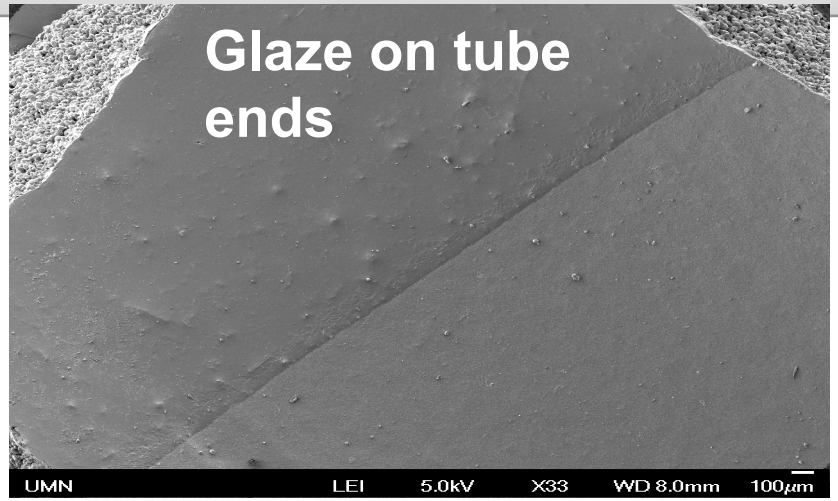




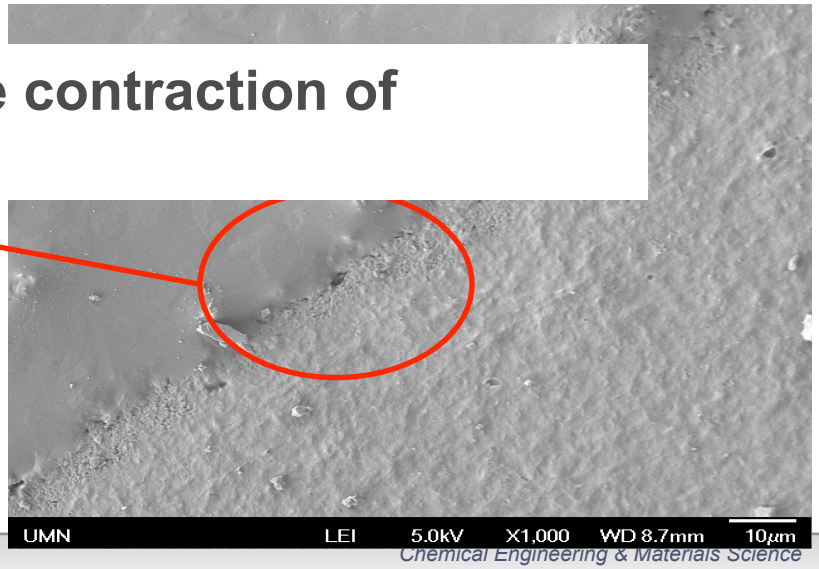


Nanosheet coating on alumina tubes





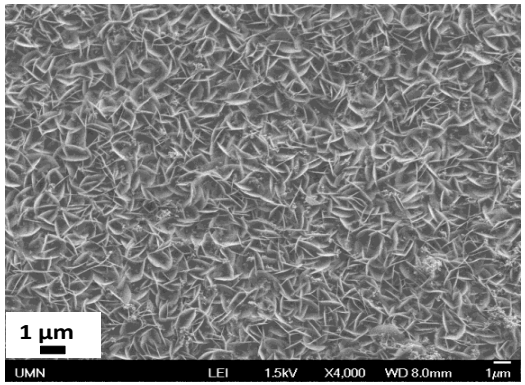
Leak areas due to the contraction of nanosheet film

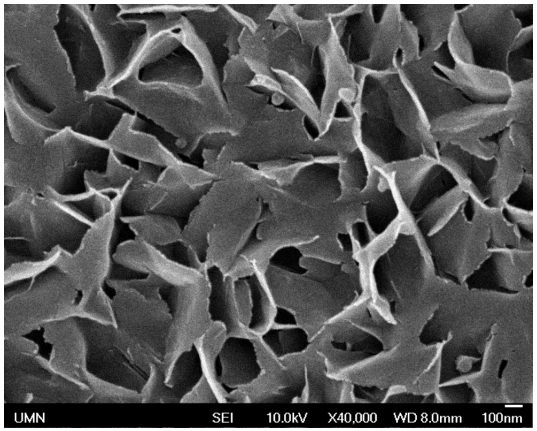


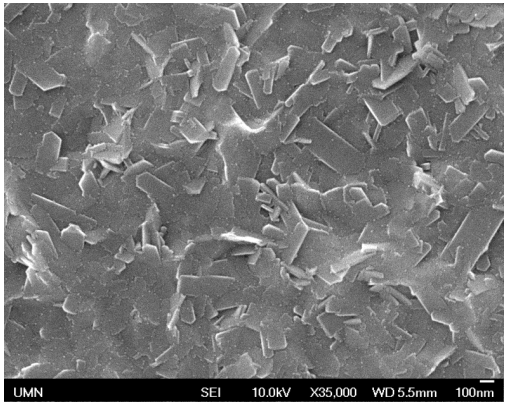
Objective: c-oriented MWW membranes

Secondary growth methods for MWW

- **Pre-crystallization of the gel and secondary growth**
- **Gel-free growth : with impregnated SDA**
- **Gel-free growth: MWW/MFI mixed matrix membrane**







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Summary of permeation results

Target at 500°C
H_2/CO_2 = 80 H_2/N_2 = 600 H_2-permeance=0.06-0.12 mol/m^2-s-atm

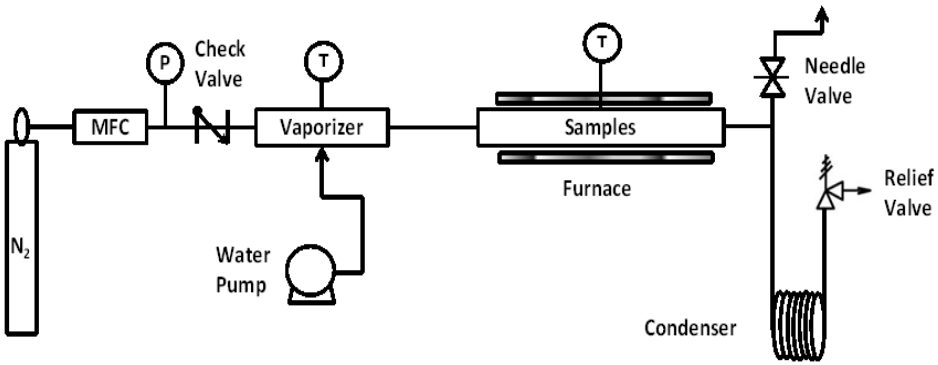
Achieved at 350°C (sealing problems did not allow higher T tests; current hydrothermal stability prohibits use above 350°C)
H_2/CO_2 = 30 H_2/N_2 = 150 H_2-permeance=0.05 mol/m^2-s-atm
[~300GPU or ~ 100 SCFH/ft^2-100psi **Δ**P]

