Utilization of Zeolite as Multi-Functional Proppant for CO_2 Enhanced Shale Gas Recovery and CO_2 Sequestration:

A Molecular Simulation Study on Gas Adsorption in Zeolite and Organic Matter

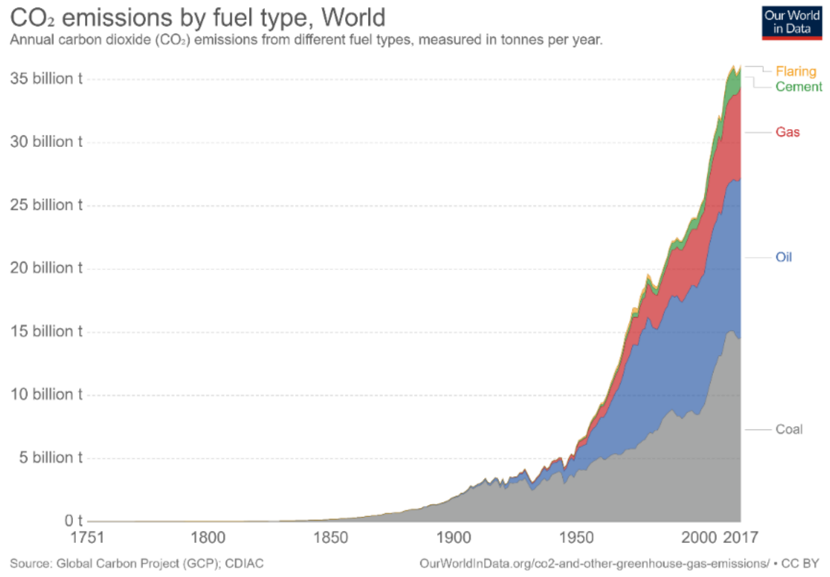
Kaiyi Zhang and Guan Qin
University of Houston
Department of Petroleum Engineering

