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University of Minnesota

DE-FE0001322 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

Total Project Funding: $993,772 , DOE/Non-DOE Share: 793,775 /199,997

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

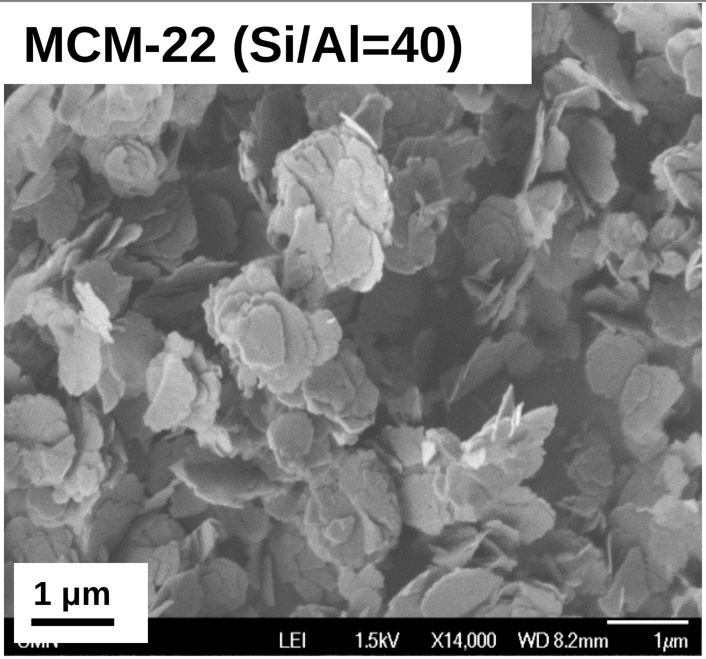
Objective

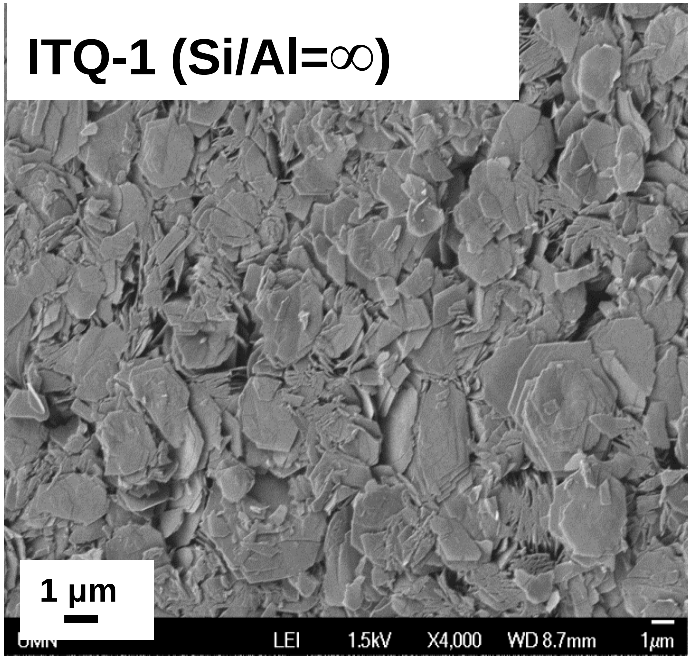
To develop a technically and economically viable membrane for H_2 separation from typical water-gas-shift (WGS) mixture feeds at high temperatures.

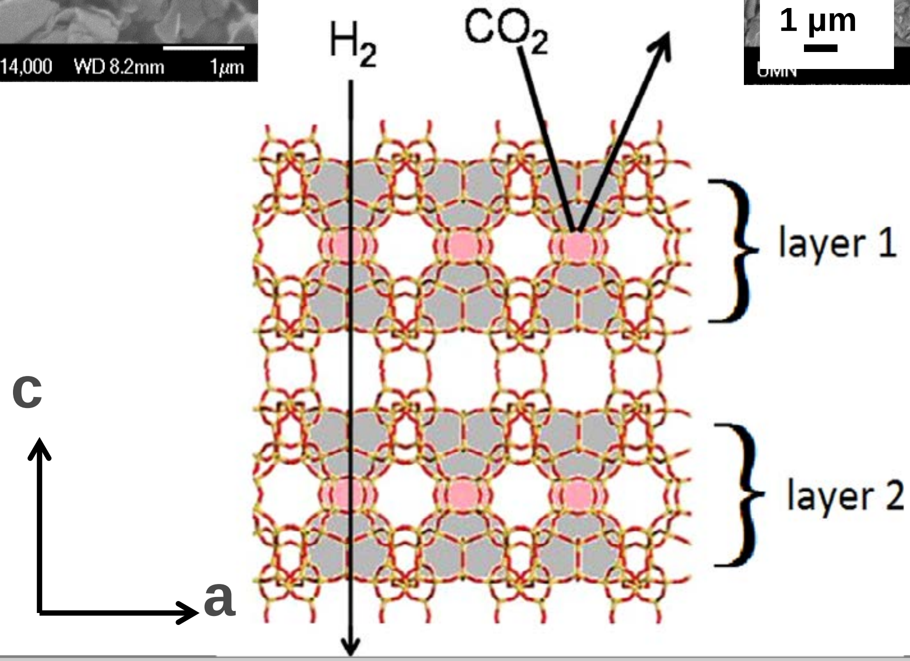
Outline

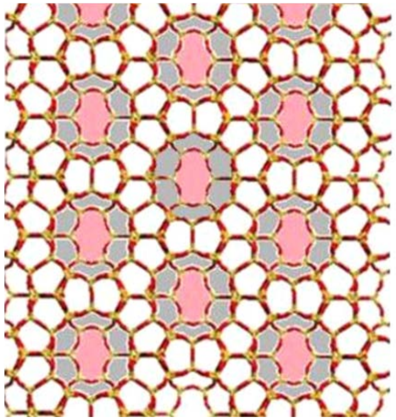
- **Preparation of hydrogen selective membranes using zeolite nanosheets.**
- **Steam stability of layered zeolites (MCM-22, ITQ-1, RUB-24, Nu-6(2)).**
- **Modeling and optimization of IGCC plant with membrane reactor.**

Layered zeolites with 6-MR pores







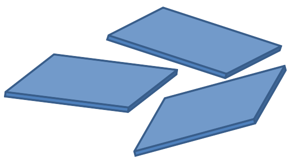


Hierarchical manufacturing of zeolite membranes

Layered zeolite
(thickness ~50 nm)

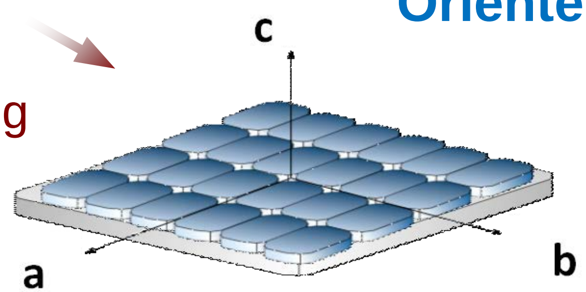
Exfoliation

Nanosheets with high aspect ratio
(thickness 2.5 nm)



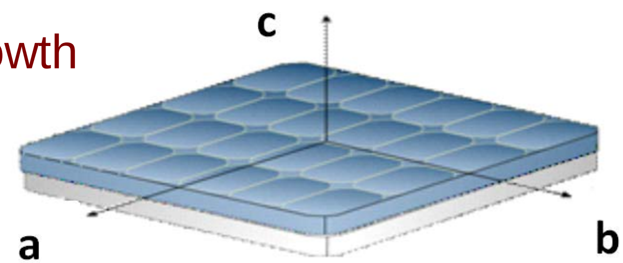
Oriented monolayer of crystals

Coating



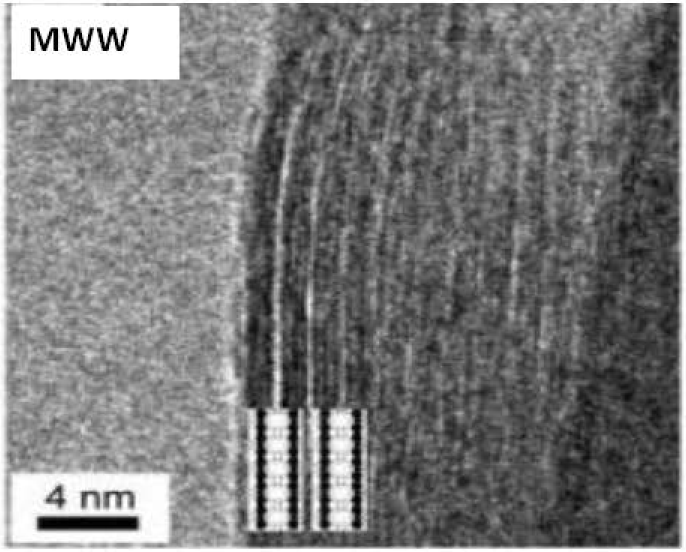
Membrane

Secondary growth

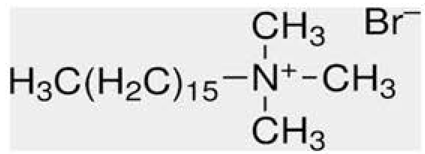


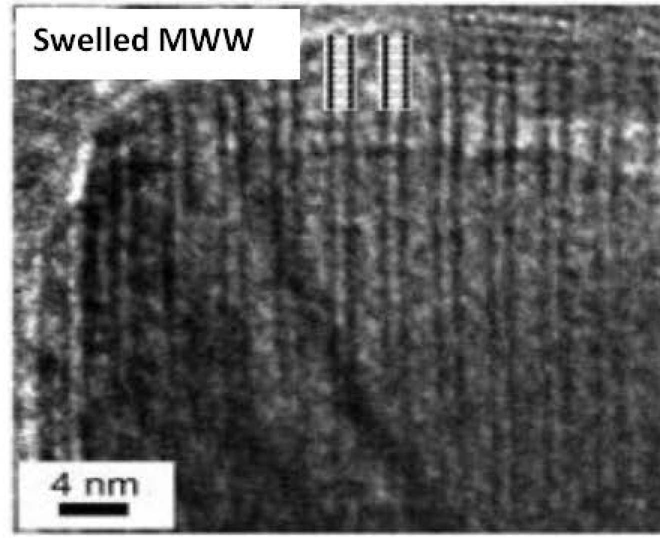
For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. **2007**, *46*, 7560–7573