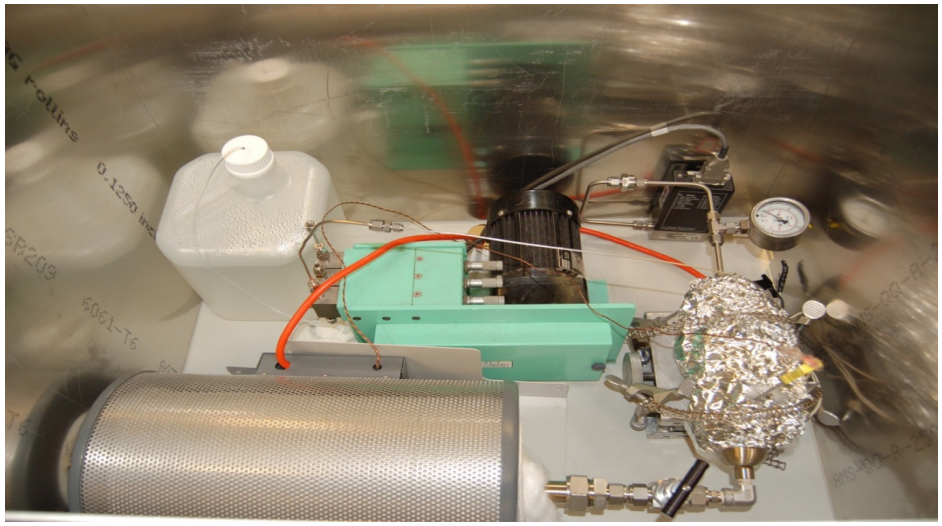
Membrane performance deteriorates by steaming at 350°C

Water and CO permeance have not been investigated.

Steam stability

- Temperature: 350°C (and 600 °C)
- Pressure: 10 bar (95% steam, 5% nitrogen)
- Samples were analyzed in 21 days intervals for 84 days





Steam stability of MCM-22, ITQ-1, and $SiCl_4$-treated ITQ-1

Gel-free growth method for MWW with HMI/TMAdaOH as the SDA

Substrates: Silica and alumina

↓

Coating: MWW nanosheets. Calcination

↓

Impregnation for 40s in OSDA aq. soln.:

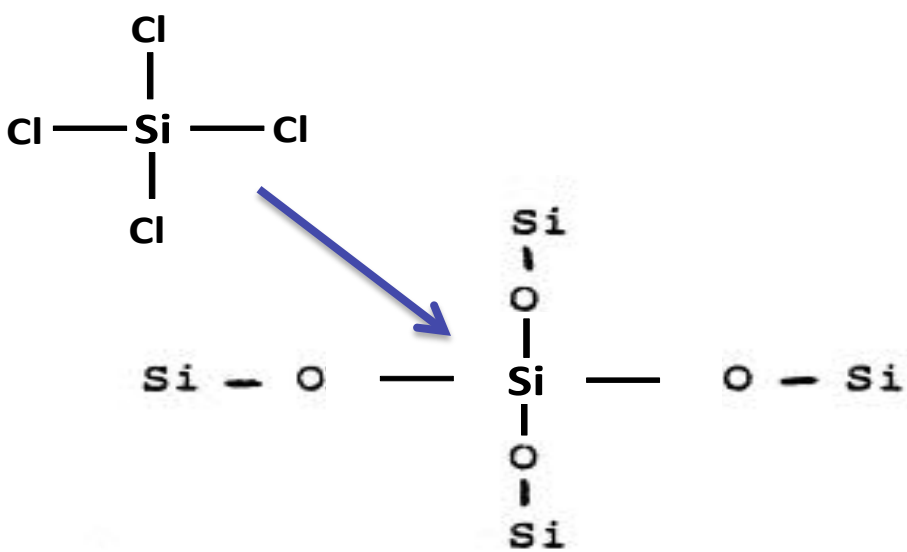
1) HMI (Conc. = 0.1 M – 1 x 10^{-4})
2) TMAdaOH (Conc. 0.025 M)

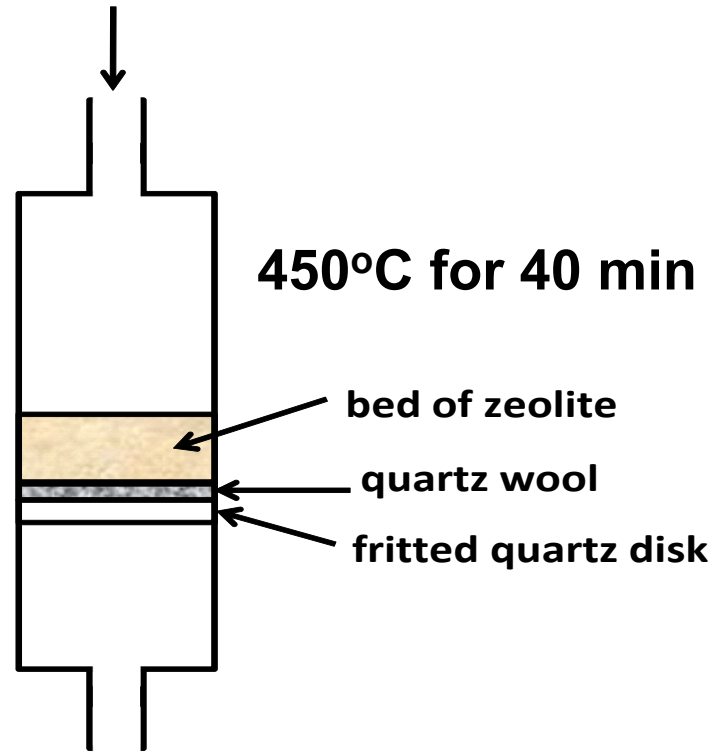
↓

Hydrothermal treatment temperatures: 190°C – 75°C
Growth time: 6h – 48h. Calcination.

