Michael Tsapatsis (PI) and Prodromos Daoutidis (co-PI)
Drs. Bahman Elyassi, Fernando Lima and Aparna Iyer (Presenter)
Department of Chemical Engineering and Materials Science
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.

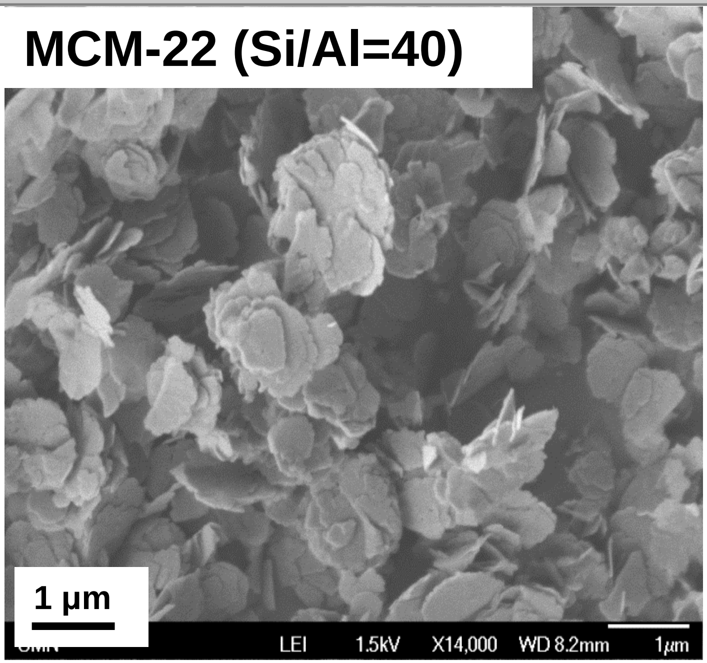
Outline

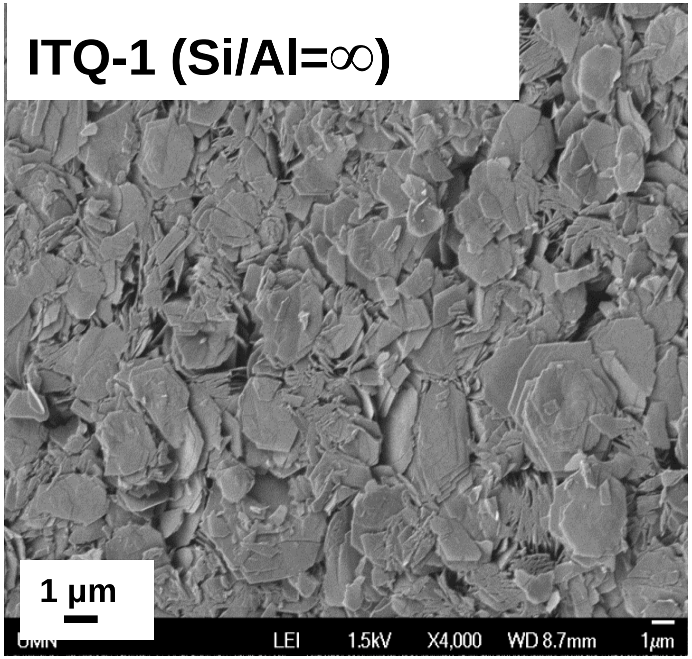
- **Preparation of hydrogen selective membranes using zeolite nanosheets.**

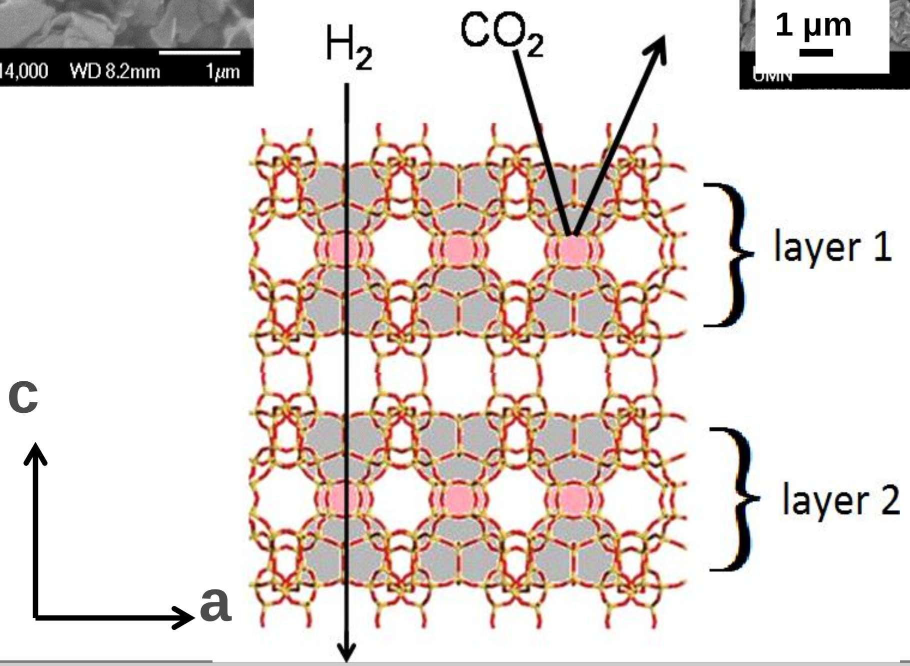
- **Steam stability of layered zeolites (MCM-22, ITQ-1, RUB-24, Nu-6(2)).**

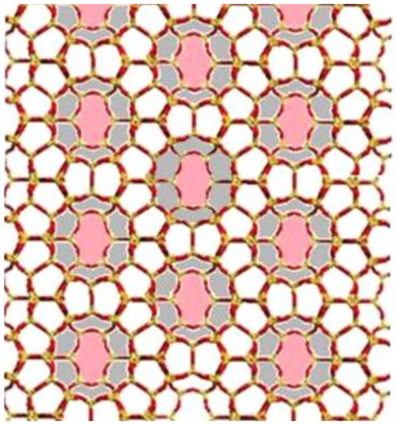
- **Modeling and optimization of IGCC plant with membrane reactor.**

Layered zeolites with 6-MR pores







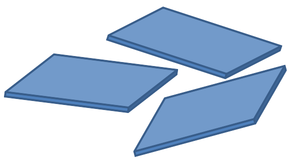


Hierarchical manufacturing of zeolite membranes

Layered zeolite
(thickness ~50 nm)

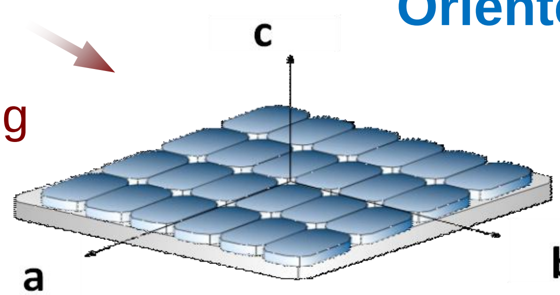
Exfoliation

Nanosheets with high aspect ratio
(thickness 2.5 nm)



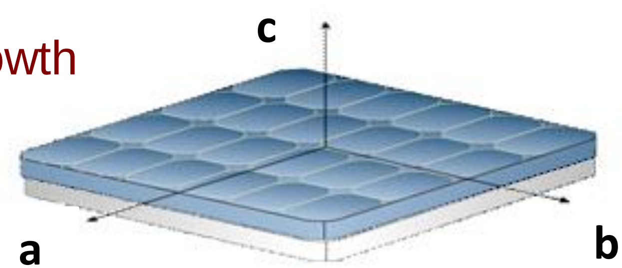
Coating

Oriented monolayer of crystals



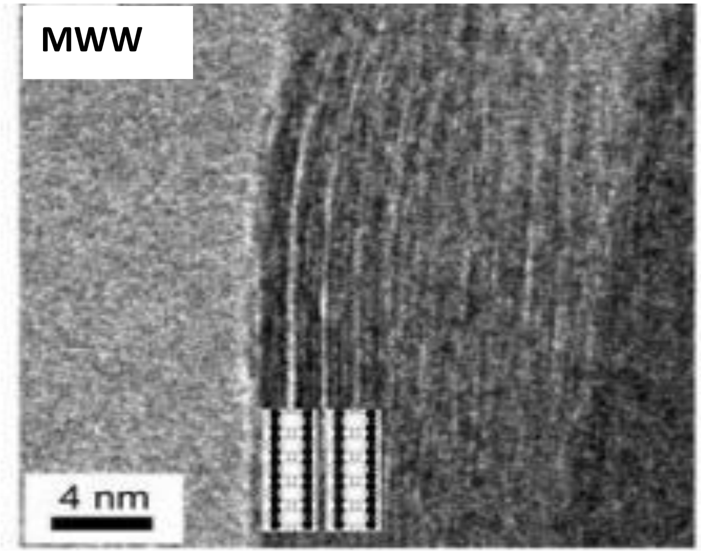
Secondary growth

Membrane

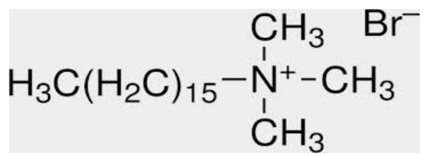


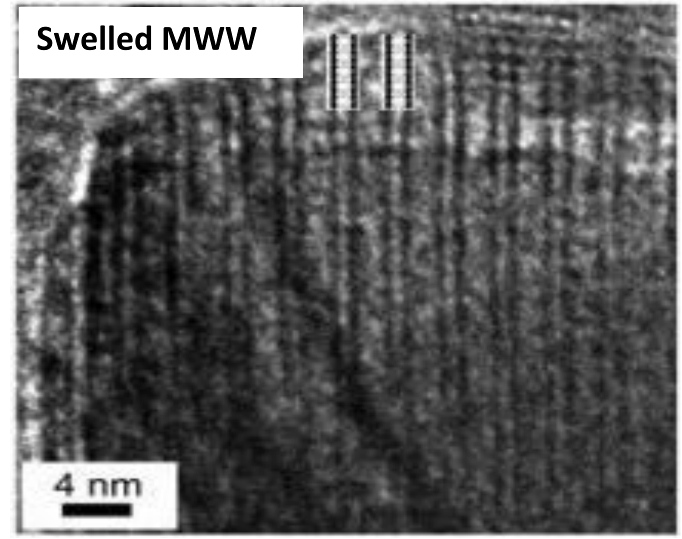
For a Review:
Mark A. Snyder, Michael Tsapatsis,
Angew. Chem. Int. Ed. **2007**, *46*, 7560–7573