Membrane preparation

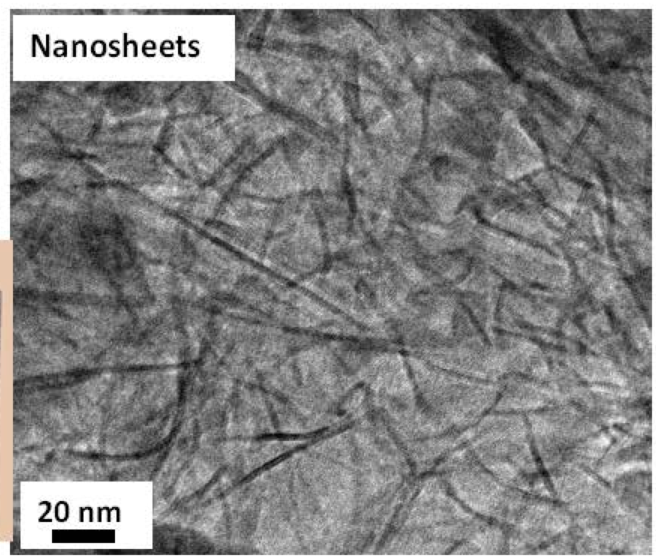


Swelling with CTAB

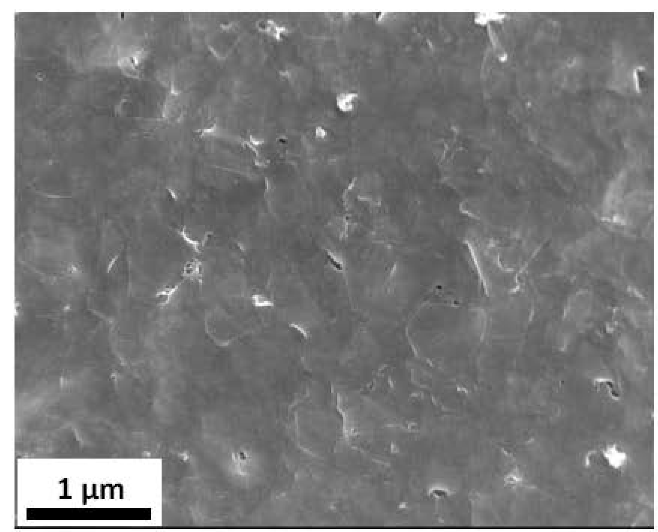




Exfoliation with polystyrene

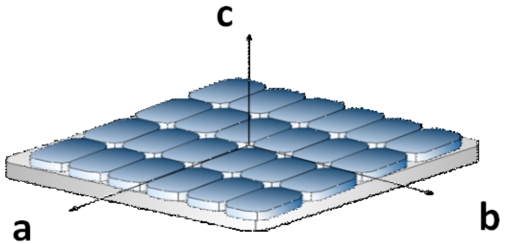


Dissolution of the nanocomposite in toluene, purification and filtration

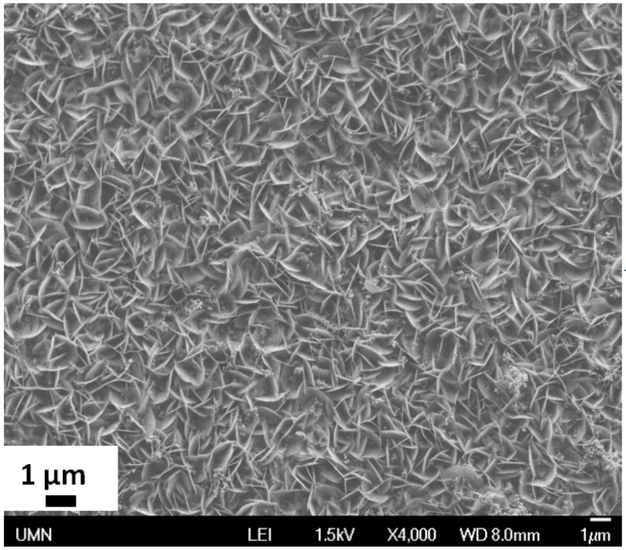


Varoon K., et al Science 334 (2011) 72–75,
Maheshwari et al J. Am. Chem. Soc. 2008, 130, 1507-1516

Membrane preparation

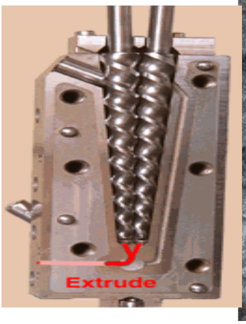


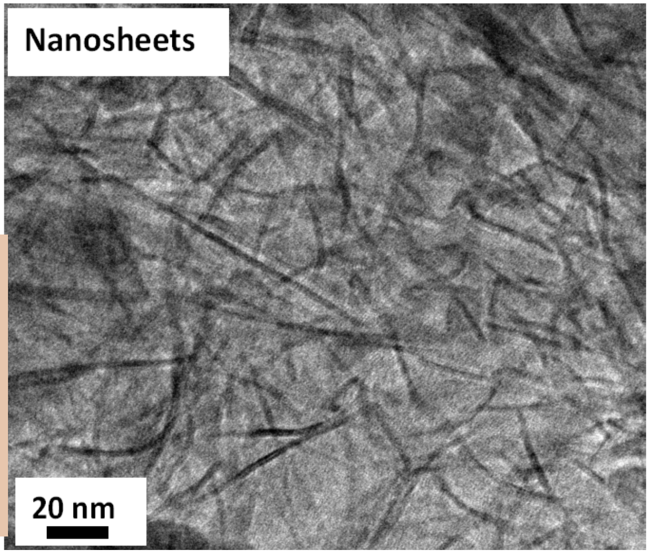
Oriented monolayer of crystals



Gel-based secondary growth (*misorientation*)

Exfoliation with polystyrene





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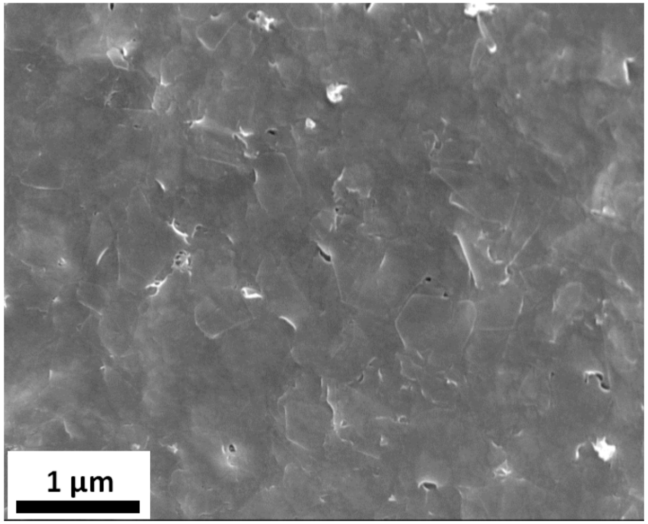
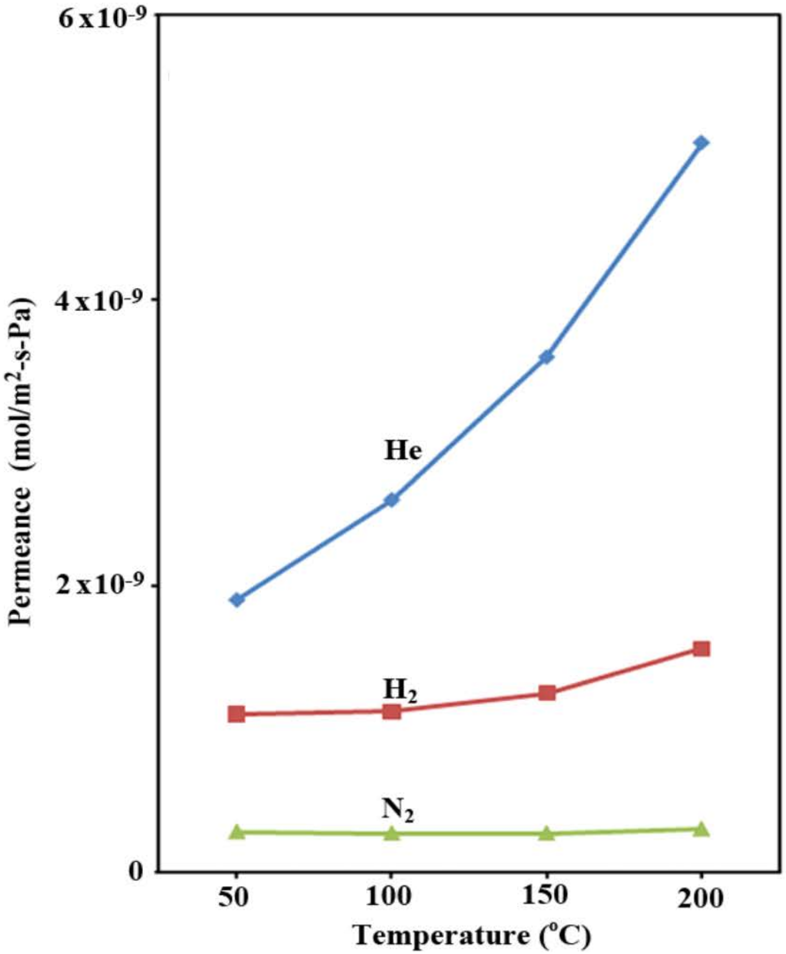
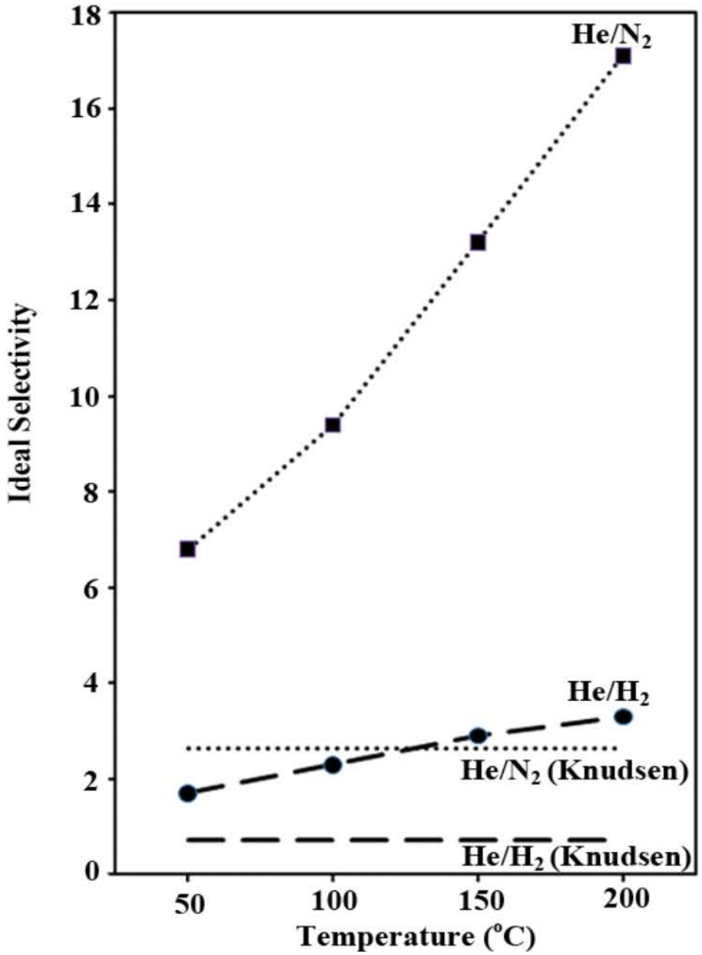