Treating ITQ-1 with $SiCl_4$ to heal structural defects

Flow of nitrogen saturated with $SiCl_4$ vapor at room temperature

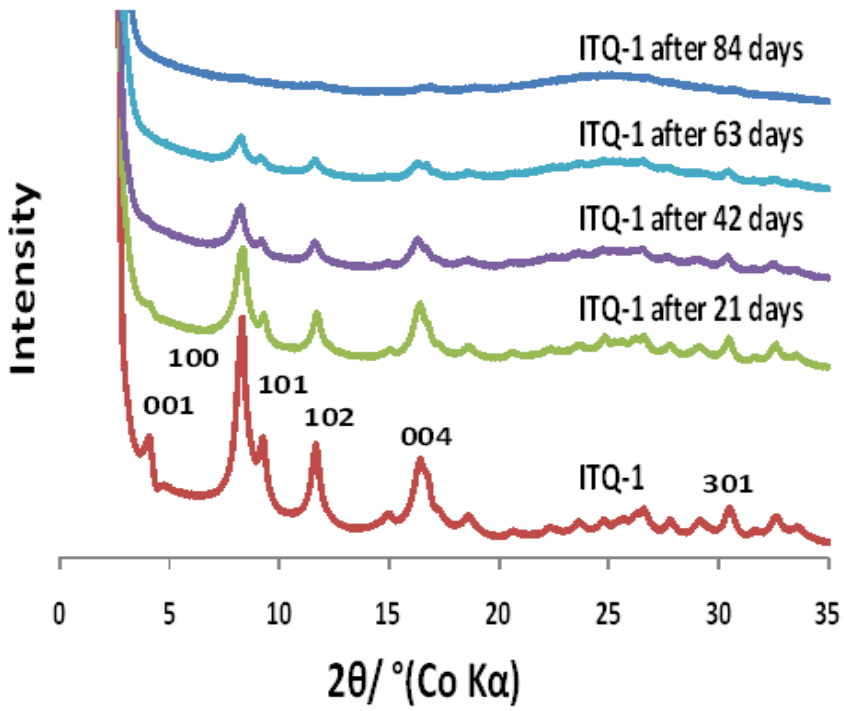


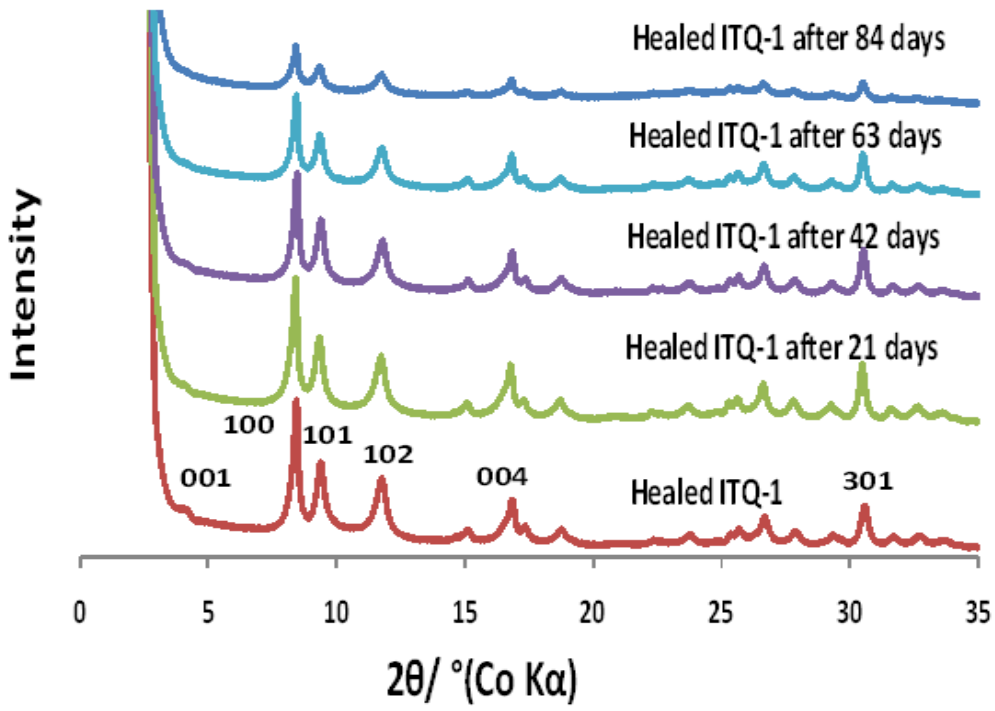


Beyer et. al., J . Chem. Soc., Faraday Trans. 1, 1985, 81, 2889-2901.

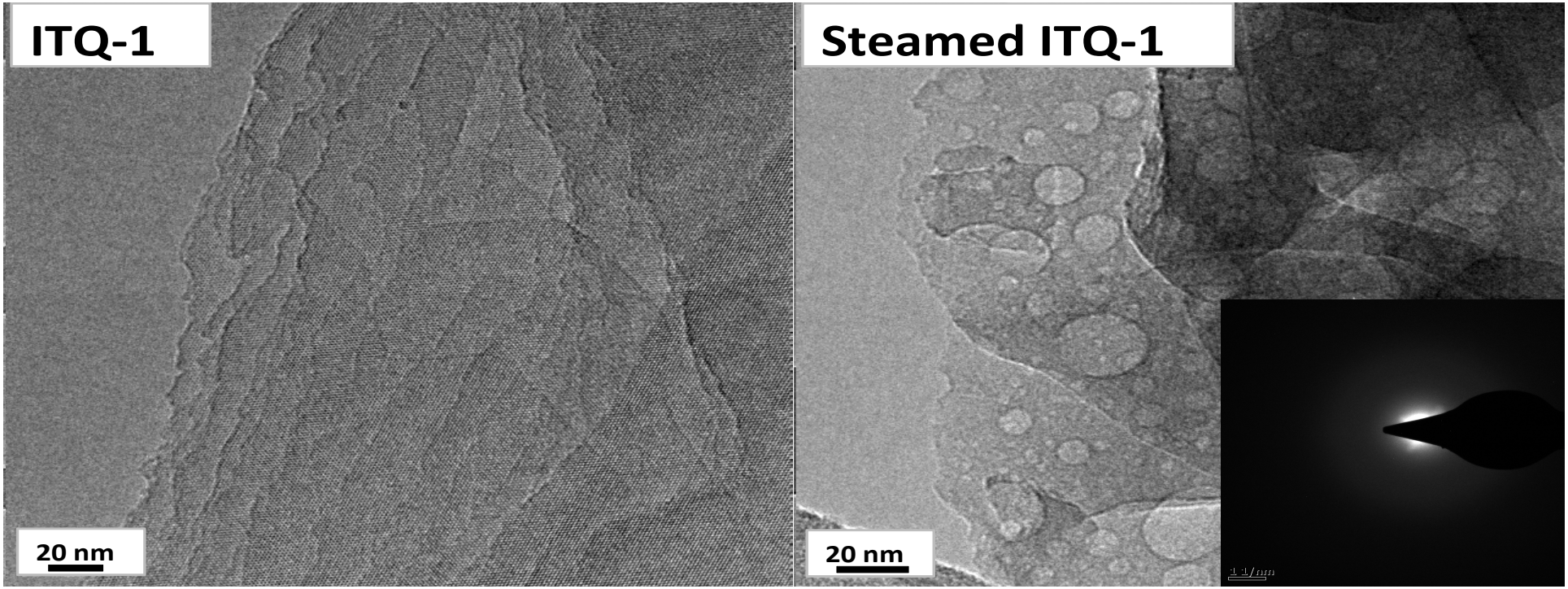
XRD of ITQ-1 and ITQ-1 treated with $SiCl_4$ at 350°C

- $SiCl_4$ treatment is effective in improving the hydrothermal stability of ITQ-1