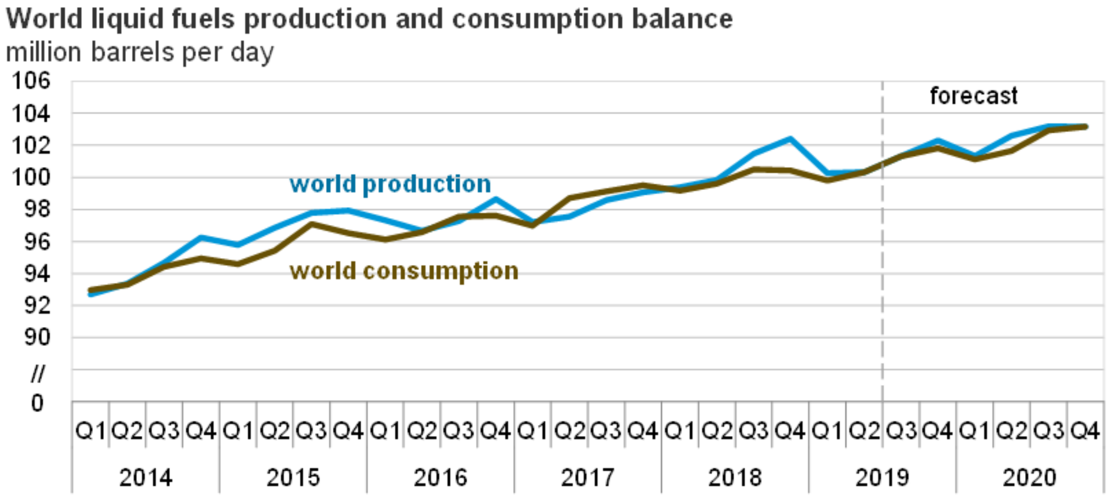
Outline

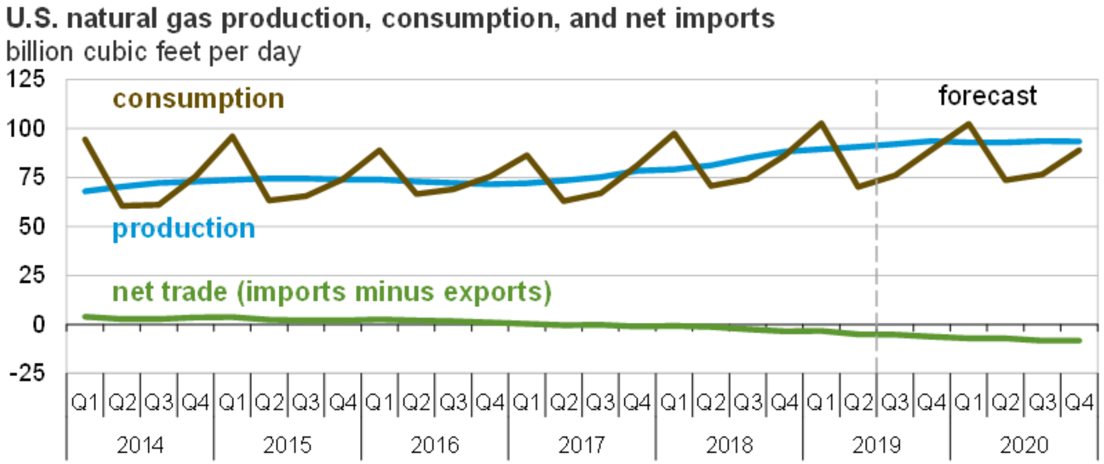
- Motivation and objectives
- Introduction
- Our approach
- Model setup
- Results and discussion
- Conclusion and future work

Motivation and Objectives

- The dual challenge
  - Meeting the energy demand
  - Reducing the carbon emissions
- Objectives
  - Enhance shale gas production by extracting tl
  - equ