Varoon K., et al Science 334 (2011) 72–75,
Maheshwari et al J. Am. Chem. Soc. 2008, 130, 1507-1516

Performance of an ITQ-1 Membrane





Varoon K., Zhang X., Elyassi B., Brewer D.D., Gettel M., Kumar S., Lee J.A., Maheshwari S., Mittal A., Sung c., Cococcioni M., Francis L.F., McCormick A.V., Mkhoyan K.A., Tsapatsis M., Science 334 (2011) 72–75.

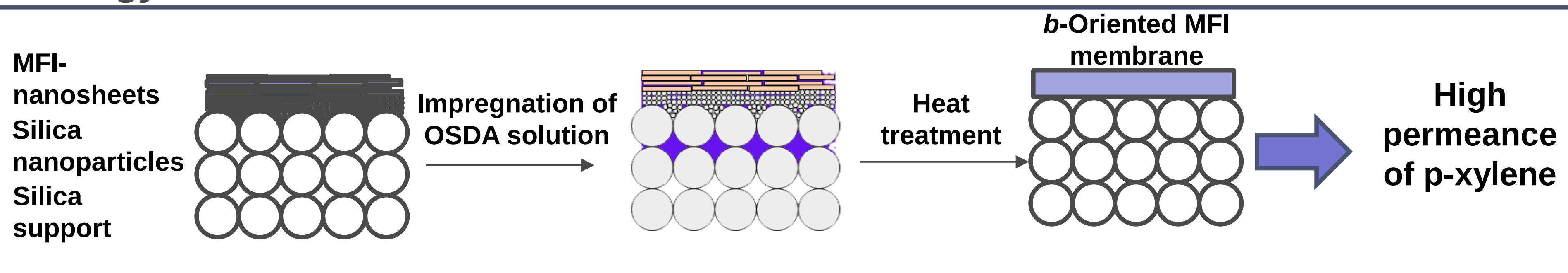
c-oriented MWW membranes

- Preserve the orientation of the MWW layers along the *ab* plane.
- Fabrication of *b*-oriented MFI membranes have shown a superior performance in the separation of xylenes.

Secondary growth methods for MWW

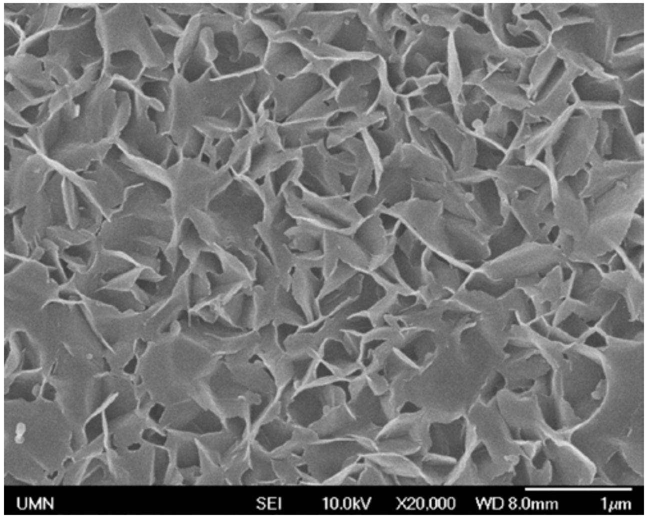
- **Pre-crystallization of the gel and secondary growth**
- **Gel-free growth : with HMI as the SDA**
- **Gel-free growth: MWW/MFI mixed matrix membrane**

Analogy: b-oriented MFI membranes

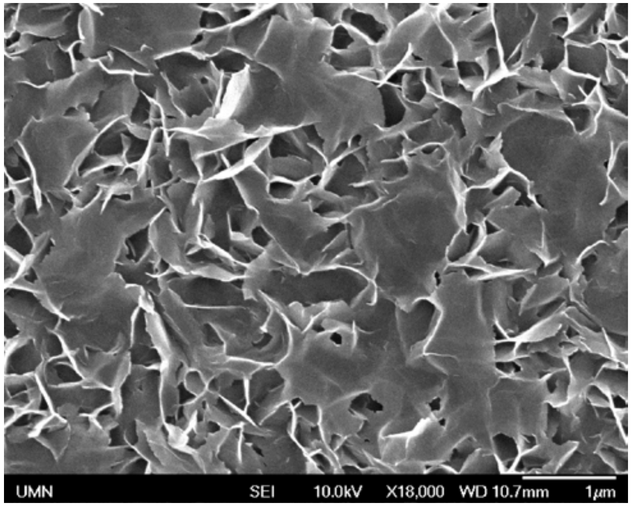


Pham et. al *Angewandte Chemie* **2013**, 125,33, 8855.

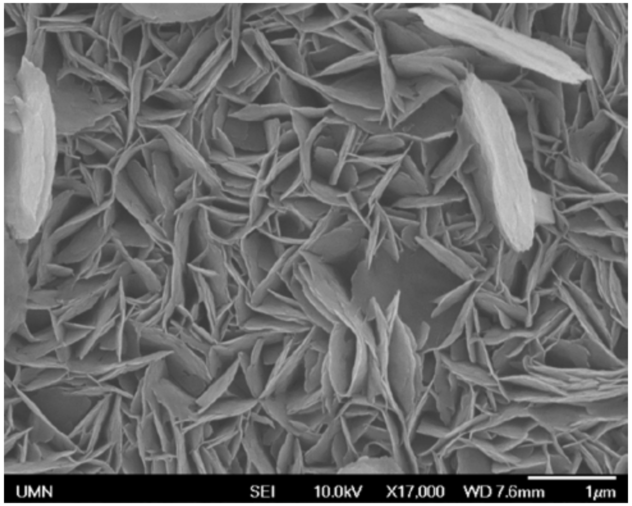
Secondary growth of MWW nanosheets – Pre-crystallization of the gel



Precrystallization of the gel 150° C/18h. SG 150° C/24h



Precrystallization of the gel 150° C/40h. SG 150° C/24h



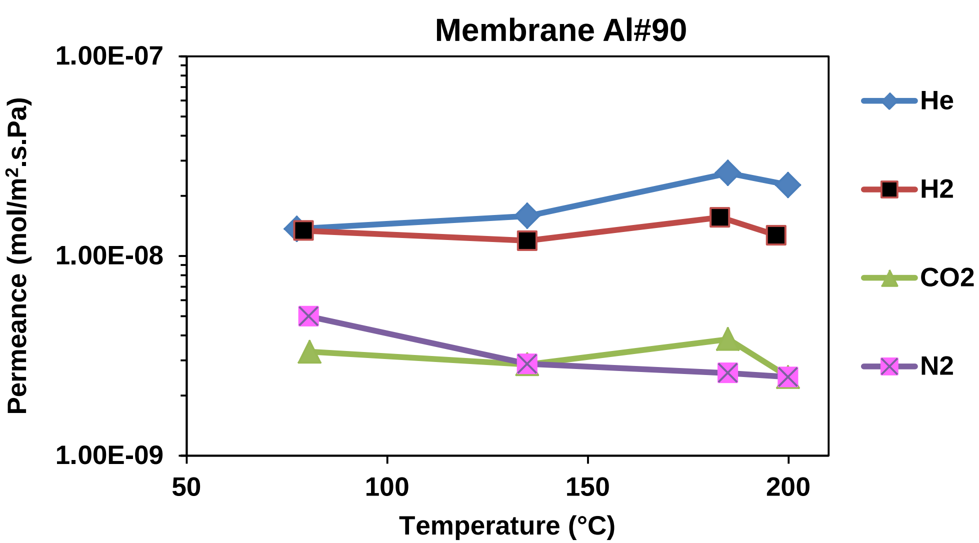
No precrystallization of the gel

- Misoriented growth on the surface of the MWW nanosheets.
- Longer pre-crystallization times of the gel prior to secondary growth might lead to *c*-oriented growth of MWW flakes.