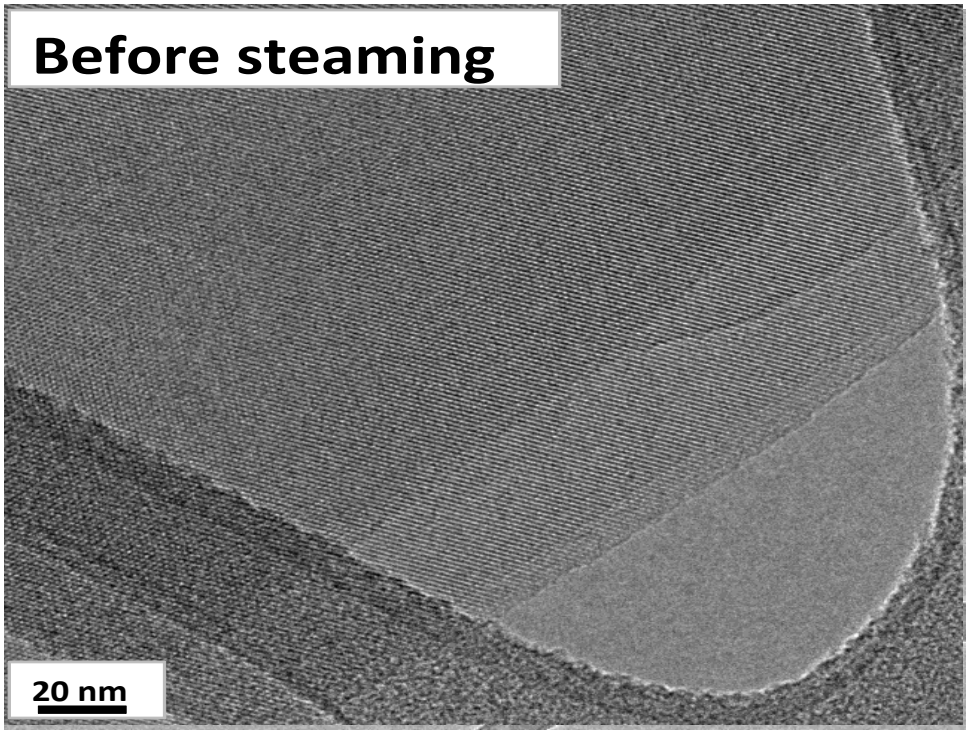


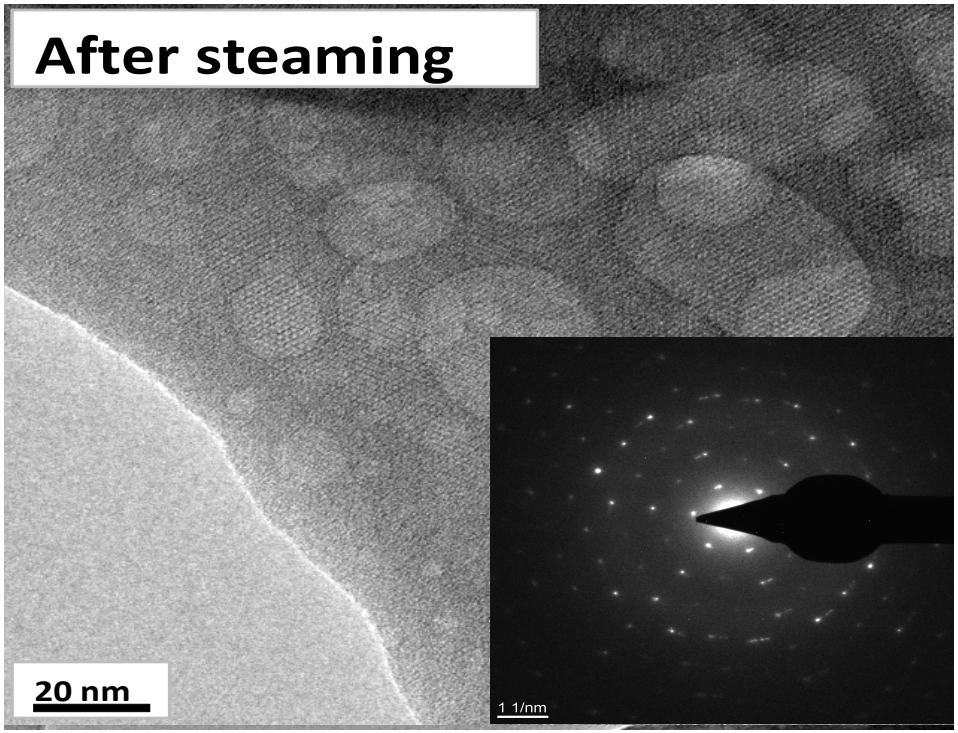


TEM images of **ITQ-1** before and after 84 days of steaming

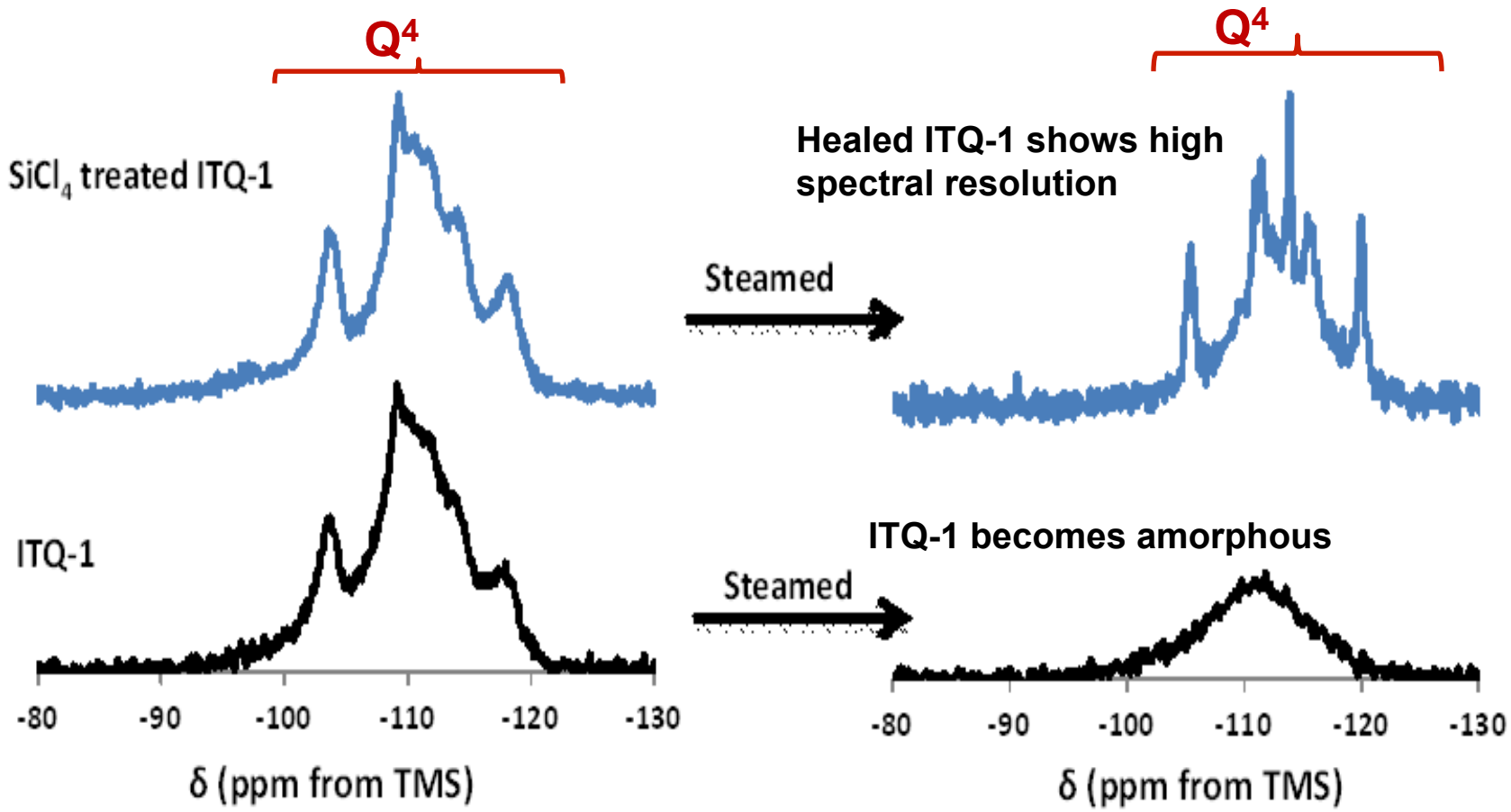