Membrane preparation

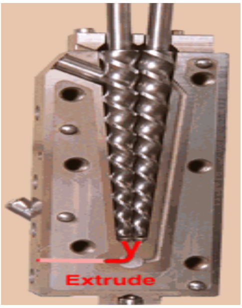


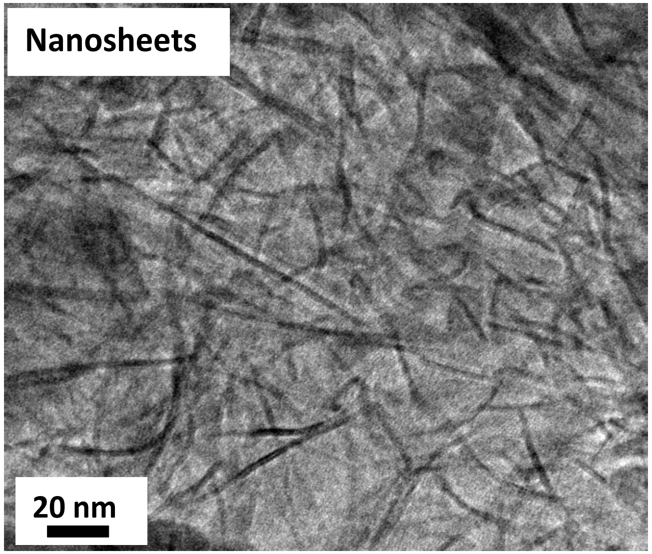
Swelling with CTAB



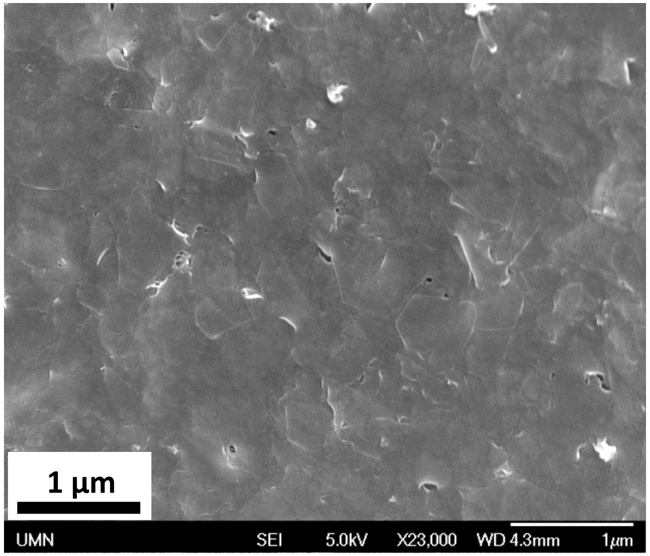


Exfoliation with polystyrene

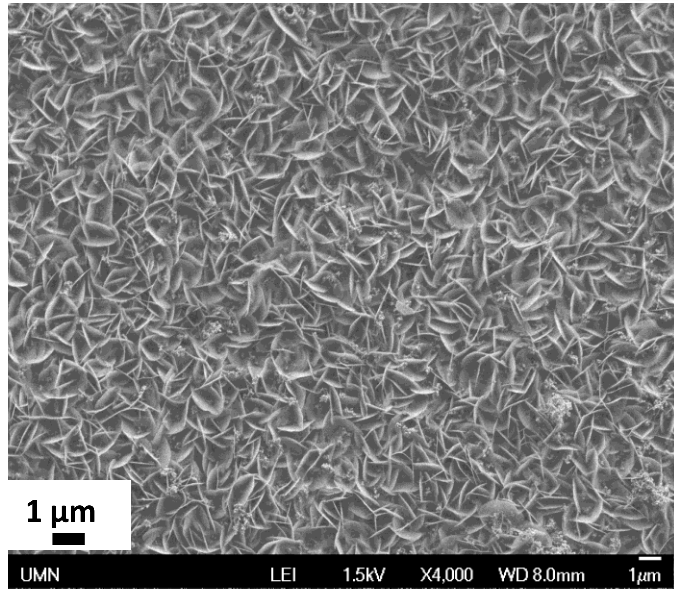




Dissolving nanocomposite in toluene, purification and filtration

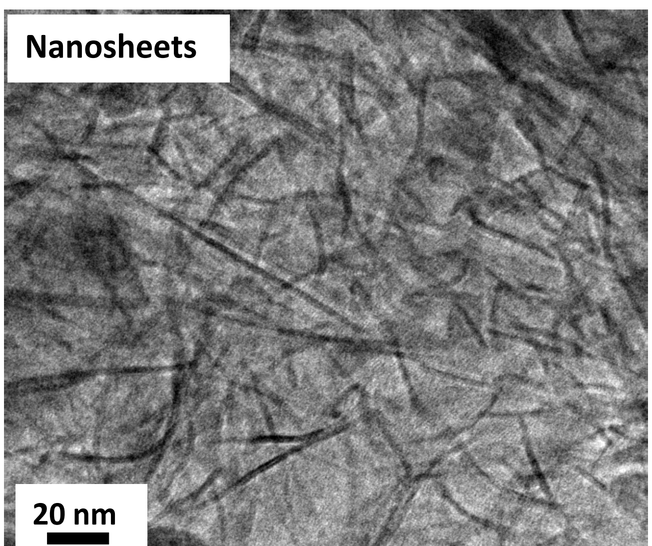


Membrane preparation

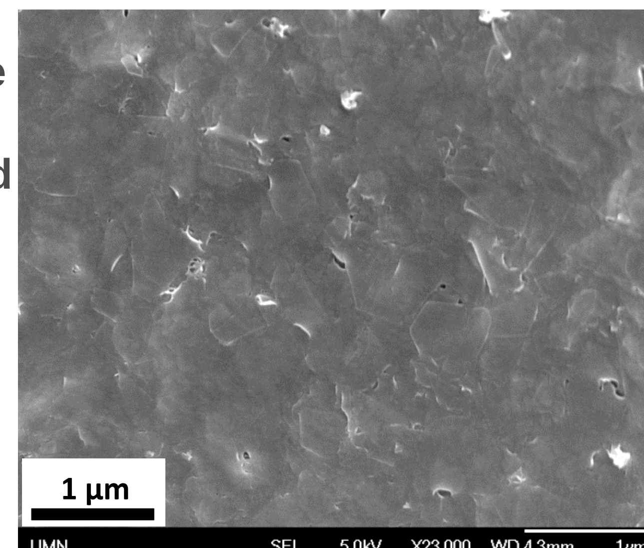


Secondary growth

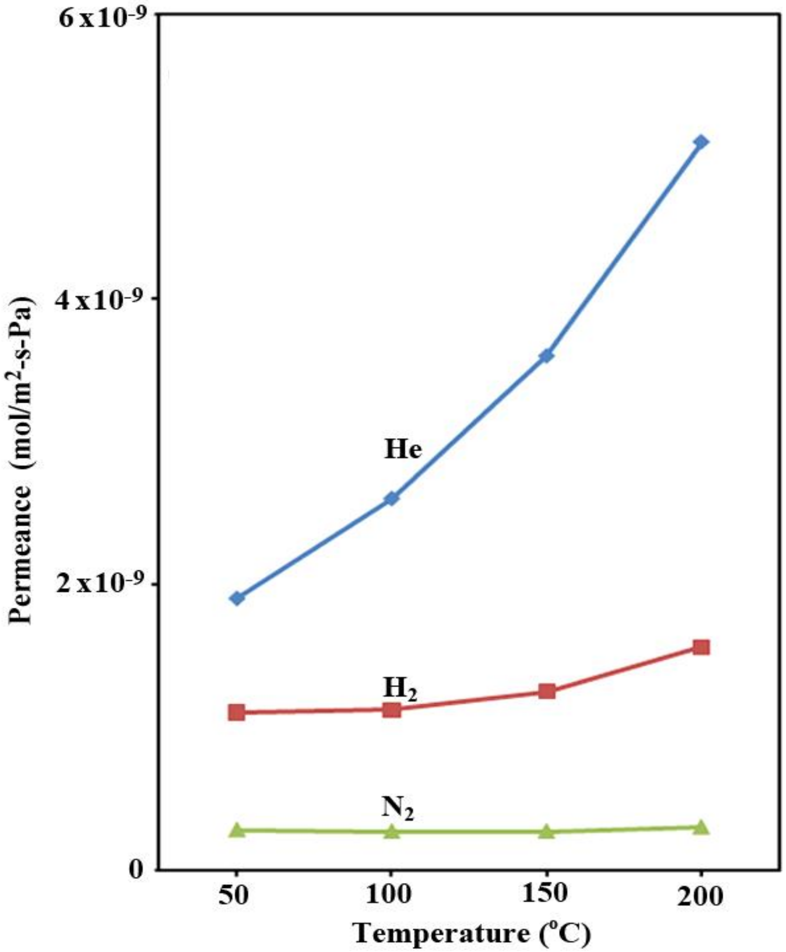
Exfoliation with polystyrene

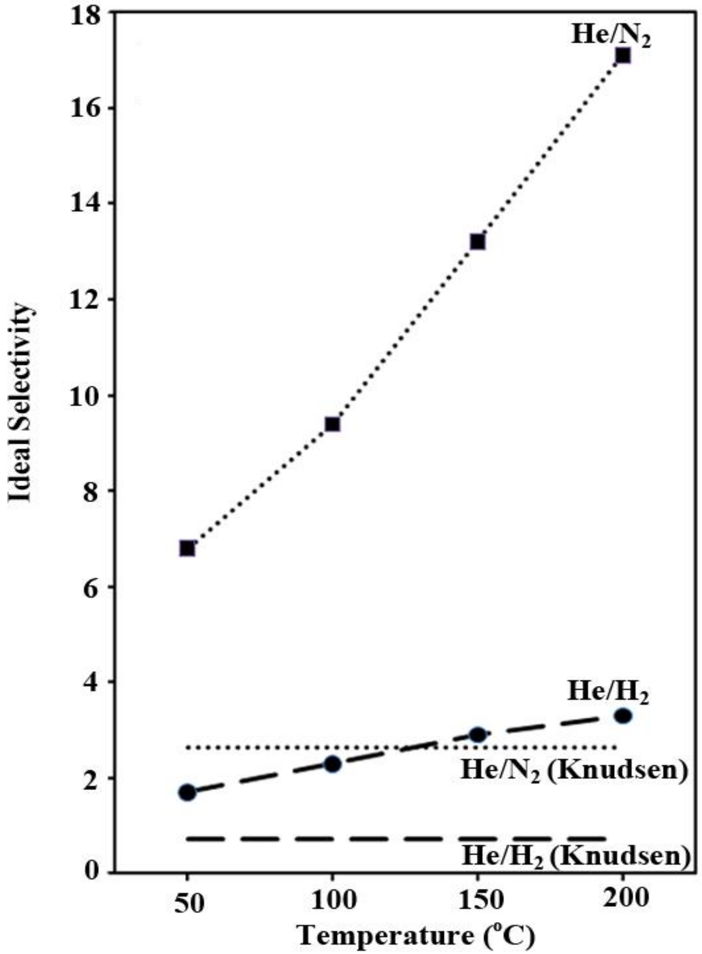


Dissolving nanocomposite in toluene, purification and filtration



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.