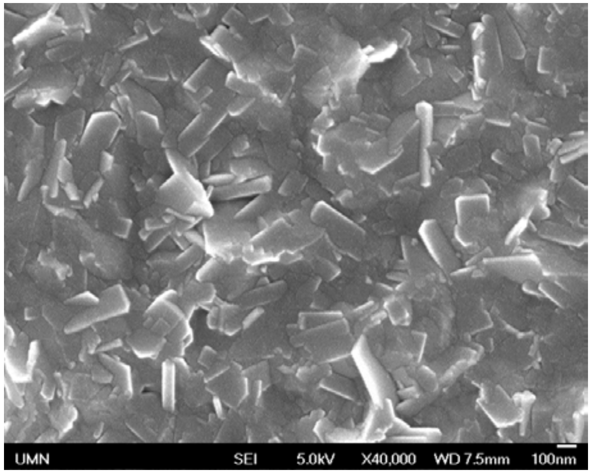
MEMBRANE 3 :

2nd growth condition: Gel aged at 150° C/40 h and secondary growth at 150° C/24 h

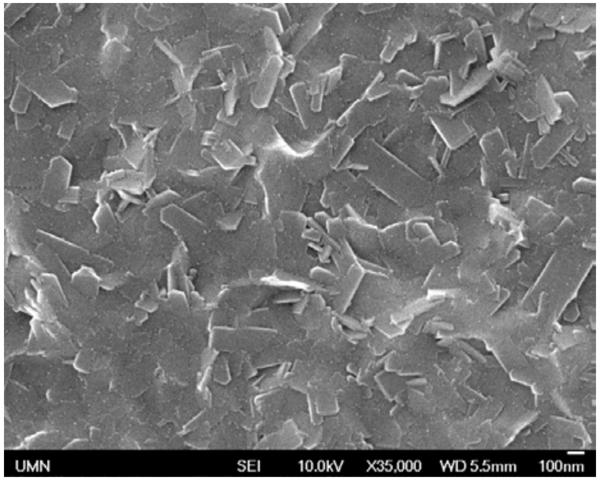
	Temp (° C)	Permeance (mol/m2.Pa.s)				Selectivity					
		He	H_2	CO_2	N_2	He/N_2	He/H_2	H_2/CO_2	H_2/N_2	CO_2/N_2	
						2.65	0.71	4.69	3.74	0.8	Knudsen
Bare Al support	22	2.53E-06	3.08E-06	8.75E-07	1.08E-06	2.35	1.22	3.51	2.86	0.81	
Membrane #90	80	1.37E-08	1.34E-08	3.31E-09	4.98E-09	2.74	1.02	4.04	2.69	0.66	
	135	1.58E-08	1.19E-08	2.86E-09	2.88E-09	5.51	1.33	4.16	4.14	1.00	
	185	2.60E-08	1.56E-08	3.83E-09	2.59E-09	10.03	1.67	4.07	6.01	1.48	
	200	2.26E-08	1.27E-08	2.47E-09	2.47E-09	9.15	1.78	5.13	5.13	1.00	



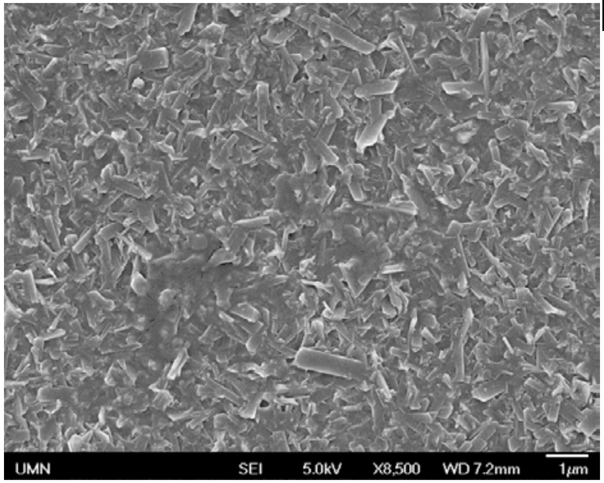
MWW / MFI (30 / 70 ratio) mixed membranes.
SG conditions: Impregnation with 0.025M TpaOH. Hydrothermal at 170° C/ (9h - 36h)



Hydrothermal at 170° C/9h.
p-xylene/o-xyleneSF= 4.2



Hydrothermal at 170° C/18h.
p-xylene/o-xylene SF = 4.7



Hydrothermal at 170° C/27h.
p-xylene/o-xylene SF = 1.7

However, these membranes gave poor separation of H_2, He, CO_2 or N_2.

MWW membranes

- With membranes made by the pre-crystallization method, a He permeance of 2.60E-08 and a He/N_2 separation of 10 was obtained.
- MWW/MFI membranes did not give high separation factors for gases.
- Under gel-free conditions with HMI, hydrothermal treatment resulted in formation of amorphous silica or destruction of MWW nanosheets.

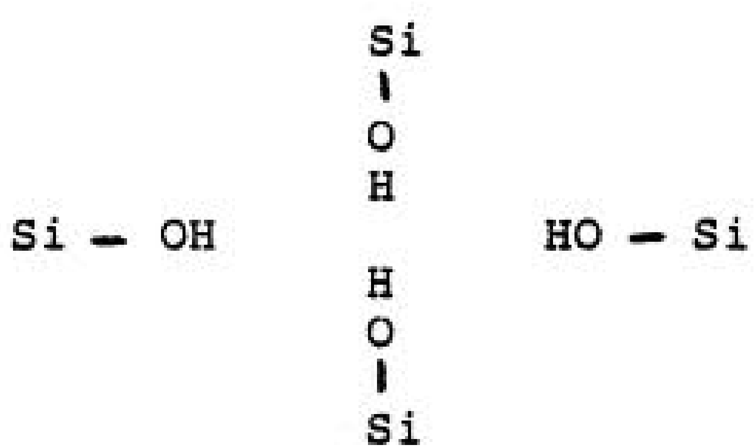
Steaming conditions for ITQ-1 and MCM-22

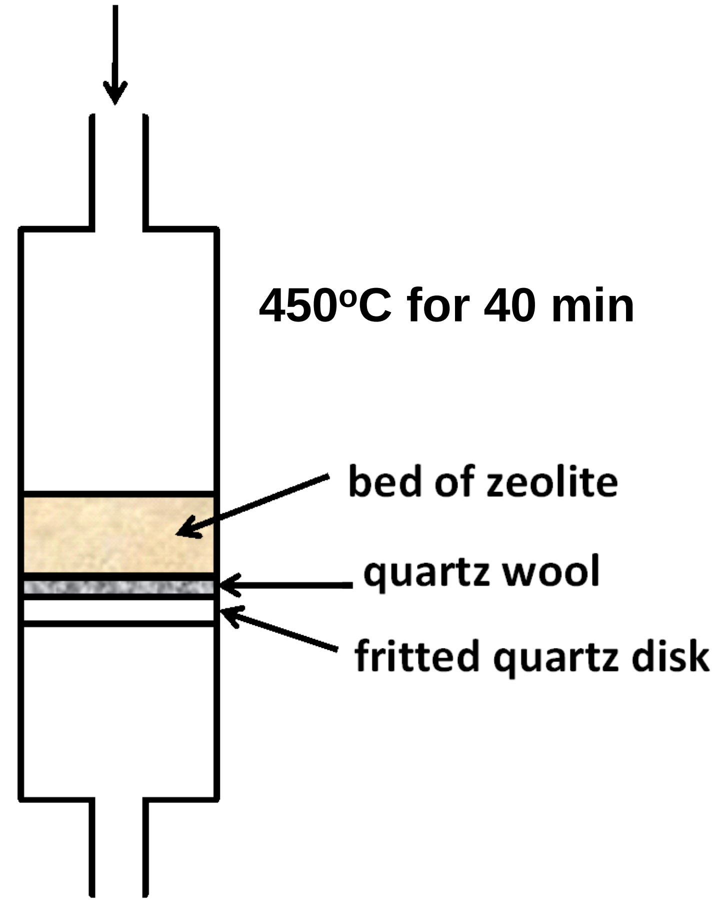
- Temperature: 350° C
- Pressure: 10 bar (95% steam, 5% nitrogen)
- Samples were analyzed in 21 days intervals for 84 days.

Stability of ITQ-1 and $SiCl_4$-treated ITQ-1

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.