TEM images of **healed ITQ-1** before and after 84 days of steaming



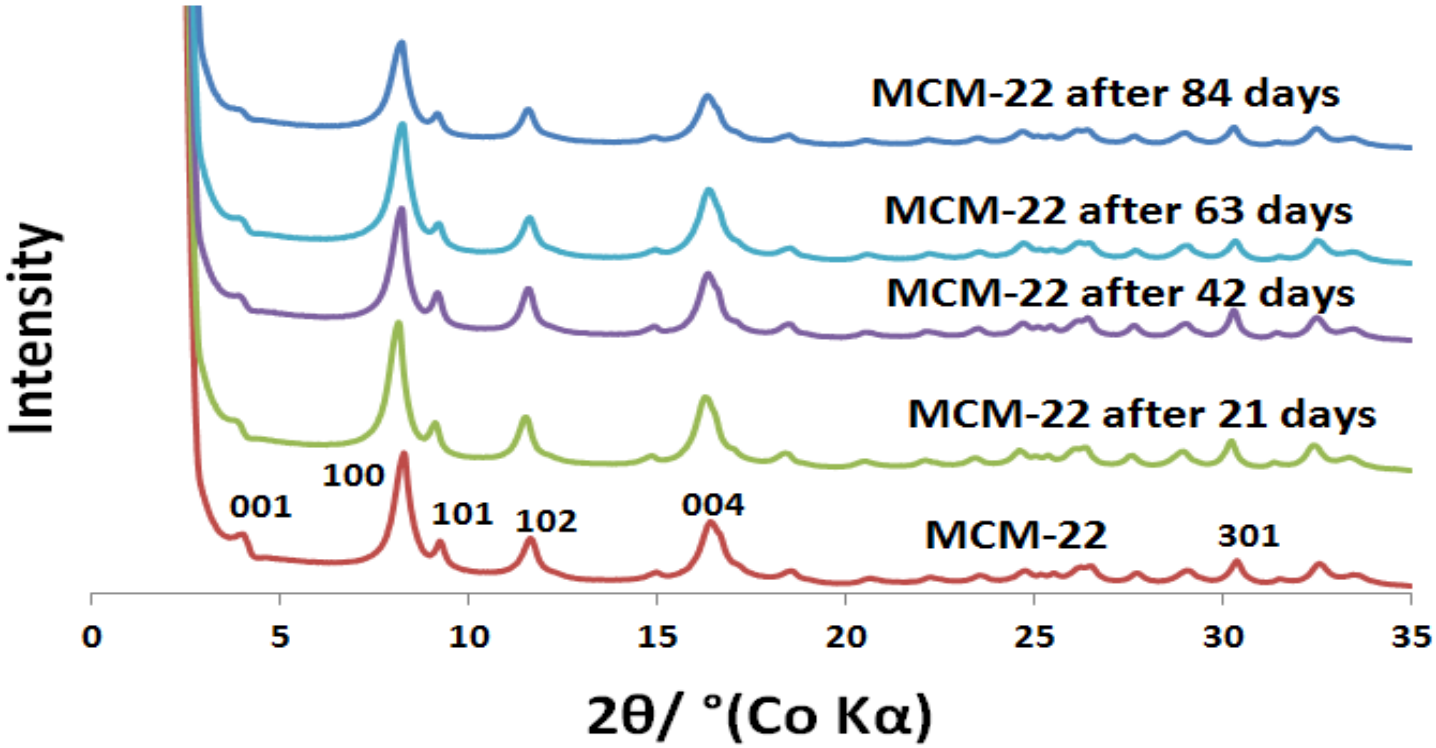


^{29}Si MAS NMR of ITQ-1 and $SiCl_4$ treated ITQ-1 before and after steaming for 84 days at 350°C