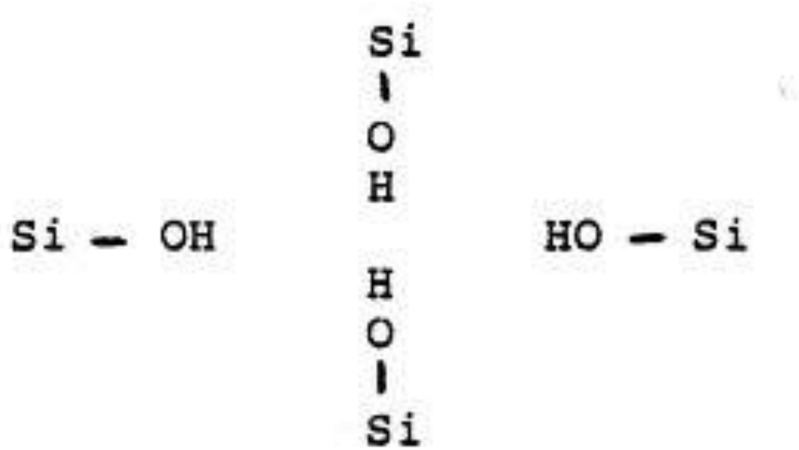
Steaming conditions for ITQ-1 and MCM-22

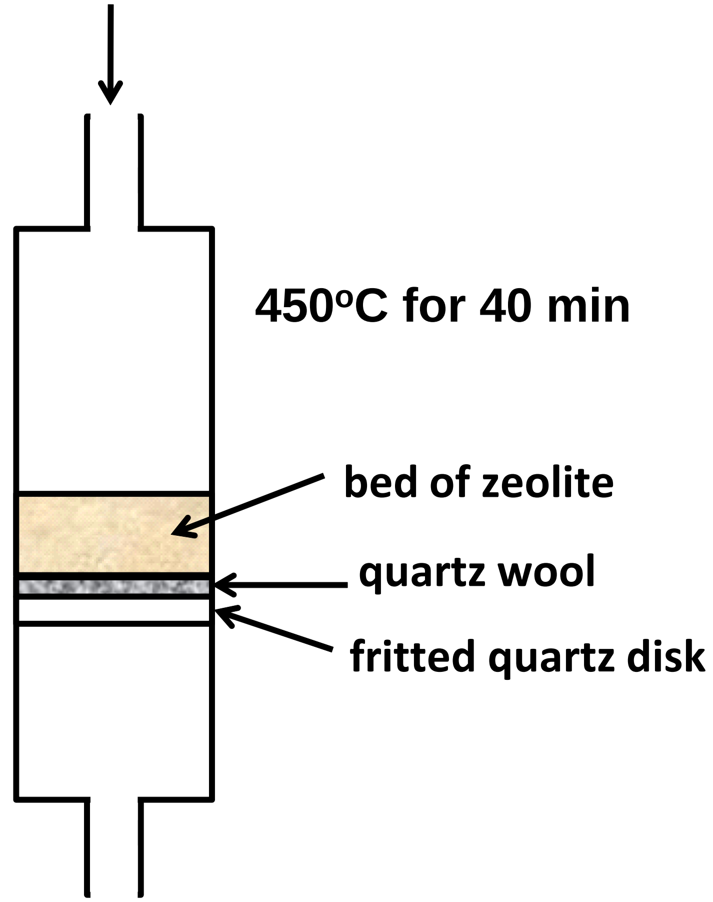
- Steaming conditions:
- Temperature: 350^{o}C
- Pressure: 10 bar (95% steam, 5% nitrogen)
- Samples were analyzed in 21 days intervals for 84 days

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



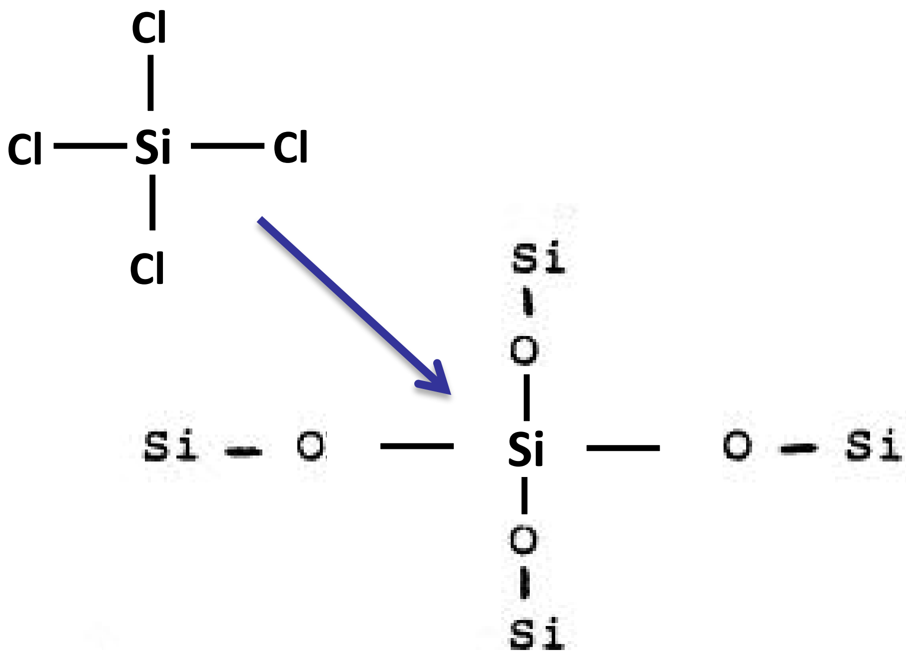


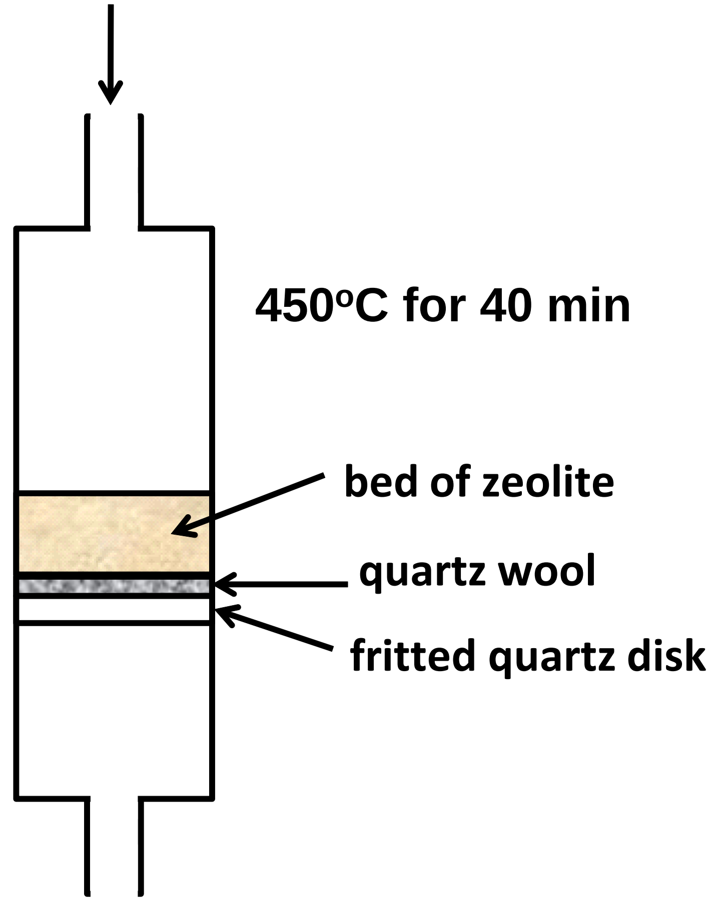
Beyer et. al., J . Chem. Soc., Faraday Trans. 1, 1985, 81, 2889-2901.