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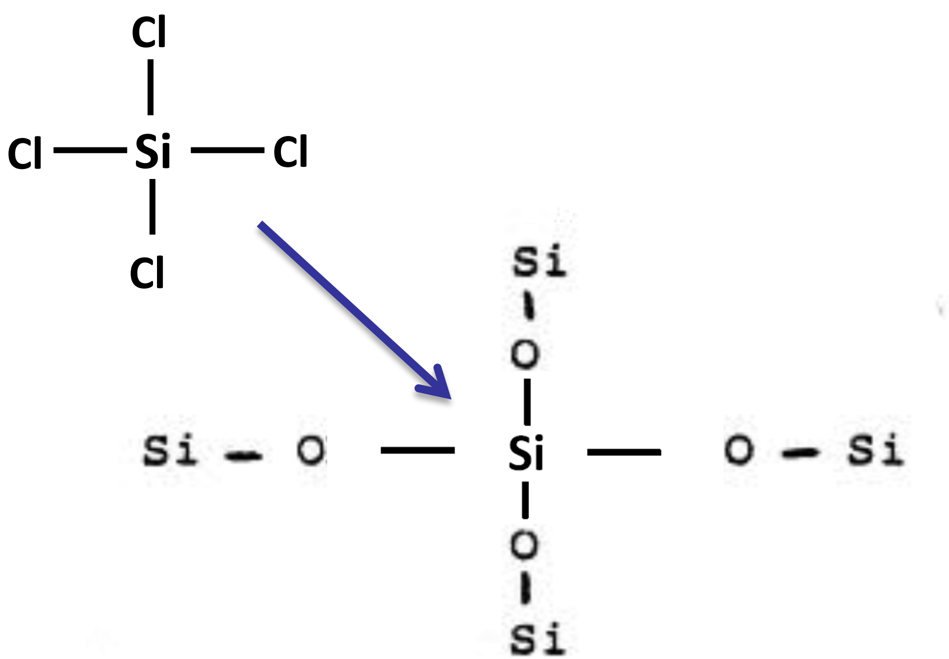
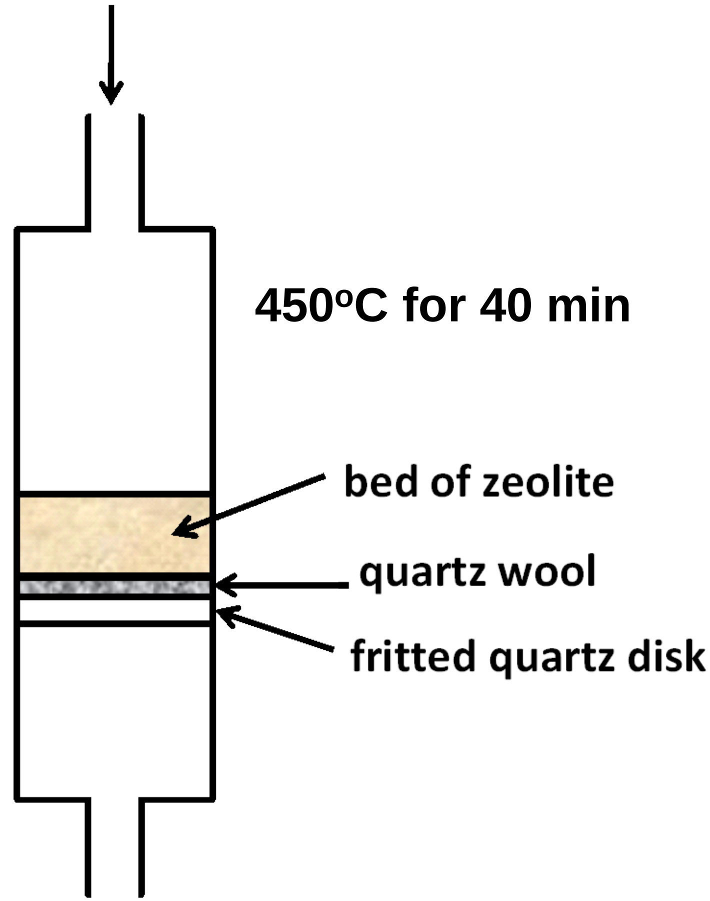
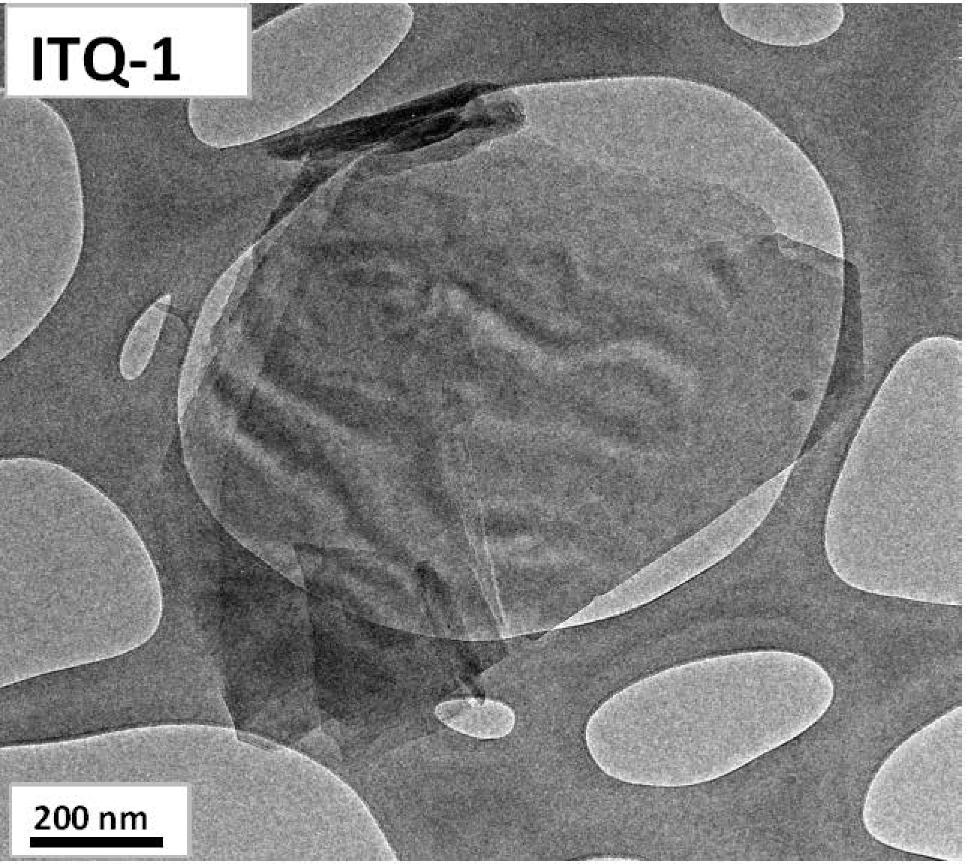
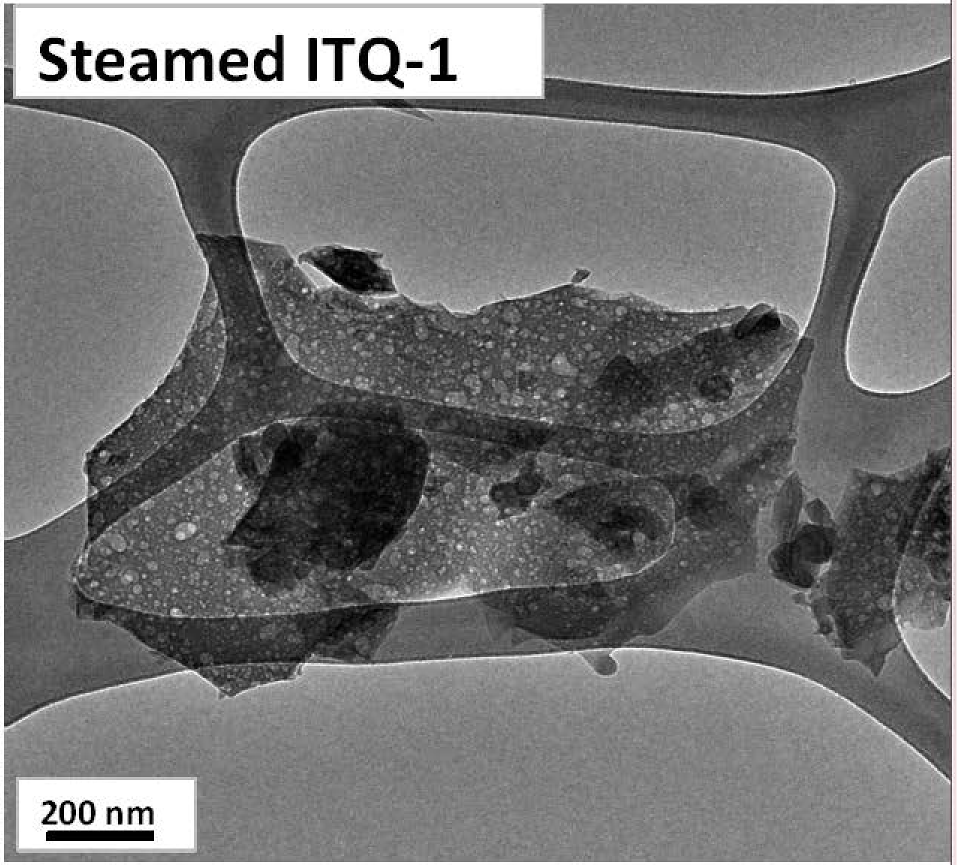




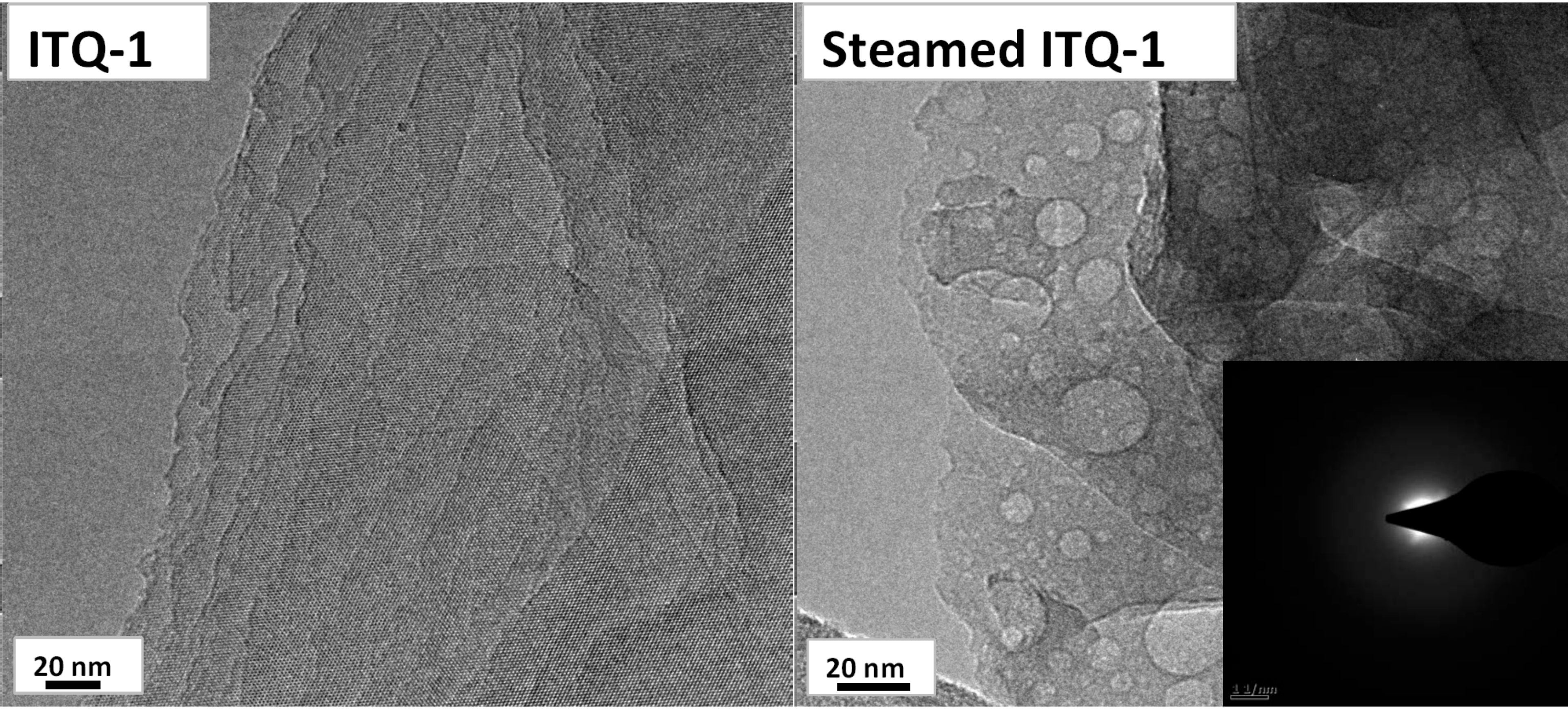
Beyer et. al., J . Chem. Soc., Faraday Trans. 1, 1985, 81, 2889-2901.