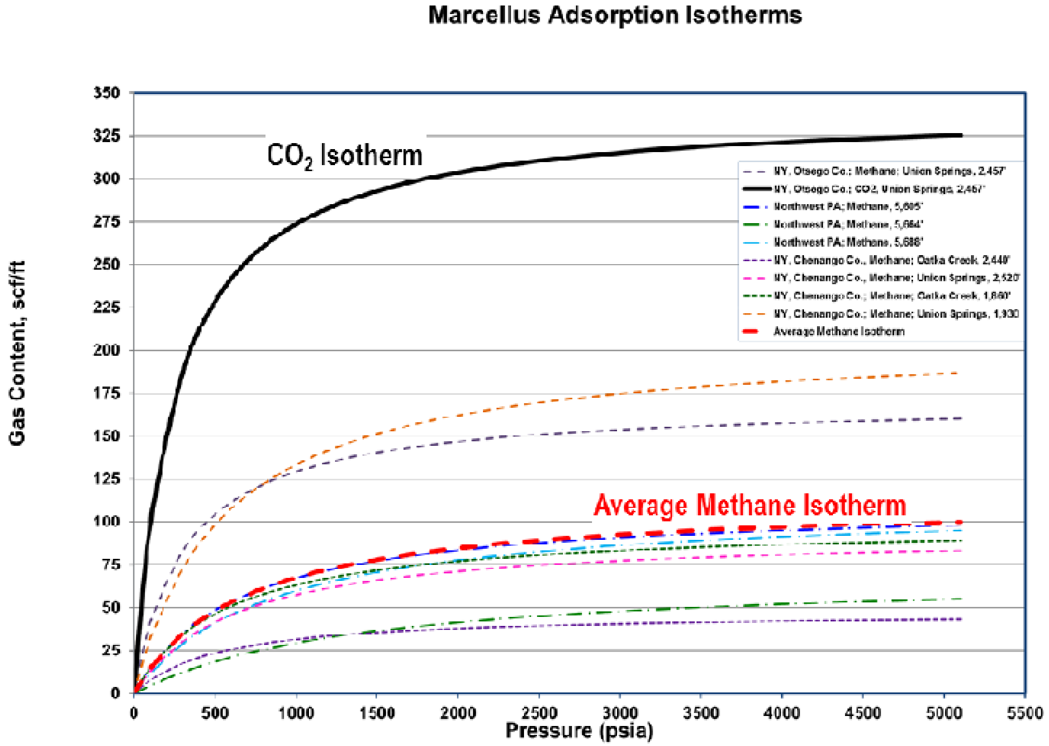




Source: Short-Term Energy Outlook, EIA, September 2019

Introduction

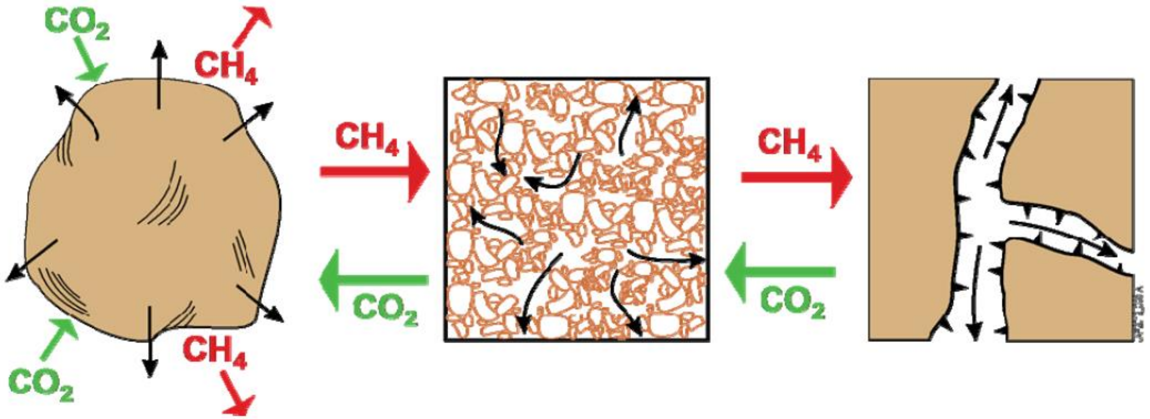
- CH_4 and CO_2 adsorptions in shale formation
  - Large amount of adsorbed gas in shale formation
  - Organic rich shales adsorb CO_2 preferentially over CH_4
  - Replace adsorbed CH_4 by CO_2 to enhance shale gas recovery



M. Godec, Potential for enhanced gas recovery and CO_2 storage in the Marcellus Shale in the Eastern United States, Int. J. Coal Geol. 118 (2013) 95–104.

Introduction

- Current CO_2-enhanced shale gas recovery methods
  - CO_2 injection:
    - **Potential issues: early CO_2 breakthrough through fractures, not long enough time for gas exchange**
  - CO_2 fracturing:
    - Well-established and results in as much as 5-fold higher gas production
    - **Potential issue: CO_2 emission from flow-back fluids, formation of CO_2 hydrates that block the tubing, low proppant-carrying capacity.**



M. Godec, Potential for enhanced gas recovery and CO_2 storage in the Marcellus Shale in the Eastern United States, Int. J. Coal Geol. 118 (2013) 95–104.

Our approach

- Use CO_2-Loaded microporous adsorbents as proppant
  - Sufficient time for gas exchange through desorption process
  - CO_2 Sequestration

CO_2 adsorbs in proppant → Proppant delivered to reservoir → CO_2 desorbs @ reservoir conditions → Replace CH_4 via competitive adsorption with OM

- Requirements on microporous adsorbents
  - High CO_2 uptake
  - Reasonably good CO_2/CH_4 selectivity, but less selective than kerogen organic matter
  - Good mechanical properties
  - Cheap and available in large quantities
  - Hydrophobic, etc.