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

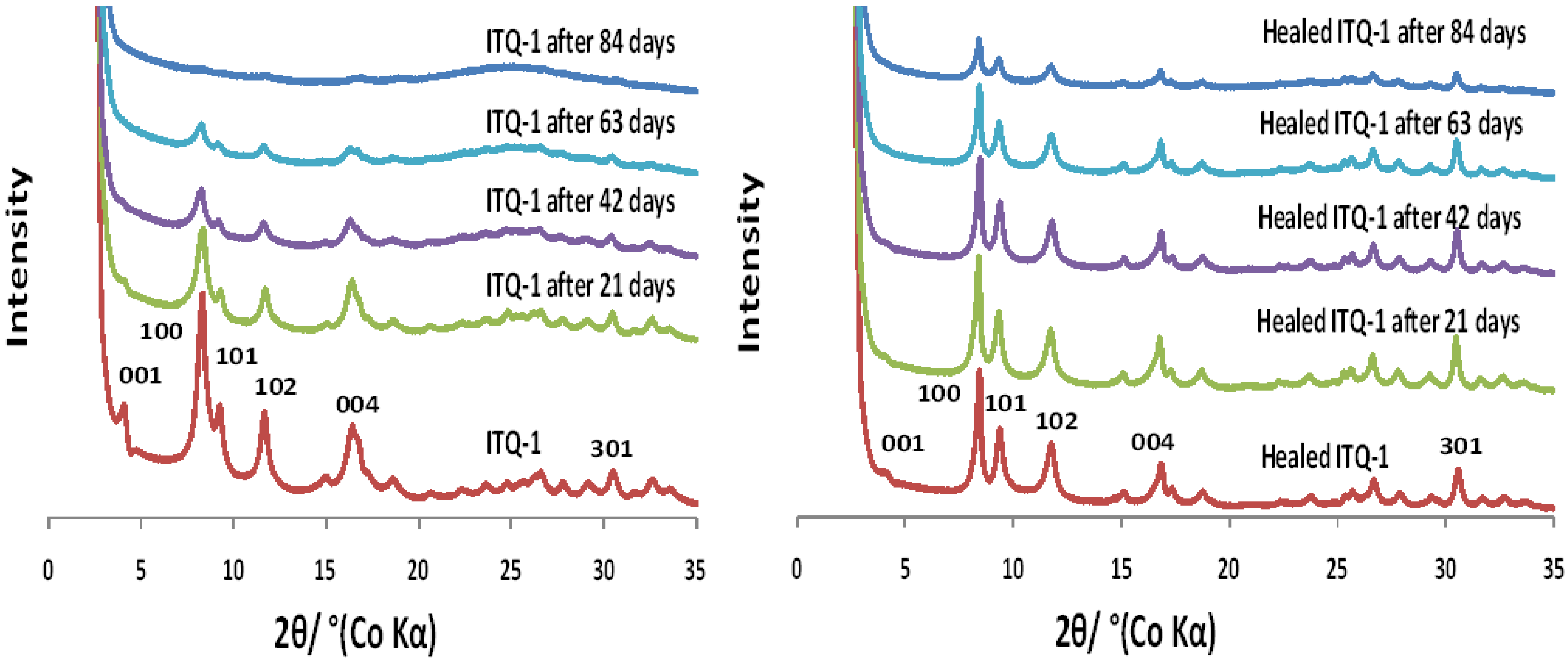




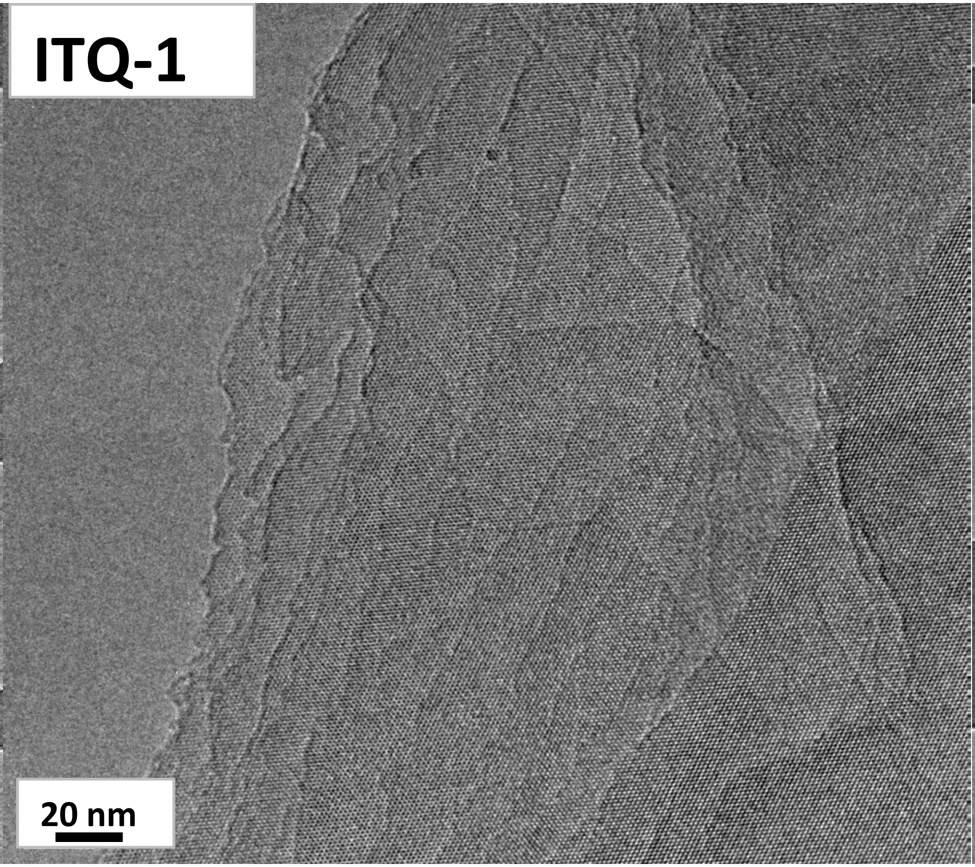
Beyer et. al., J . Chem. Soc., Faraday Trans. 1, 1985, 81, 2889-2901.

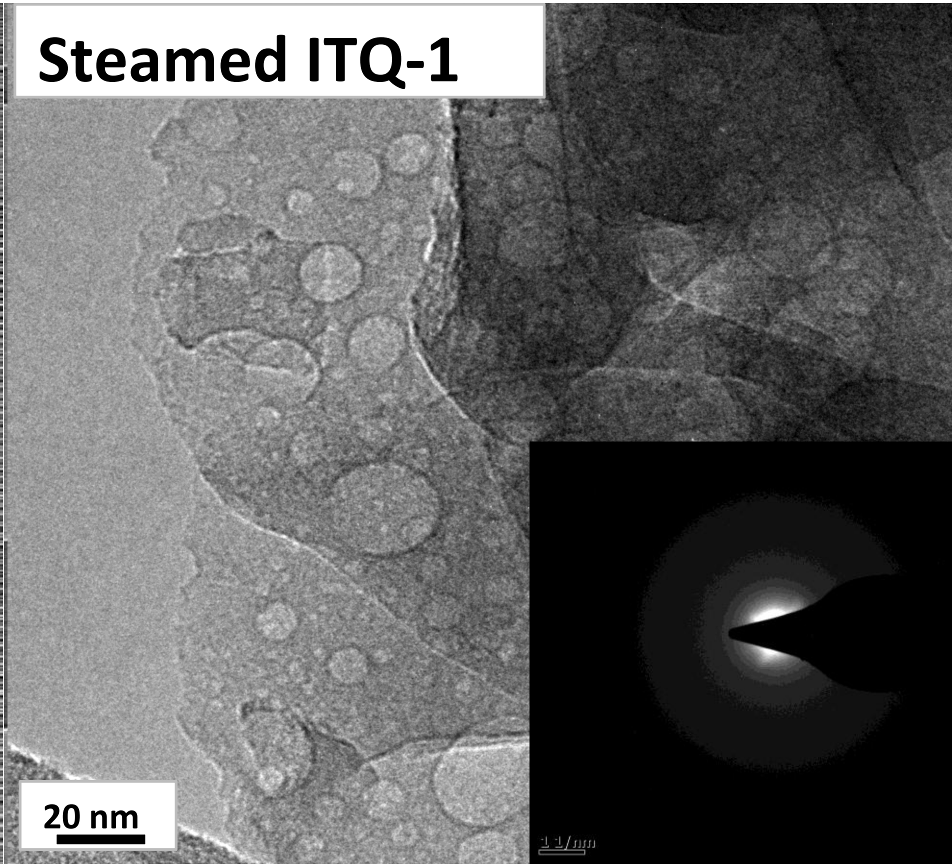
XRD of ITQ-1 and ITQ-1 treated with $SiCl_4$ at 350ºC