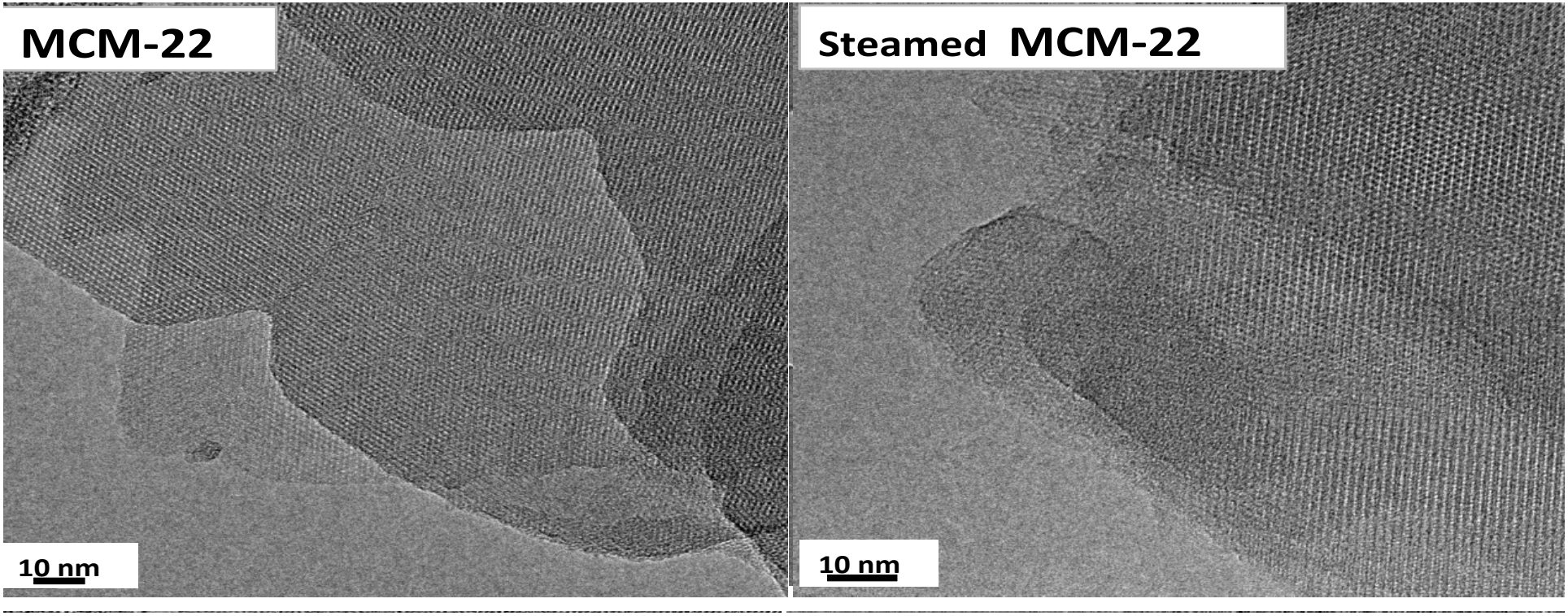


XRD of MCM-22 steam treated at 350°C

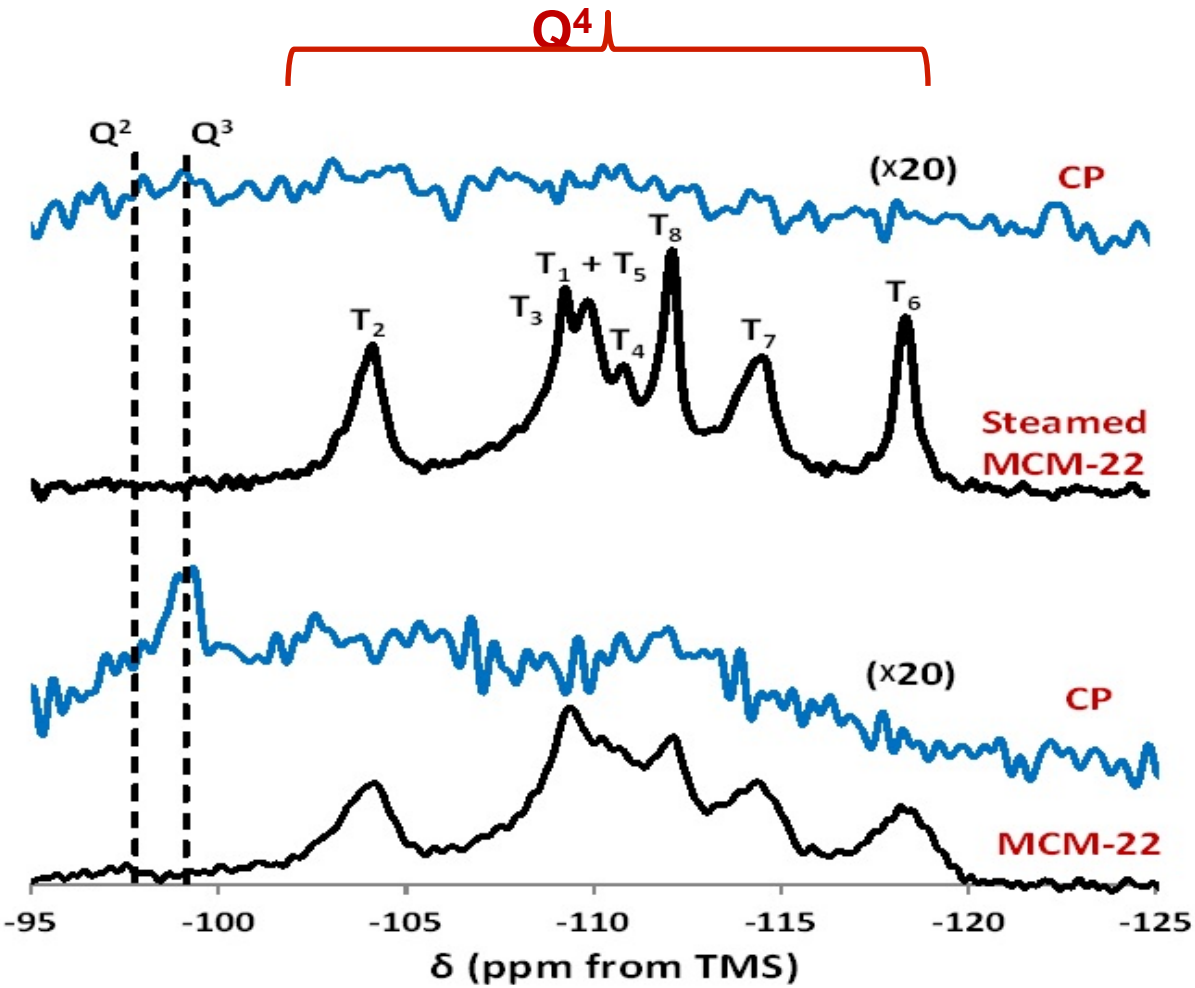
- MCM-22 keeps its crystallinity.
- No change in crystal morphology was seen in the SEM pictures.



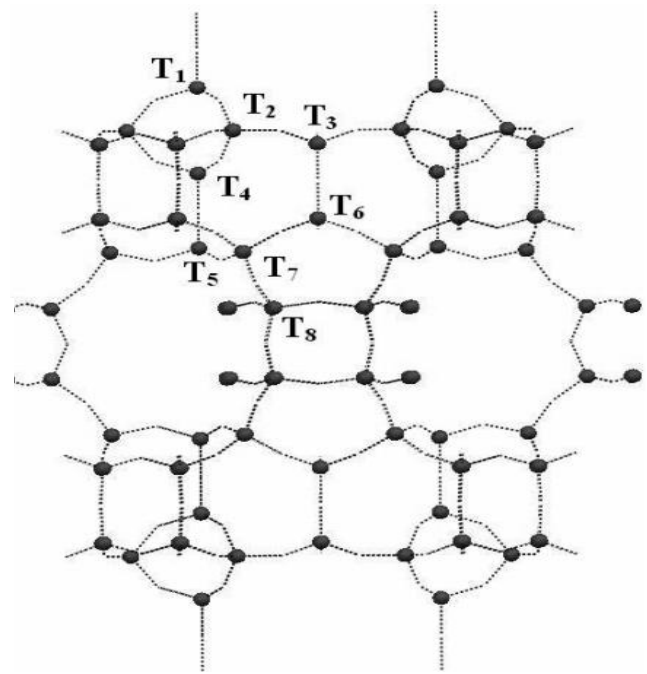
TEM images of MCM-22 before and after 84 days of steaming