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

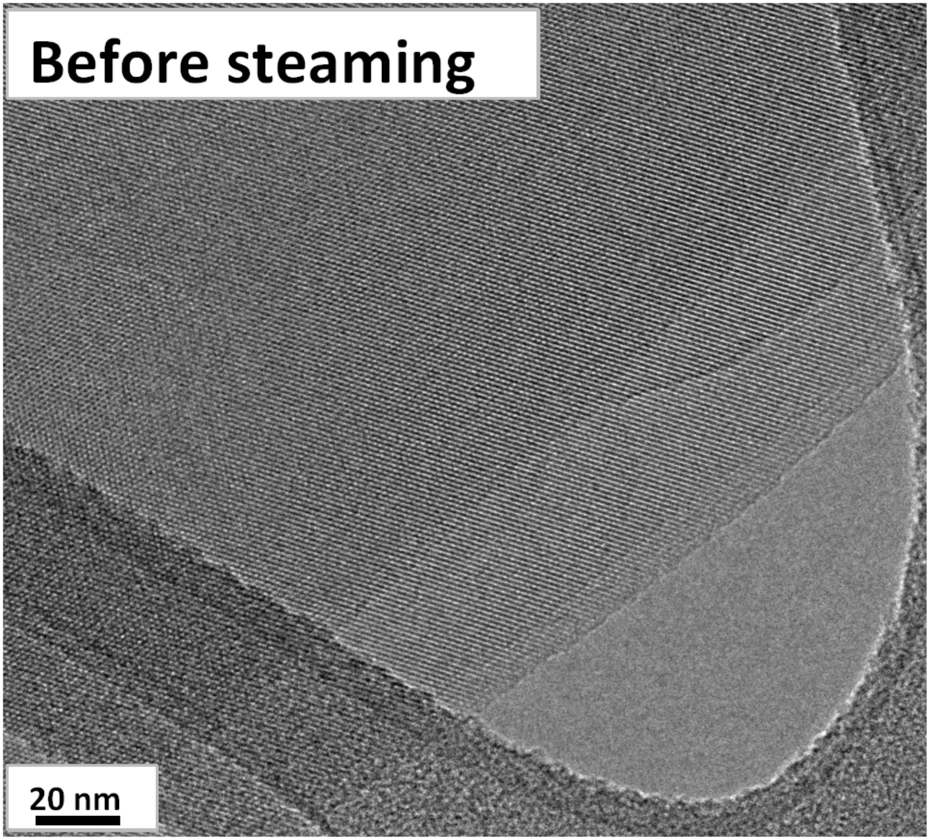


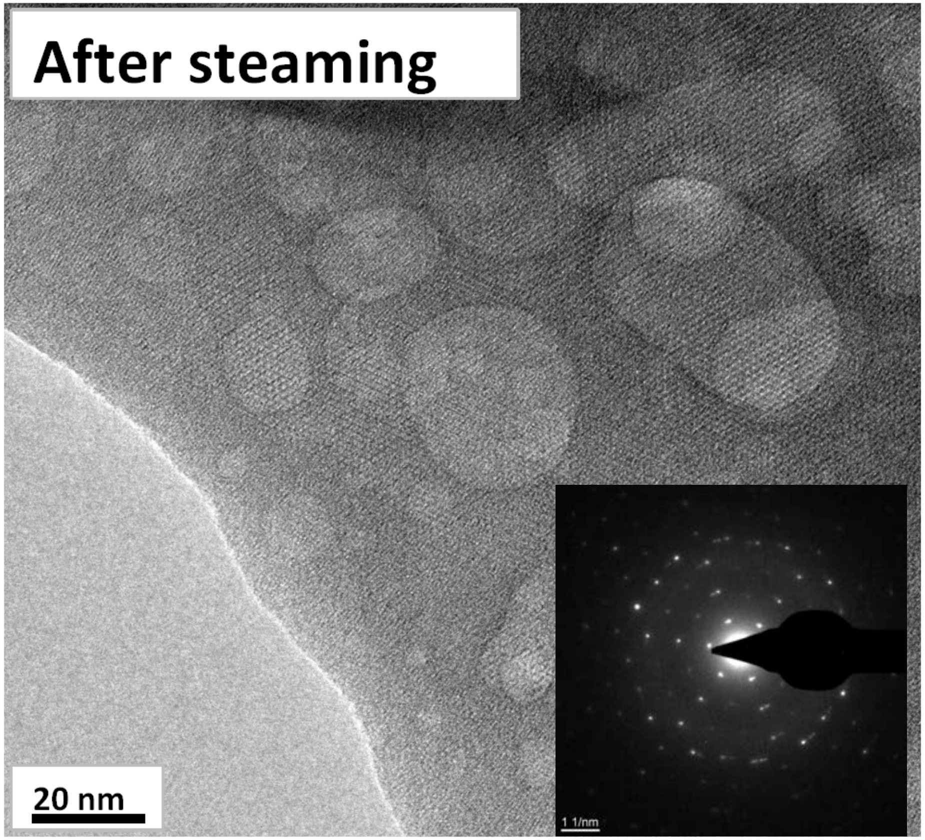


TEM images of ITQ-1 before and after 84 days of steaming



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

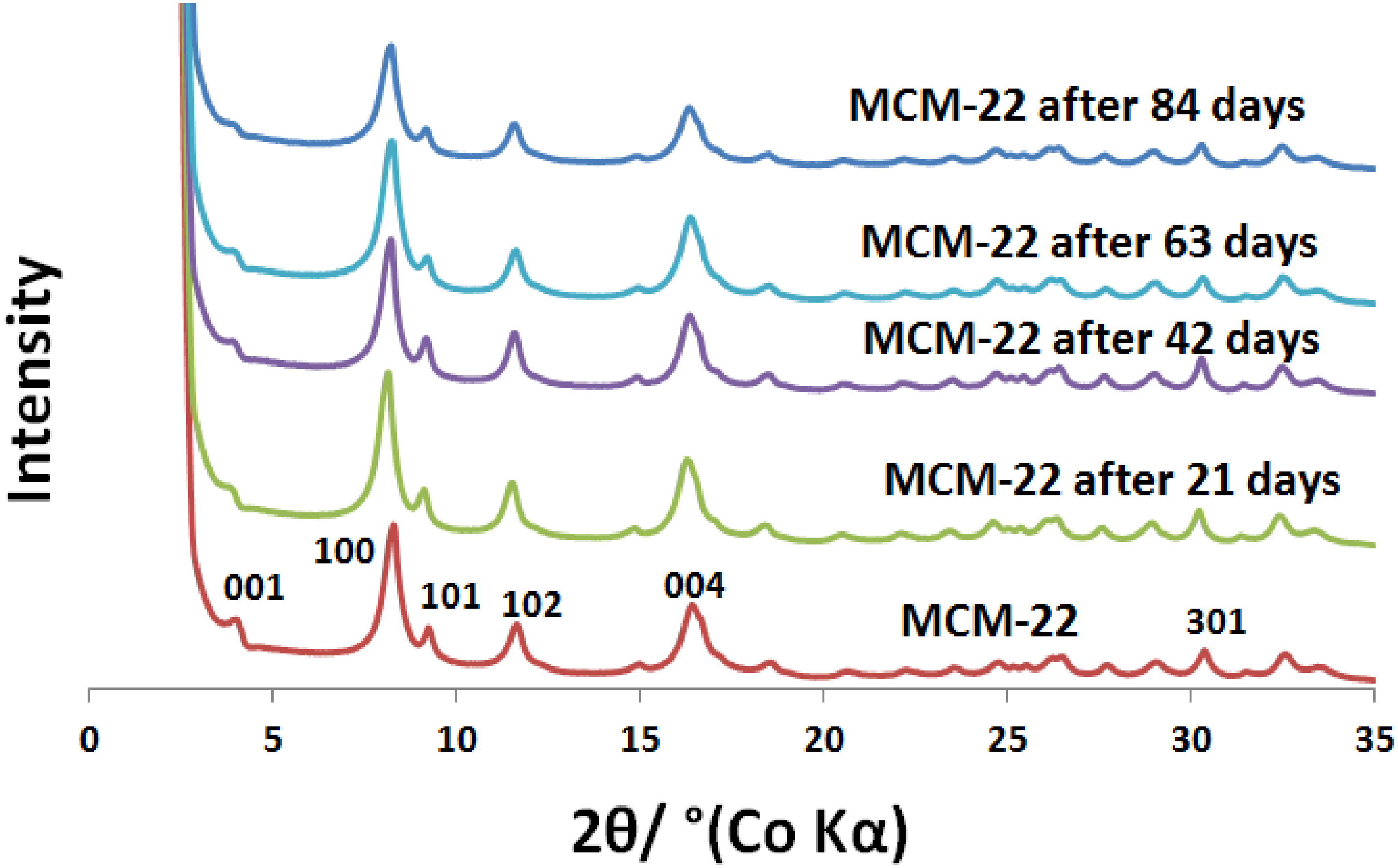




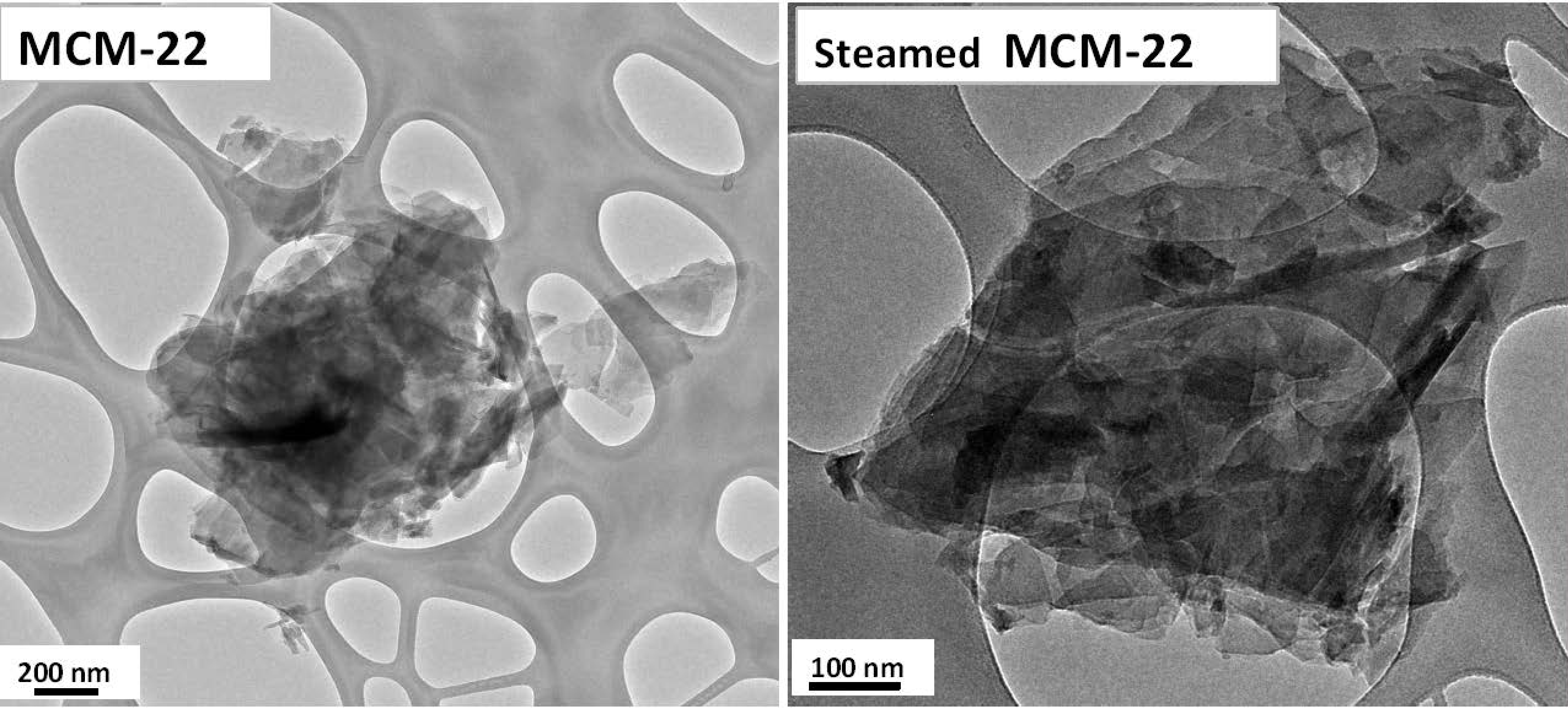
- **In ITQ-1, there is a major loss in crystallinity after steaming.**
- **$SiCl_4$ treatment improved the resistance of the ITQ-1 to water vapor attack.**
- **Holes are seen in the flakes of healed ITQ-1. However, regions around the cavities are crystalline.**

XRD of MCM-22 steam treated at 350°C

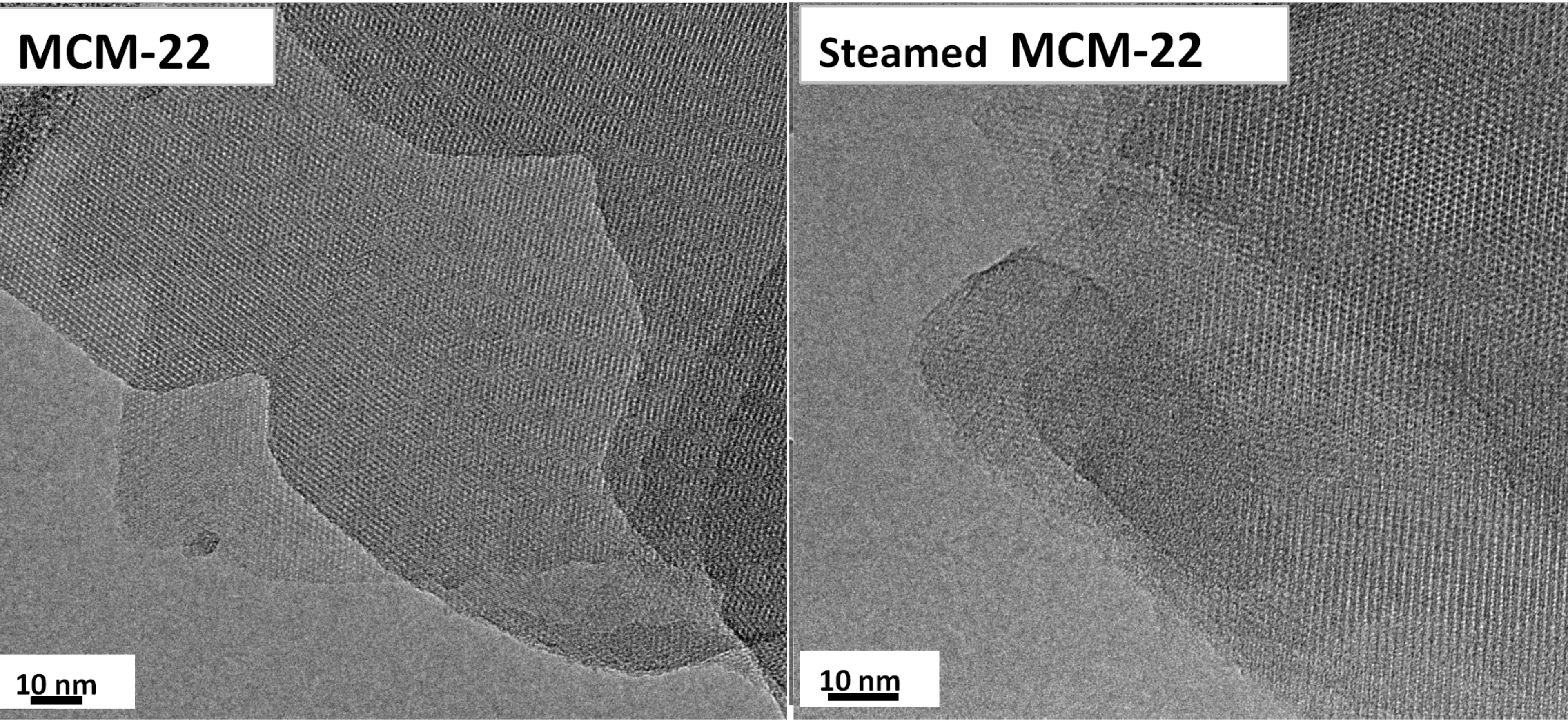
- MCM-22 keeps its crystallinity.
- No change in crystal morphology was seen in the SEM pictures.