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

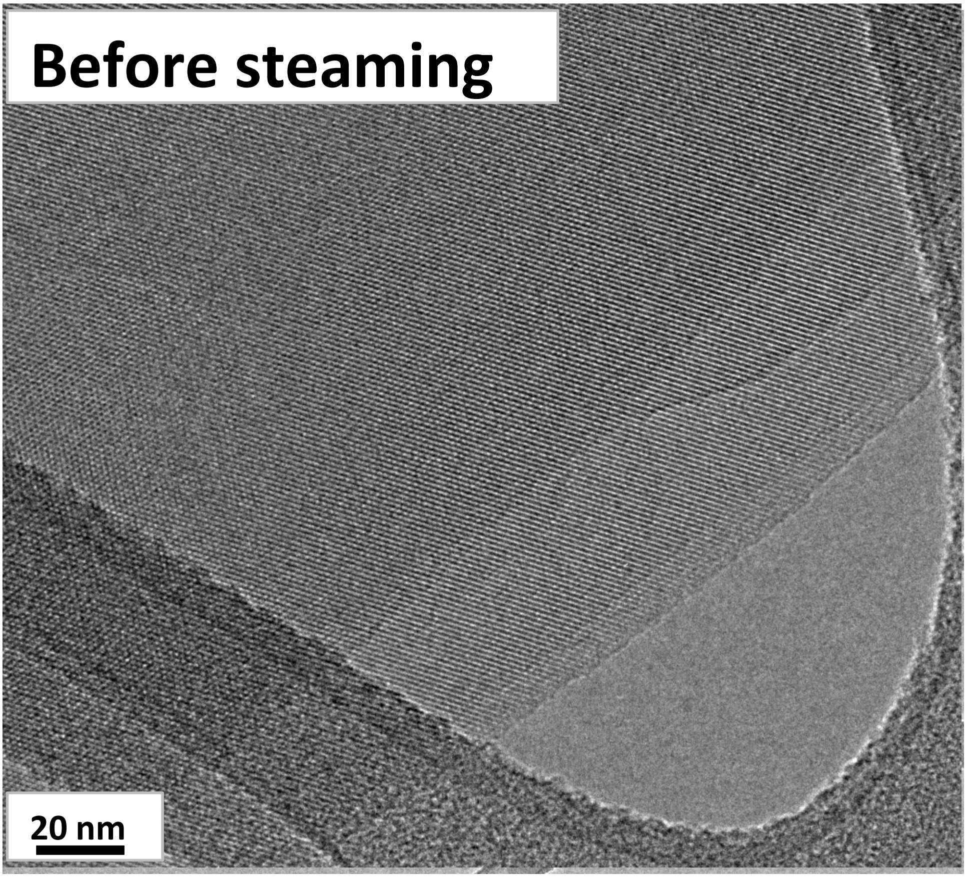


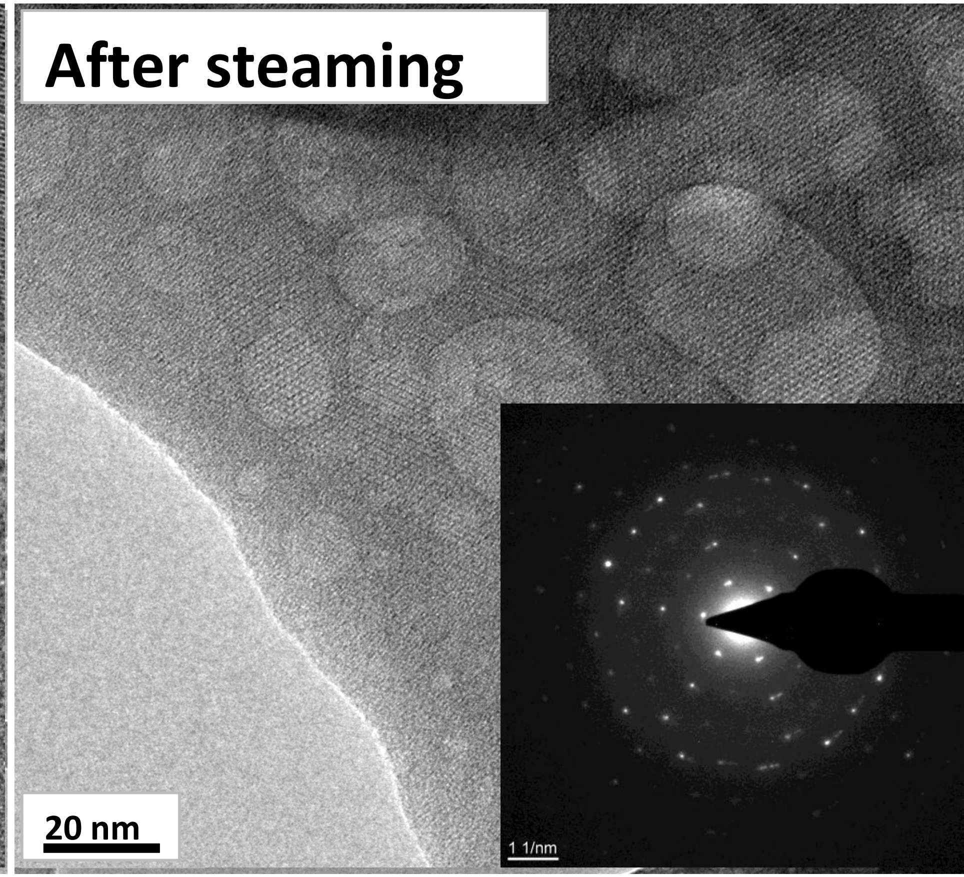
TEM images of ITQ-1 before and after 84 days of steaming



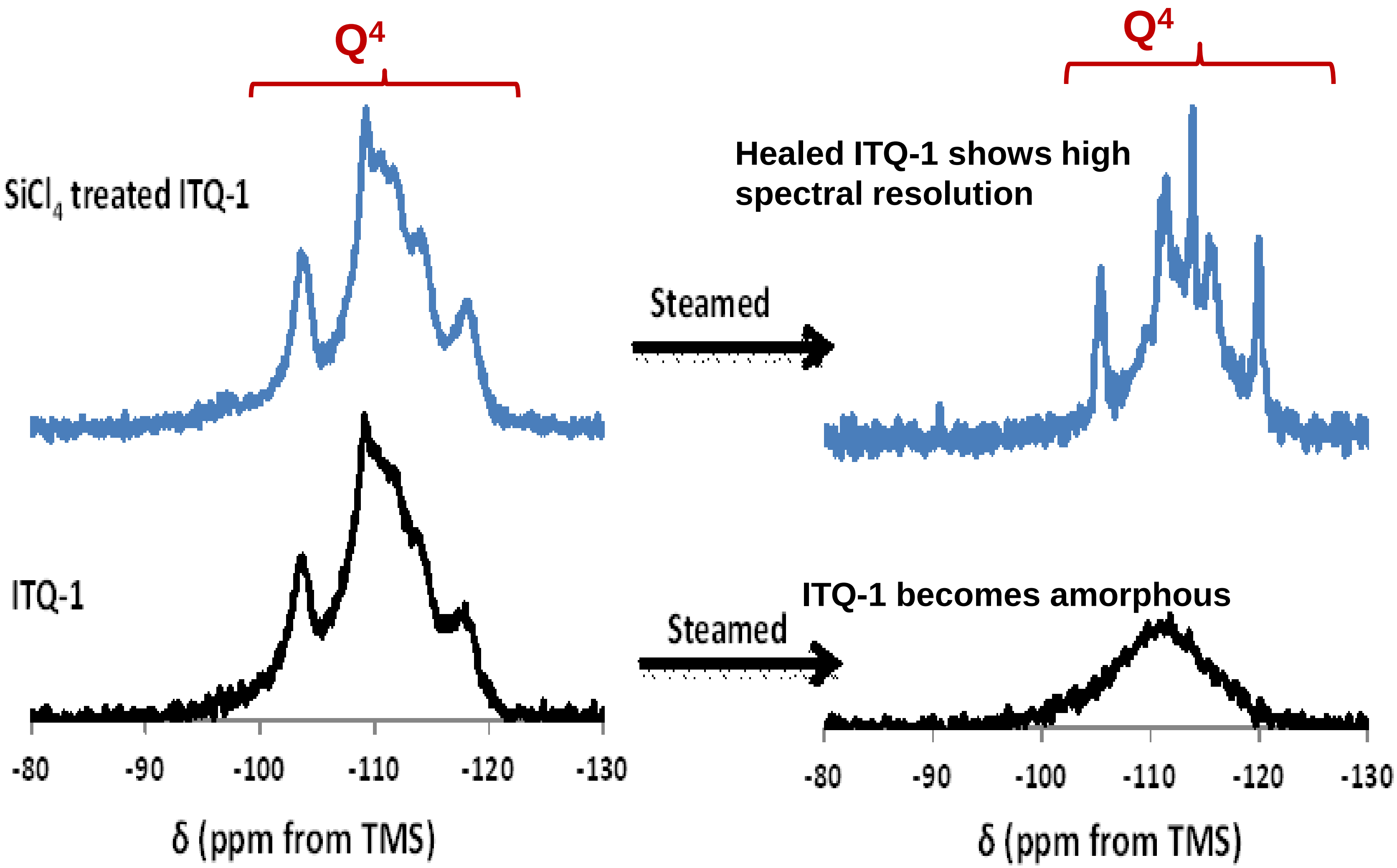


TEM images of **healed ITQ-1** before and after 84 days of steaming



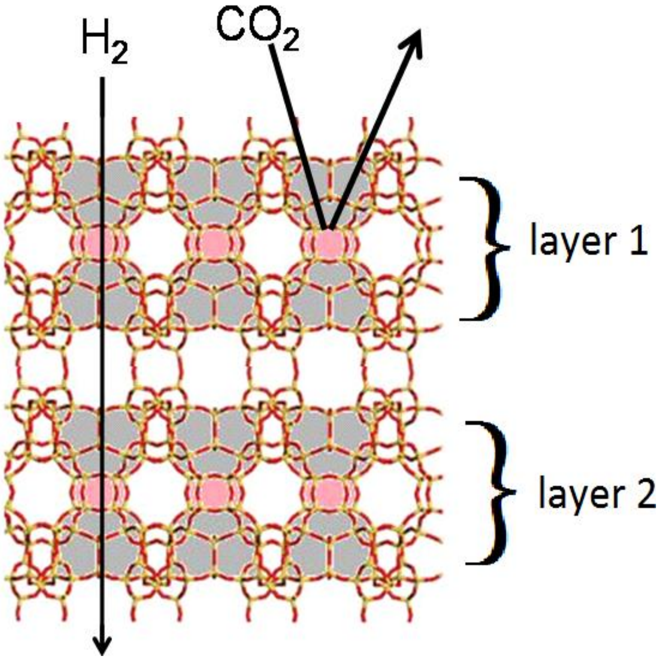


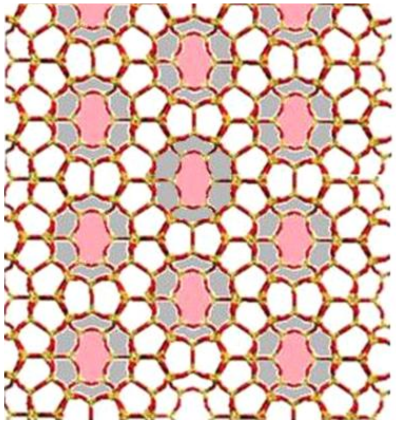
^{29}Si MAS NMR of ITQ-1 and $SiCl_4$ treated ITQ-1 before and after steaming for 84 days at 350°C