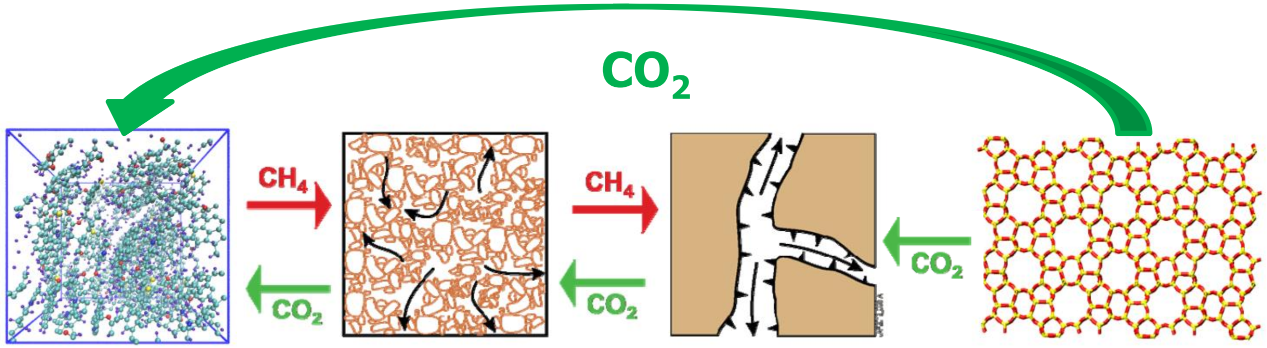
Our approach

- Potential candidates for microporous adsorbents

Candidate	Key features
Zeolite	• Naturally occurs and can be synthesized in large quantities • Long-term stability with well defined micropore size distribution • Has been extensively studied for CO_2 sequestration
Metal Organic Framework (MOF)	• Structure can be tailored and surface properties are tunable • Large surface area and pore size; high adsorption selectivity • Expensive and structure less “rigid”, less water stability
Zeolitic Imidazolate Framework (ZIF), etc.	• A class of MOF that have zeolite-like topologies • Hydrophobic and water stability

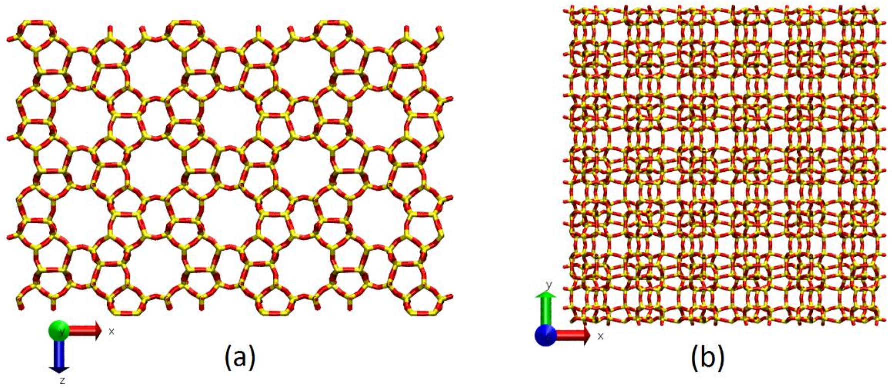
Scope of the work

- Investigate the thermodynamic feasibility of the replacement process
  - Competitive adsorption of CO_2 and CH_4 in organic matter and zeolite
  - The impact of water on the CO_2/CH_4 selectivity



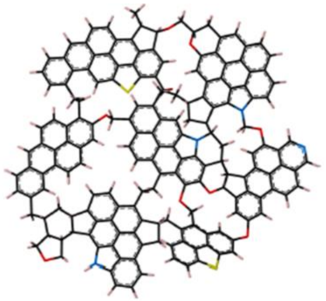
Model Setup

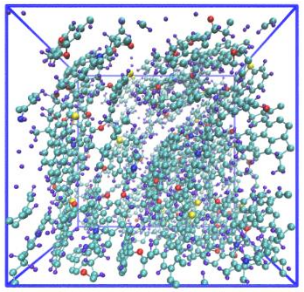
- Select silicalite-1 (Si-ZSM-5 or MFI) to represent zeolite
  - All silica zeolite, formula: SiO_2
  - Pore size: ~5.5Å in diameter
  - Hydrophobic and organophilic
  - Good chemical and thermal stability
  - Widely used in catalysis, adsorption and separation



- Type II-D overmature kerogen model[1] to represent shale organic matter
  - Characteristic kerogen type in gas-prone shale
  - Formula: $C_{175}H_{102}O_9N_4S_2$
  - Use molecular dynamics simulation (LAMMPS) to build 3D kerogen model at 400K and 30MPa