^{29}Si and CP/MAS NMR of MCM-22, before and after steaming at 350°C for 84 days



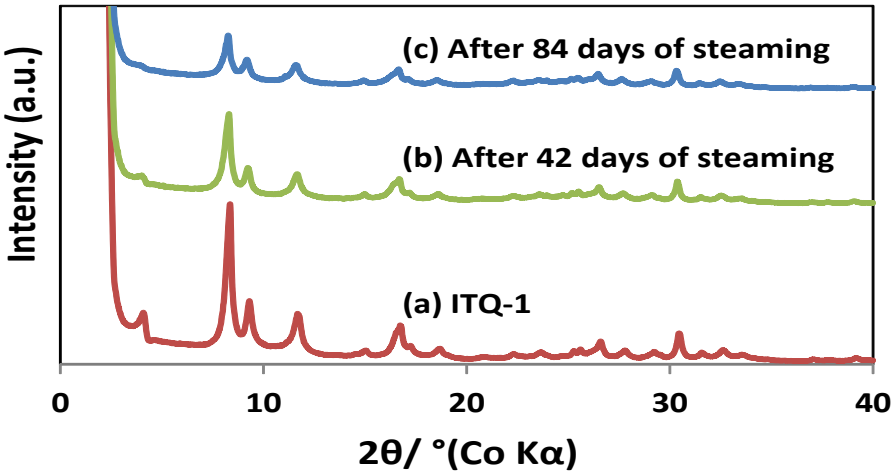
- **Higher spectral resolution can be seen after hydrothermal treatment**
- **Intensity reduction at -97 and**

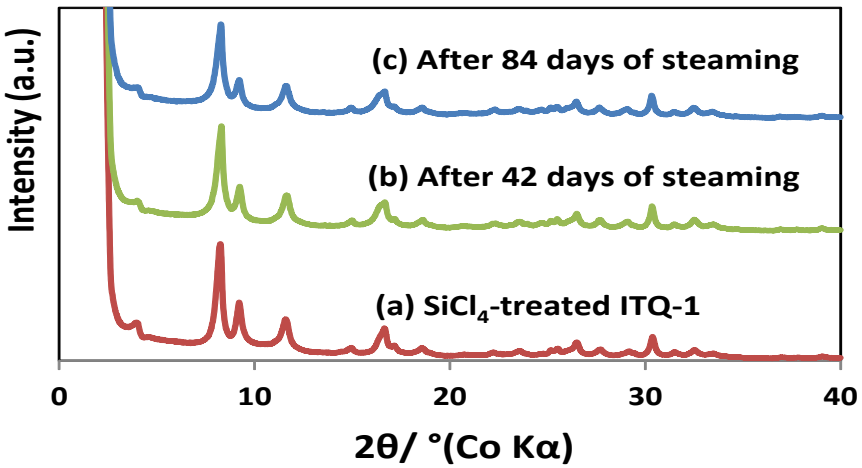


$$\sigma = -0.6192\Theta - 18.68$$

G. Engelhardt, R. Radeglia, Chem. Phys. Lett. 108 (1984) 271-274.

Steaming effect on ITQ-1 samples calcined at the lower temperature of 580°C





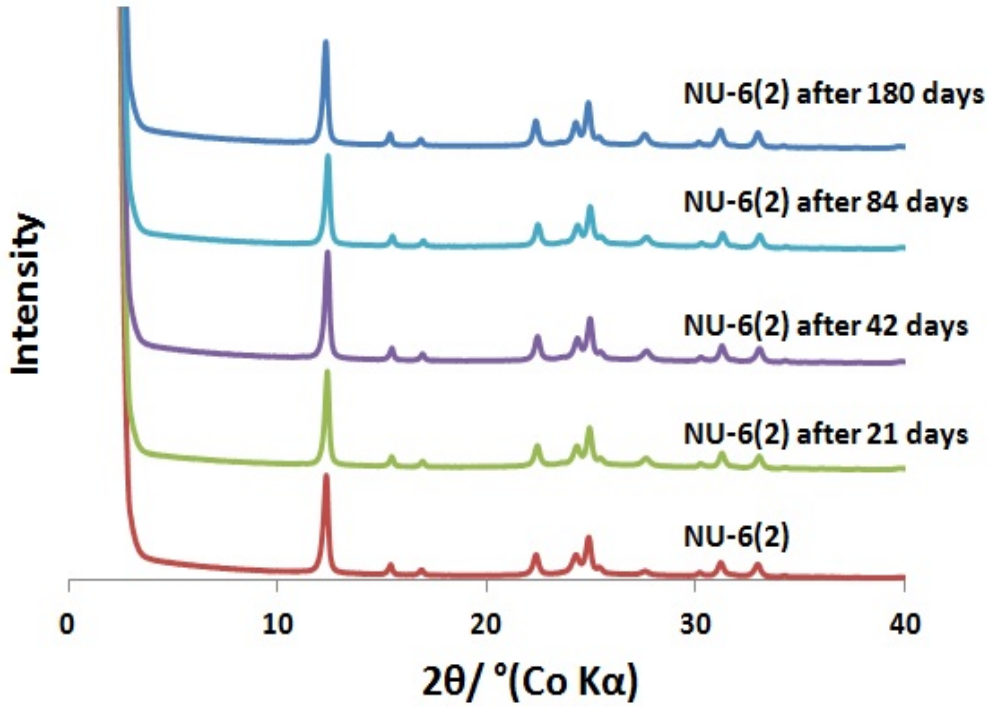
XRD patterns of ITQ-1 (left, calcined at 580 °C, 4 h in air) and $SiCl_4$-treated ITQ-1 (right,, calcined at 580 °C, 4 h in air): before (a) and after 42 days (b), and 84 days (c) of steaming at 350 °C and 10 barg (95% H_2O, 5% N_2).

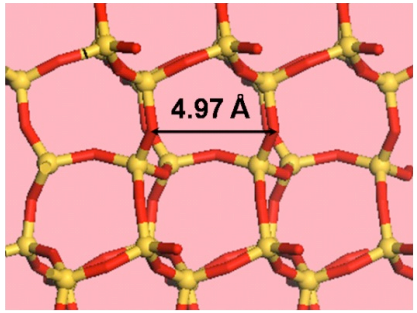
N_2/Ar adsorption studies of MWW structure zeolites

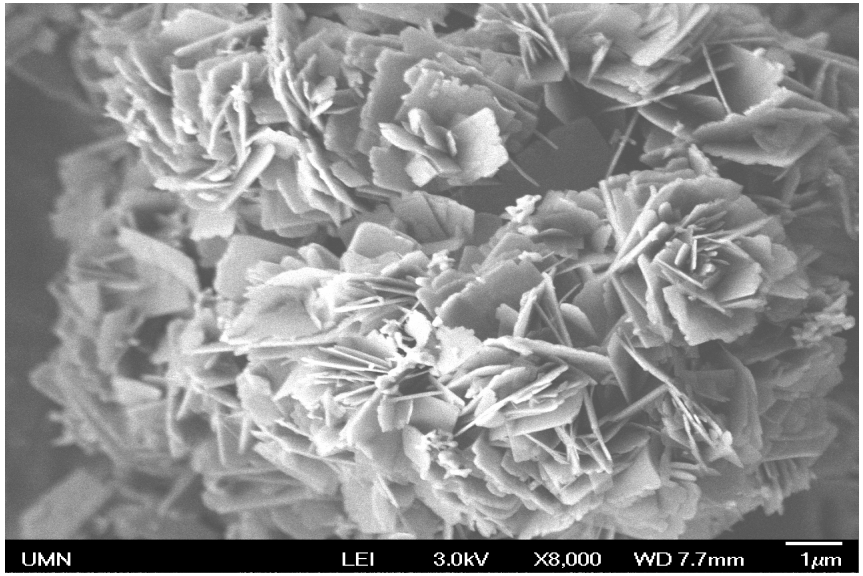
	Before steaming			After steaming for 84 days		
	S_{BET} [a] (m^2/g)	V_{micro} [b] (cm^3/g)	V_{micro} [c] (cm^3/g)	S_{BET} [a] (m^2/g)	V_{micro} [b] (cm^3/g)	V_{micro} [c] (cm^3/g)
MCM-22-H (calcined at 900°C)	490	0.163	0.198	340	0.113	0.133
ITQ-1-H (calcined at 900°C)	402	0.138	0.186	13	0	0
S-ITQ-1-H ($SiCl_4$-treated ITQ-1)	470	0.160	0.195	110	0.027	0.034
ITQ-1-C (calcined at 580°C)	550	0.182	0.254	158	0.048	0.069
S-ITQ-1-C ($SiCl_4$-treated ITQ-1)	521	0.181	0.239	308	0.103	0.142