$Q_n = Si(OSi)_n(OH)_{(4-n)}$

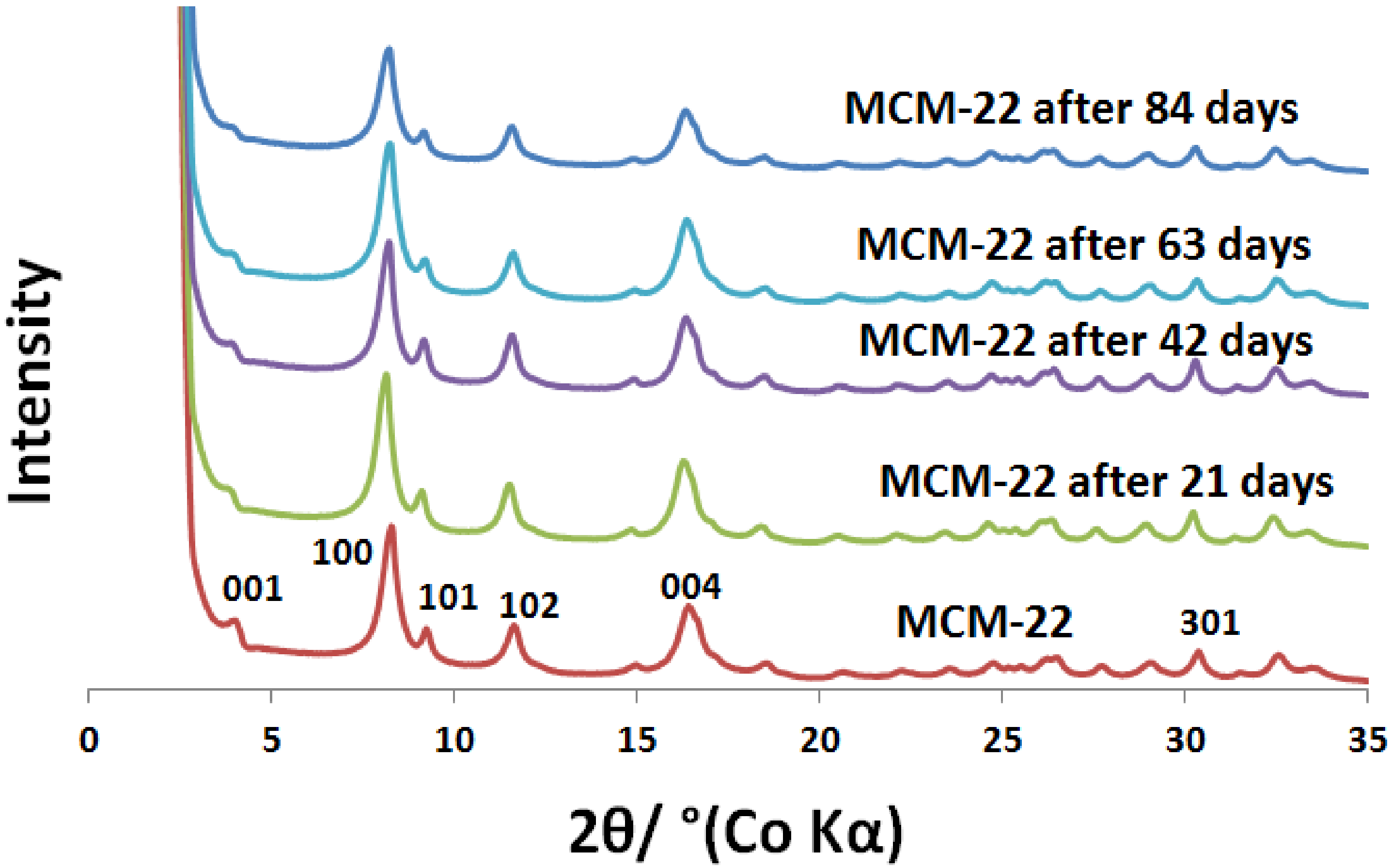
Steam stability of MCM-22 (Si/Al=40)



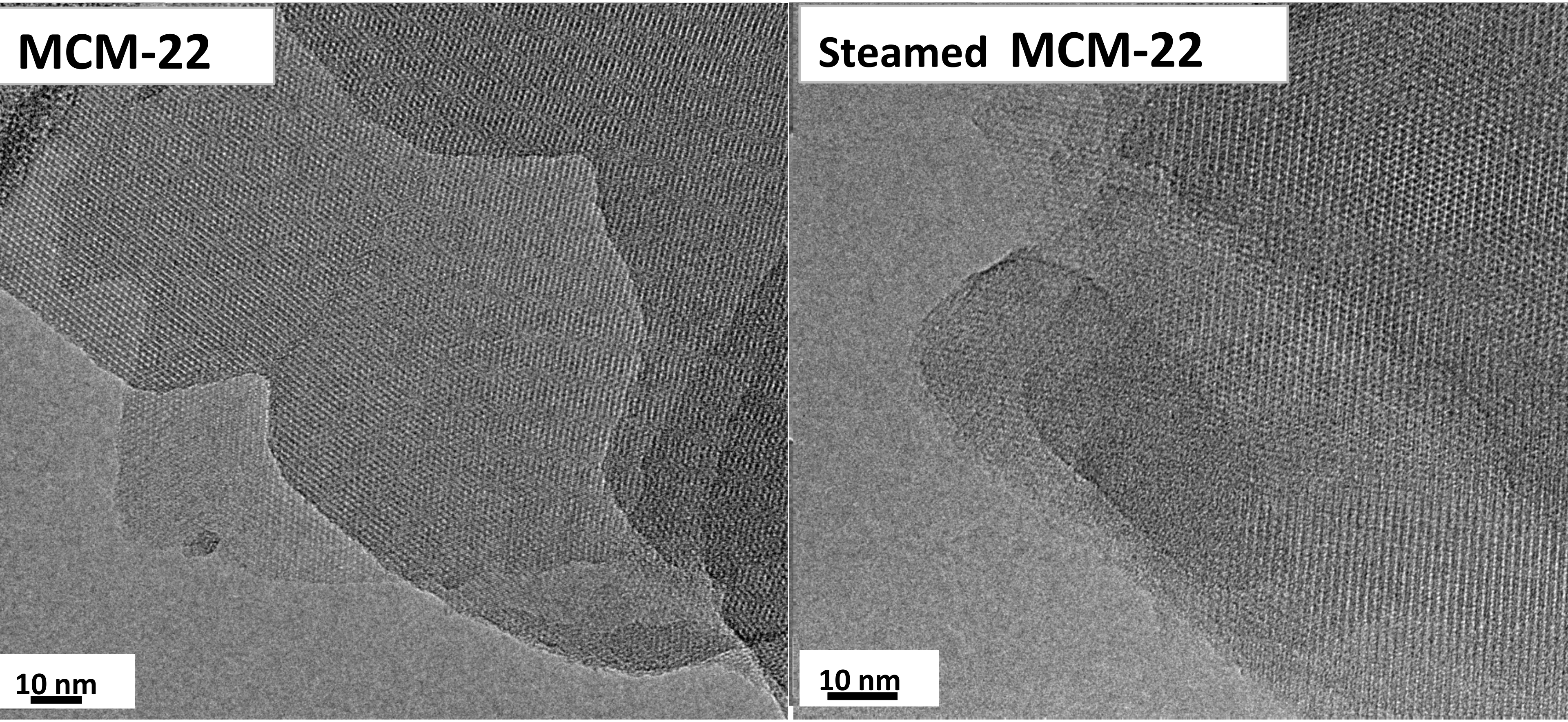


XRD of MCM-22 steam treated at 350°C

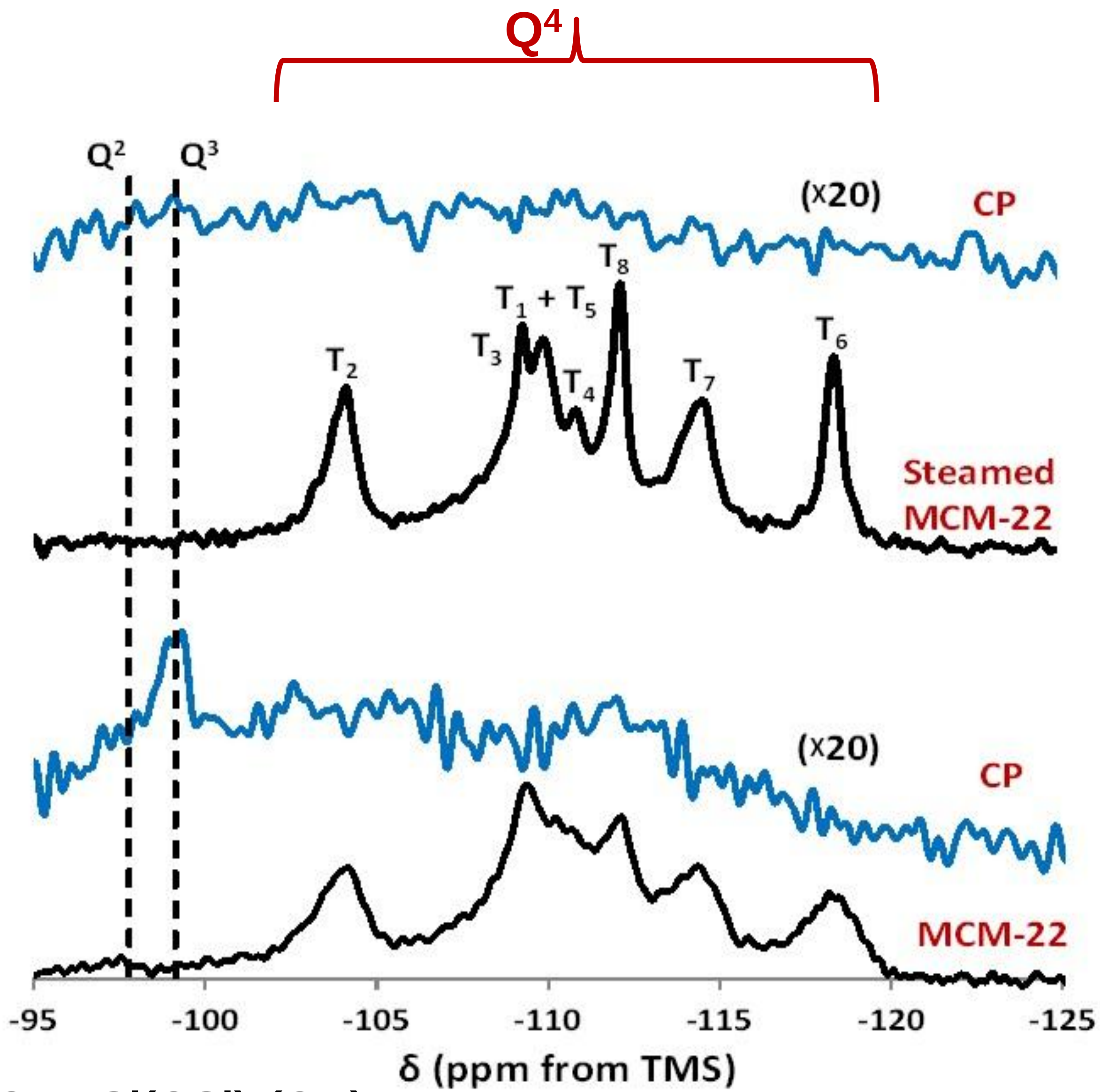
- MCM-22 keeps its crystallinity.
- No change in crystal morphology was seen in the SEM pictures.