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



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



Summary of membranes and stability analysis

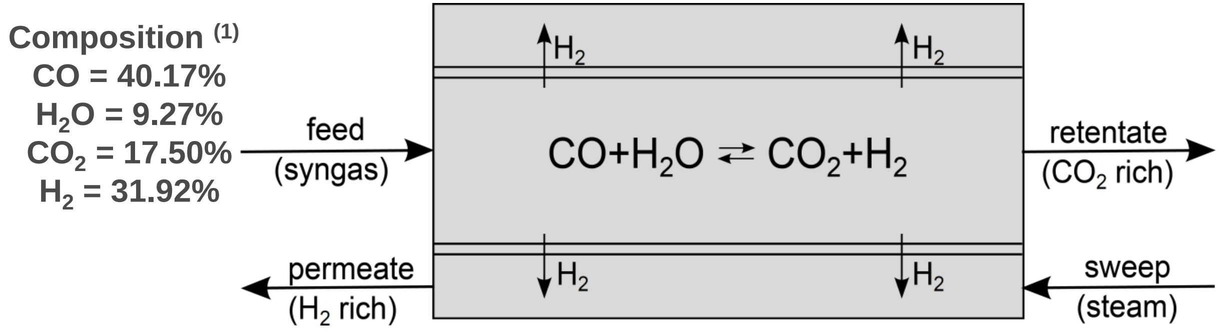
- MWW membranes were tested for gas separation.
- Depending on the secondary growth method applied, misoriention of the MWW channels or destruction of MWW nanosheets were observed.
- Hence, these membranes did not show optimum performance in gas separation.
- Systematic studies on the long-term steam stability of zeolites: MCM-22, ITQ-1, NU-6(2), and RUB-24 were completed.
- MWW may not be a suitable candidate for membrane reactor applications as structural defects developed due to water vapor attack.
- Healing of defects in the ITQ-1 crystal enhanced its steam stability.