[a] BET area from N_2 adsorption isotherm.
[b] Micropore volume from t-method using N_2 adsorption isotherm.
[c] Micropore volume using the NLDFT kernel "Ar at 87 K zeolites- silica, cylindrical pore model".

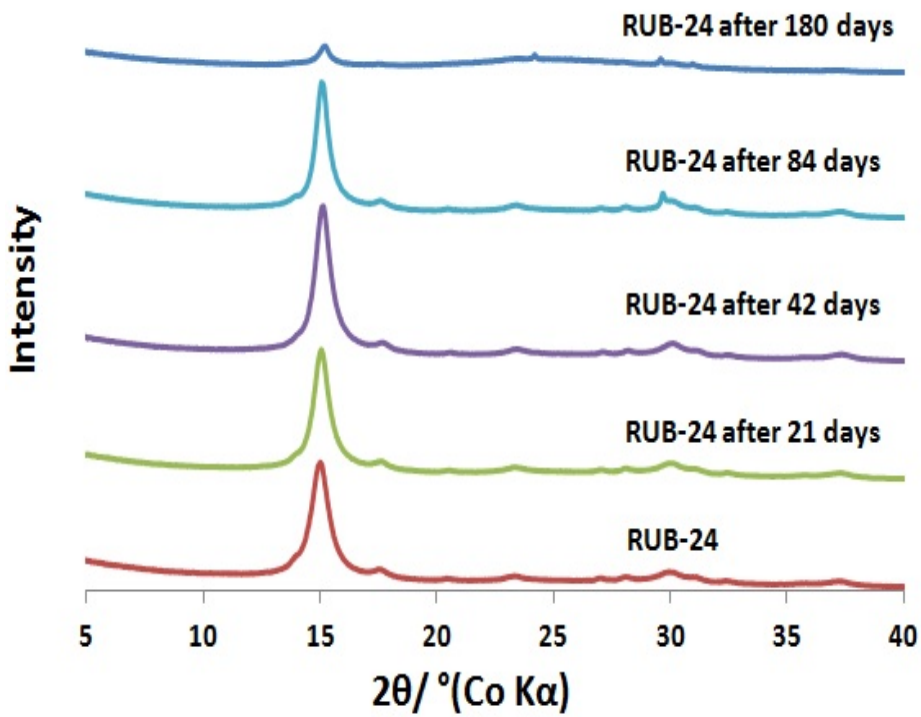
XRD of patterns of Nu-6(2) zeolite:
Steamed at 350°C and 10 bar (35% H2O in N2) for 6 Months

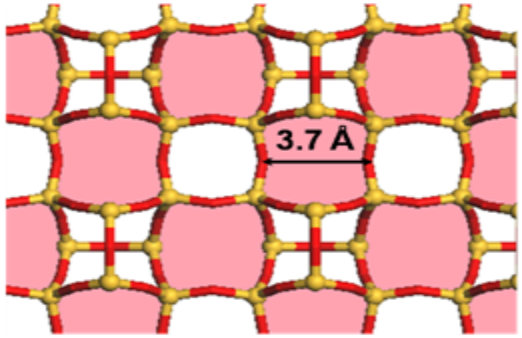


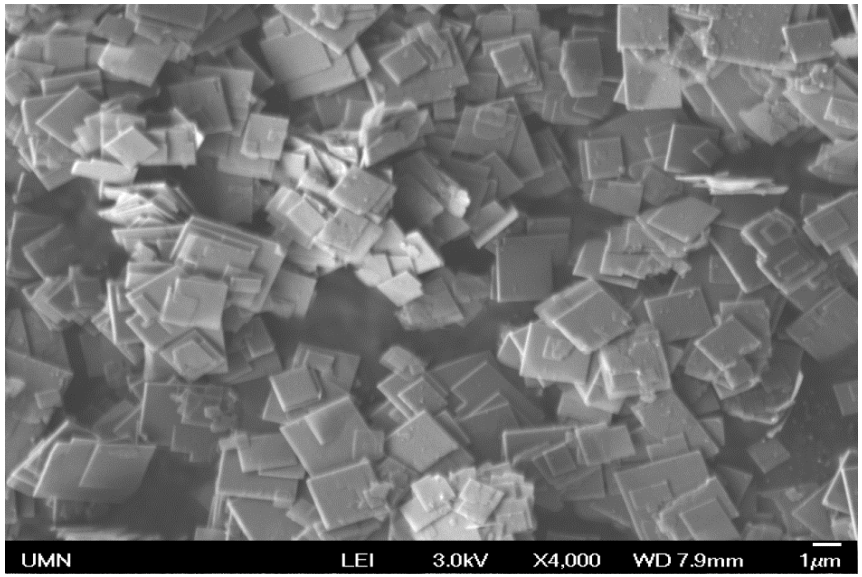




XRD of patterns of RUB-24 zeolite: Steamed at 350°C and 10 bar (35% H2O in N2) for 6 Months







On steam stability:

MWW (and other layered zeolites) are structurally stable for months under intense steaming at 350 ^{O}C.

Higher T compromises crystallinity

(i) Presence of Al during synthesis; (ii) defect healing by $SiCl_4$ treatment and (iii) lower T for 1st calcination improve stability

Steaming improves local order and possibly hydrophobicity

Although crystallinity is retained, nm-sized hole formation is observed and may lead to pinhole formation. It may explain loss of membrane performance after steaming.

Conclusions and Outlook

- Top down exfoliation approach and compact membrane fabrication achieved
- Nanosheet membranes exhibit performance close to process design targets under dry conditions
- Original hypothesis that siliceous zeolites can be steam-stable confirmed and several factors affecting stability were identified
- Membrane performance deteriorates under steaming at 350°C probably due to pinhole formation.

Outlook:

- Improvements of steam stability possible by detail study of identified factors
- Process design targets achievable by improving membrane synthesis to obtain:
  - Higher aspect ratio, defect (Si-OH) - free nanosheets
  - Highly oriented compact membranes