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

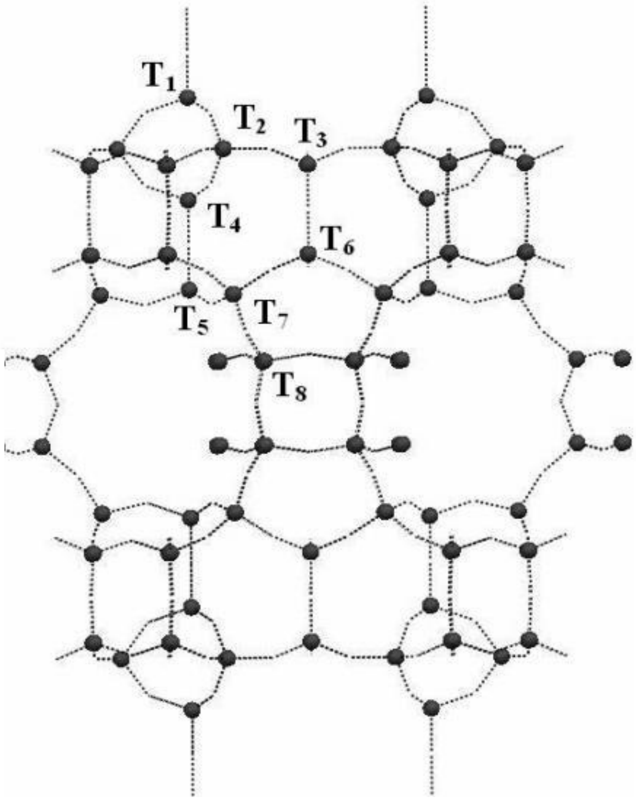


^{29}Si and CP/MAS NMR of MCM-22, before and after steaming at 350°C for 84 days



$Q_n = Si(OSi)_n(OH)_{(4-n)}$

- Higher spectral resolution can be seen after hydrothermal treatment.
- Intensity reduction at -97 and -99 ppm (defect sites).



$\sigma = -0.6192\Theta - 18.68$

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

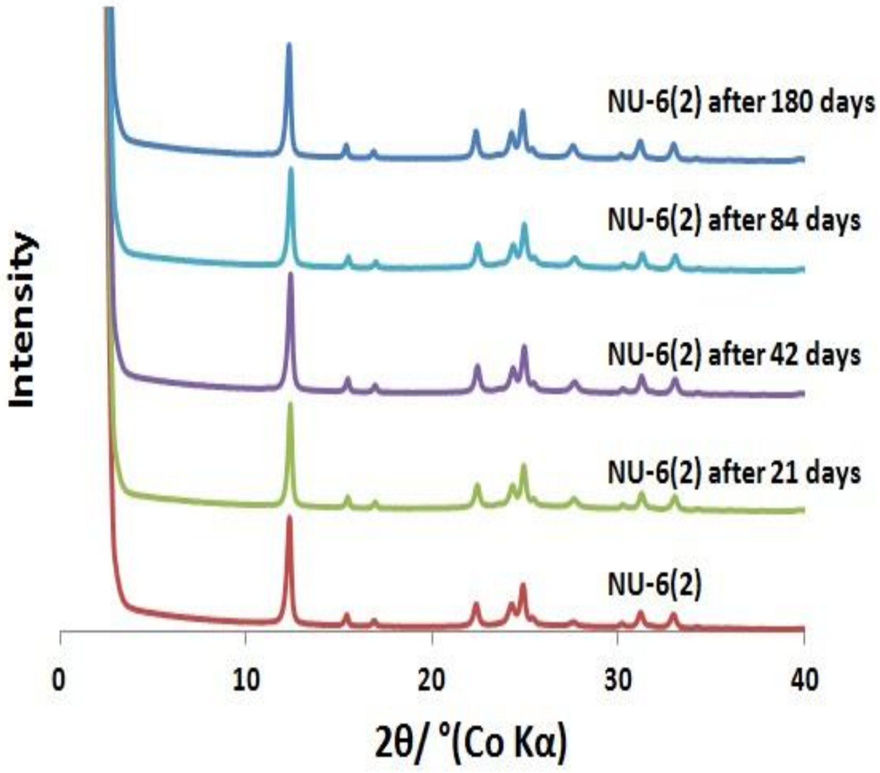
Effect of steaming on textural properties

	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	490	0.163	0.198	340	0.113	0.133
ITQ-1-900	402	0.138	0.186	13	0	0
ITQ-1-H900	470	0.160	0.195	110	0.027	0.034
ITQ-1-580	550	0.182	0.254	158	0.048	0.069
ITQ-1-H580	521	0.181	0.239	308	0.103	0.142

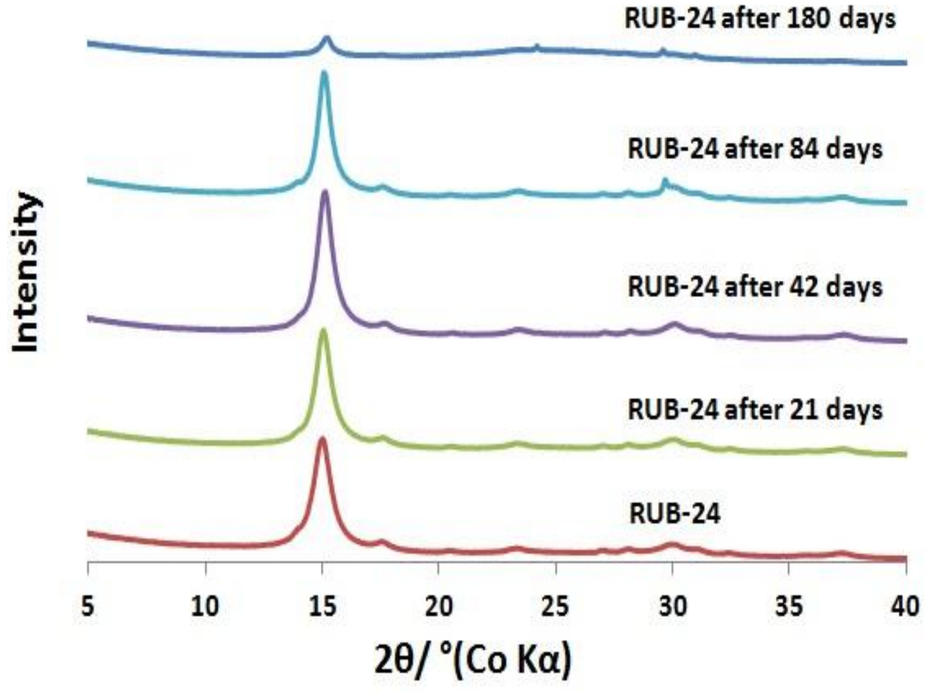
[a] BET surface area from N_2 adsorption isotherm.
[b] Micropore volume from t-method using N_2 adsorption isotherm.
[c] Micropore volume using the NLDFT kernel “Ar at 87 K zeolites- silica, cylindrical pore model”.

XRD of patterns of Nu-6(2) and RUB-24 zeolites: Steamed at 350ºC and 10 bar (35% H_2O in N_2) for 6 months

Nu-6(2)



RUB-24



Summary of stability analysis & future work

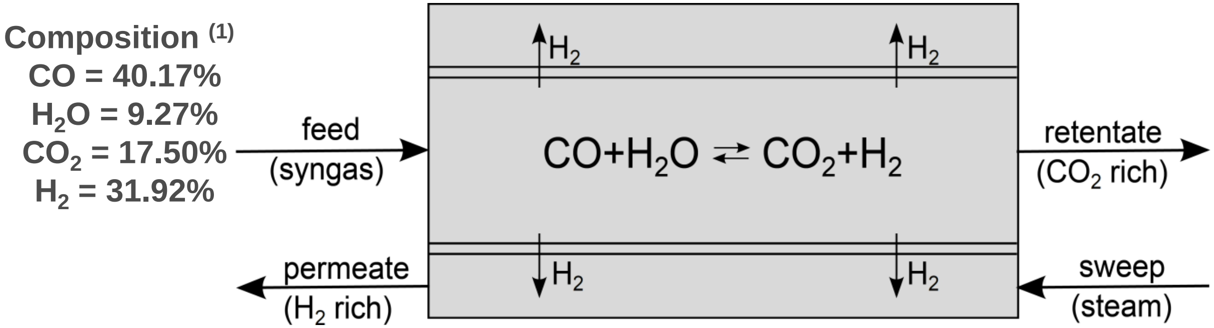
- **Achievements**
  - **Systematic studies on the long-term steam stability of zeolites: MCM-22, ITQ-1, NU-6(2), and RUB-24 were completed.**
  - **Healing of defects in the ITQ-1 crystal enhanced its steam stability.**
  - **NU-6(2) preserved its crystallinity after 6 months of steaming (35% H_2O, 65% N_2) at 350°C.**
  - **Permeation cell construction and its sealing evaluation at high temperatures.**
- **Future Work**
  - **Study of membranes' performance at high temperatures and under steaming.**

Systems Modeling: Objectives and Approach

- **Work done by Dr. Fernando Lima 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