Systems Modeling: Objectives and Approach

- **Work done by Dr. Fernando Lima (now at WVU) and Prof. Prodromos Daoutidis (UMN)**
- **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 process efficiency and 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

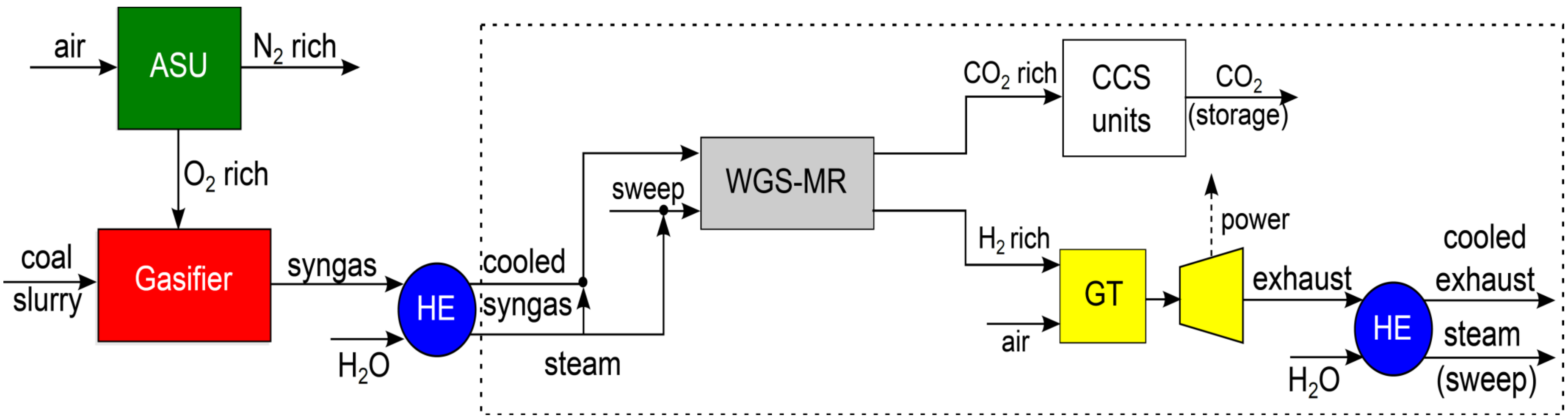


- **Assumptions**
  - **1-dimensional shell and tube reactor**
  - **catalyst packed in tube side**
  - **thin membrane layer placed on surface of tube wall**
  - **sweep gas flows in shell side**
  - **plug-flow operation**
  - **constant temperature and pressure**
  - **steady-state operation**
  - **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) Jillson et al., **J. Proc. Cont.** 19, 1470-1485 (2009)
(2) Choi and Stenger, **J. Power Sources** 124, 432-439 (2003)
(3) Lima et al., **Ind. Eng. Chem. Res.** 51, 5480-5489 (2012)

Integration of MR into IGCC Plant (MATLAB)

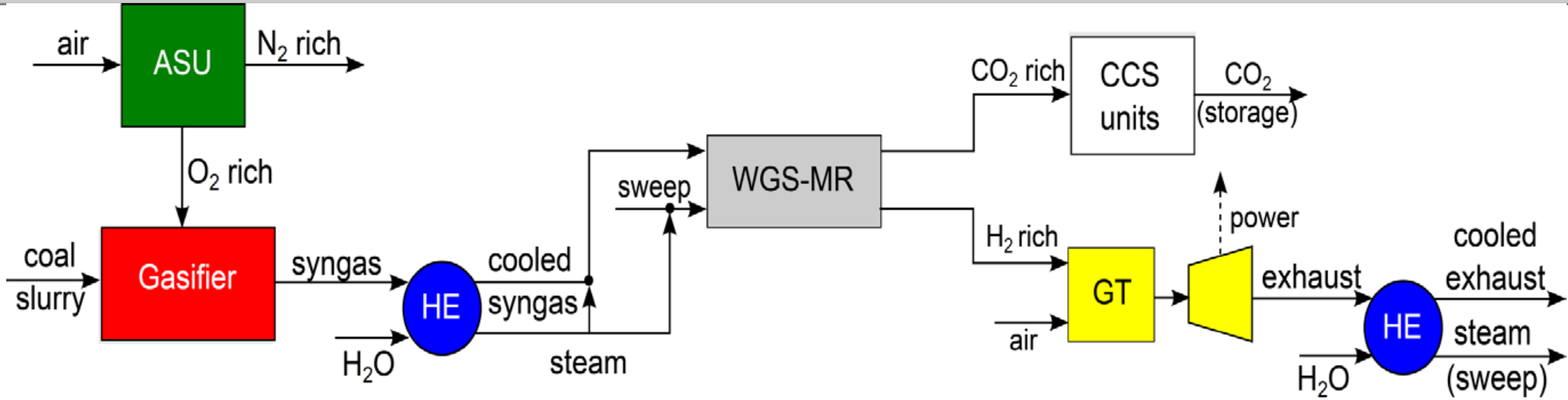


- Scale up MR model at steady state
- MR integration downstream of gasifier [(1),(2)]
- Effect on turbines/heat exchangers
- Steam integration for MR utilization

- Simulation studies performed
- Novel optimization problem formulation
  - 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)

IGCC-MR Optimization Results: Different Membrane Characteristics

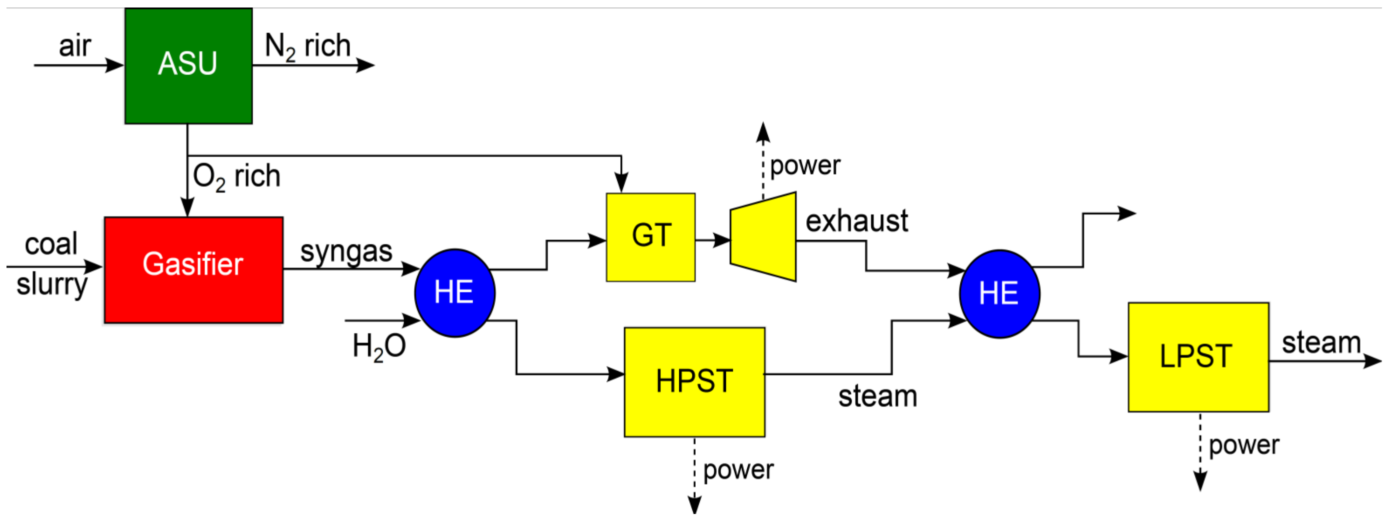


IGCC Performance Variable	Nominal ($S_{H2/all}$ = 1000, Q_{H2} = 0.2)	Nominal Optimal	Case I ($S_{H2/all}$ = 100, Q_{H2} = 0.2)	Case II ($S_{H2/all}$ = 1000, Q_{H2} = 0.1)
$A_m = \text{membrane area}\ [m^2]$	6800	4989	4739	7271
$C_{CO_2} = \frac{\text{carbon captured}}{\text{carbon in feed}}\ [\%]$	98.54	99.02	91.13	99.28
$\eta = \frac{\text{power generated}}{\text{HHV energy in coal}}\ [\%]$	47.96	47.55	47.63	46.96
$W = \text{power generated}\ [MW]$	614.07	617.60	618.41	615.00

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

IGCC 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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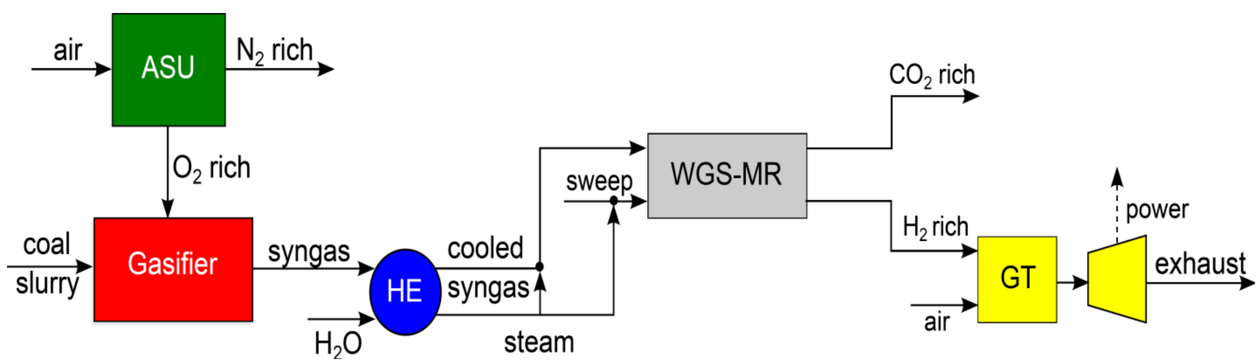

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(2) Turton et al., **Analysis, Synthesis and Design of Chemical Processes** (2012)

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**

- **Calculate MR cost to break even in a 30 year period**
- **Results based on present value of annuity calculation – 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)

Modeling Conclusions

- **Conclusions**
  - **MR model 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 (estimated to be \$1000-10000/m^2).**

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