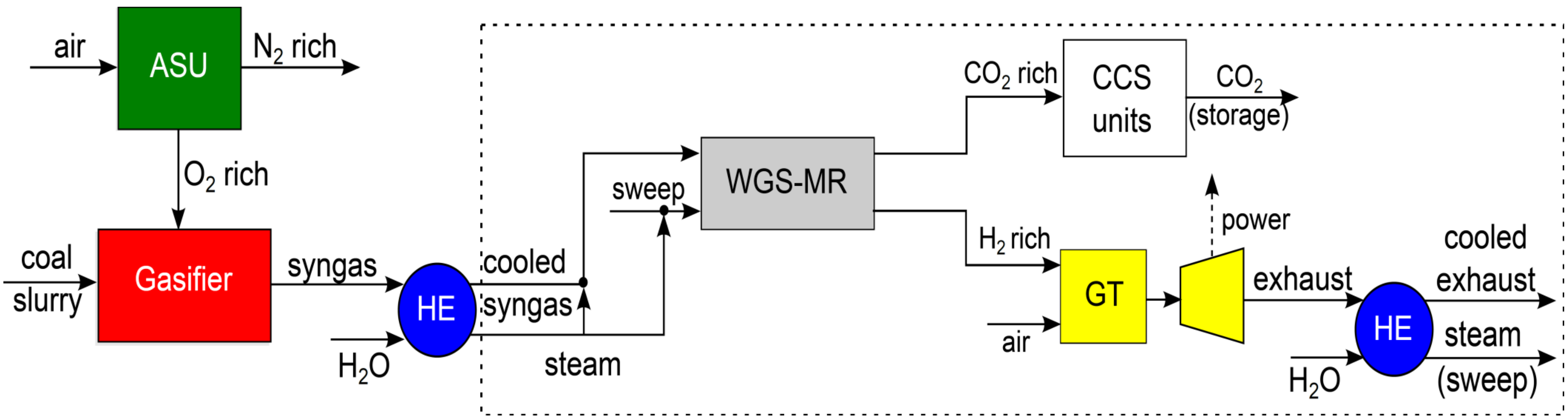


- **Assumptions**
  - **1-dimensional shell and tube reactor**
  - **catalyst packed in tube side**
  - **thin membrane layer placed on surface of tube wall**
  - **sweep gas flows in shell side**
  - **plug-flow operation**
  - **constant temperature and pressure**
  - **steady-state operation**
  -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

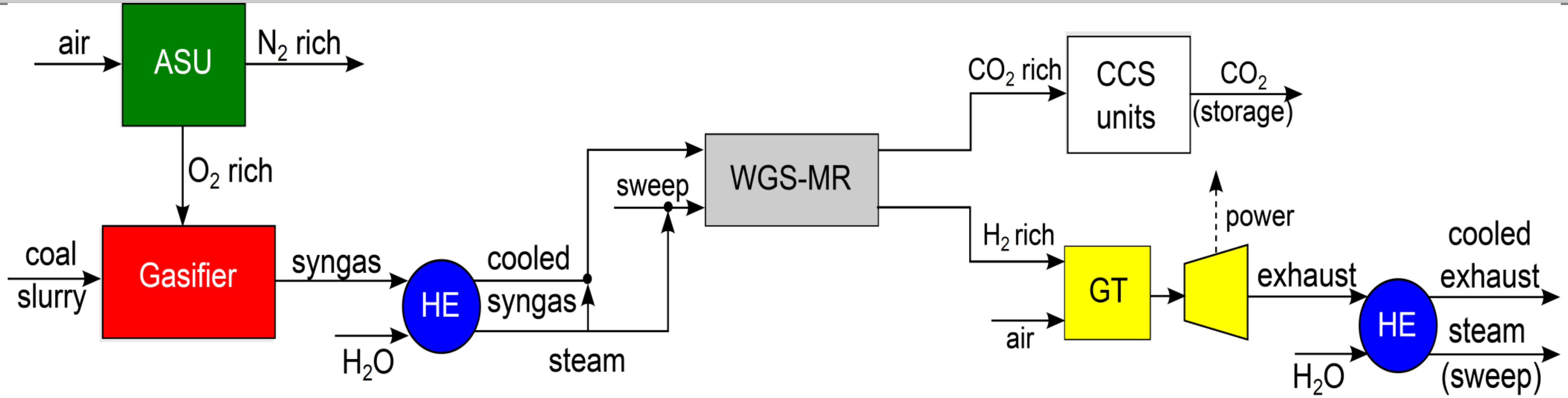
Integration of MR into IGCC Plant (MATLAB)



- **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

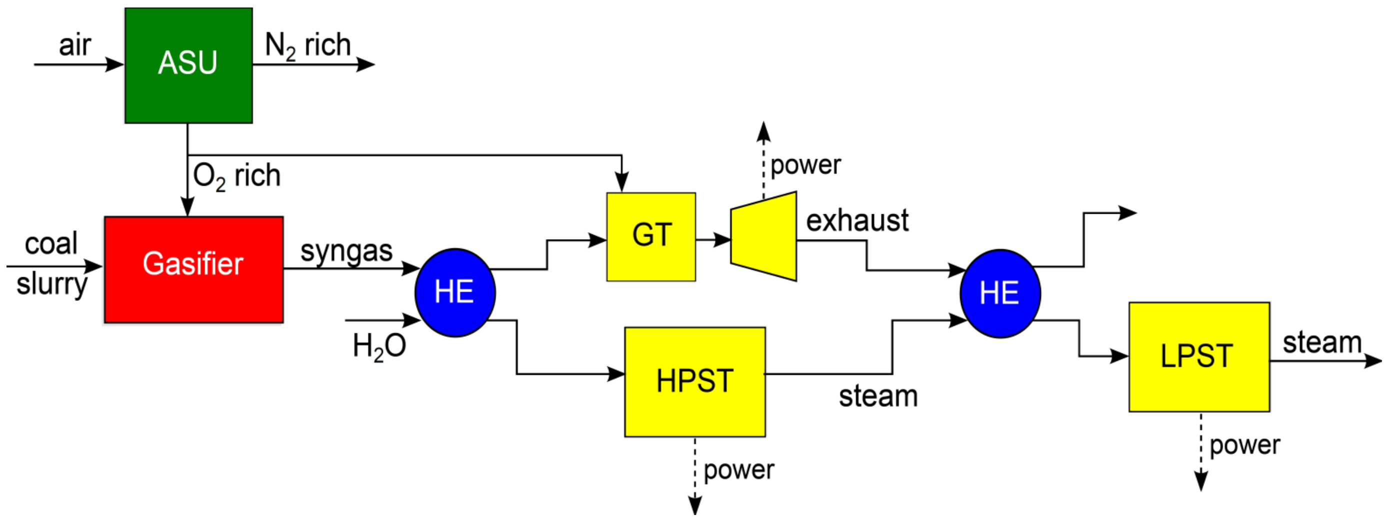


IGCC Performance Variable	Nominal ($S_{H2/all}$ = 1000, Q_{H2} = 0.2)	Nominal Optimal	Case 1 ($S_{H2/all}$ = 1000, Q_{H2} = 0.1)	Case 2 ($S_{H2/all}$ = 100, Q_{H2} = 0.2)
A_m = membrane area $\left[m^2\right]$	6800	4989	7271	4739
$C_{CO_2} = \frac{\text{carbon captured}}{\text{carbon in feed}} \left[\%\right]$	98.54	99.02	99.28	91.13
$\eta = \frac{\text{power generated}}{\text{HHV energy in coal}} \left[\%\right]$	47.96	47.55	46.96	47.63
W = power generated $\left[MW\right]$	614.07	617.60	615.00	618.41

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

IGCC-MR Differential Cost Analysis

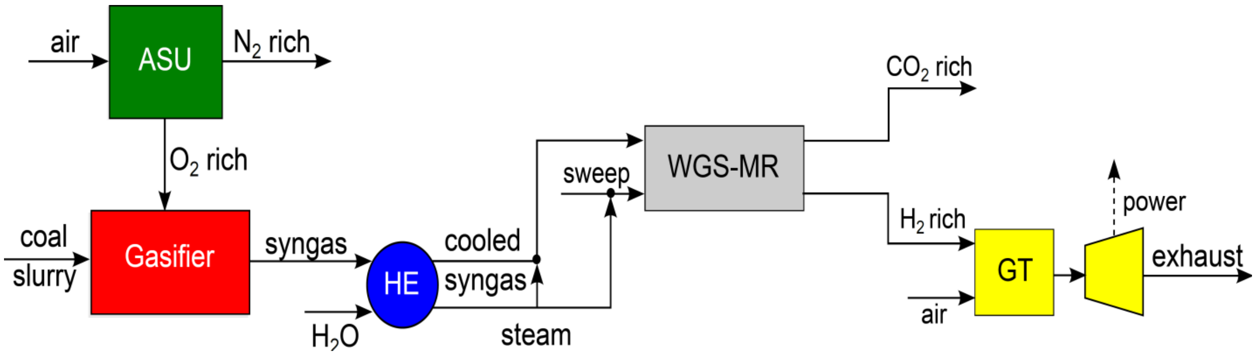
- Cost comparison between IGCC with and without MR
- Same amount of coal and power generation (≈ 615 MW)
- Cost differences
  - larger ASU (IGCC) [(1)]: \$291.01 million/30 years
  - steam and gas turbines differences (IGCC) [(1)]: \$41.53 million/30 years
  - extra heat exchangers (IGCC-MR) [(2)]: \$3.78 million/30 years
  - added MR with A_m = 5000 m^2 (IGCC-MR): ≈ \$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)

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): \$291.01 million/30 years**
  - **steam and gas turbines differences (IGCC) (1): \$41.53 million/30 years**
  - **extra heat exchangers (IGCC-MR) (2): \$3.78 million/30 years**
  - **added MR with A_m = 5000 m^2 (IGCC-MR): ≈ \$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)

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): $291.01 million/30 years**
  - **steam and gas turbines differences (IGCC) (1): $41.53 million/30 years**
  - **extra heat exchangers (IGCC-MR) (2): $3.78 million/30 years**
  - **added MR with A_m = 5000 m^2 (IGCC-MR): ≈ $5-50 million/lifetime**

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

Lifetime [year]	Cost [$/$m^2$]
1	5,840
2	11,680
3	17,520

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

Modeling Conclusions & Future Work

- **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**
- **Future work (Aspen)**
  - **Carry out simulation studies for different flowsheet alternatives**
  - **Perform techno-economic analysis using integrated model**

Acknowledgements

U.S. Department of Energy (DOE) (grant DE-09FE0001322).

The University of Minnesota Characterization Facility, which receives partial support from NSF through the National Nanotechnology Infrastructure Network.