2D model





3D model

Model Setup

- Grand Canonical Monte Carlo (μVT) Simulation
  - Guest-Host interaction

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon r_{ij}},$$

12-6 Lennard-Jones Coulombic interaction

  - Forcefield
    - Silicalite: TraPPE-zeo
    - Kerogen: TraPPE-EH (Explicit Hydrogen)
    - CO_2: TraPPE
    - CH_4: TraPPE-UA (United Atom), no Coulombic site
    - H_2O: SPC
  - Cutoff distance: 14Å
  - Ewald summation with an accuracy of 10^{-5} for Coulombic interaction
  - Rigid solid assumption

Model Setup

- Single-component adsorption
  - Adsorption of CH_4 and CO_2 at 5 temperatures (300, 350, 375, 400, 425 K)
- Competitive gas adsorption w/o water
  - Adsorption of binary mixture (CH_4 and CO_2) with different bulk-phase composition (CH_4:CO_2 = 1:9, 1:1 and 9:1)
  - Compare the CO_2/CH_4 adsorption selectivity between silicalite and kerogen

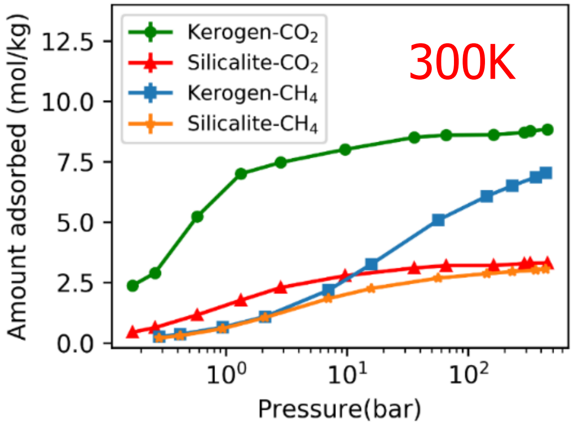
$$S_{\frac{CO_2}{CH_4}} = \frac{x_{CO_2}/x_{CH_4}}{y_{CO_2}/y_{CH_4}}$$

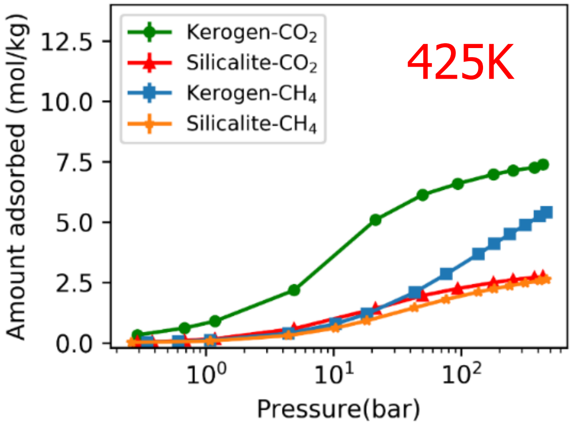
- Competitive gas adsorption with water
  - Add water to the binary mixture at different water chemical potential (μ_{water}= -46, -45, and -44 kJ/mol)
  - Compare the CO_2/CH_4 selectivity with the non-water case

Results and discussion

- Single-component adsorption
  - Adsorption of CO_2, CH_4 and water in kerogen and silicalite

CO_2 & CH_4





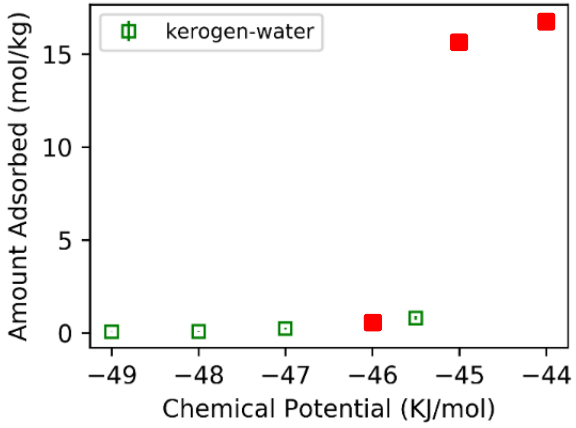
At 300 K

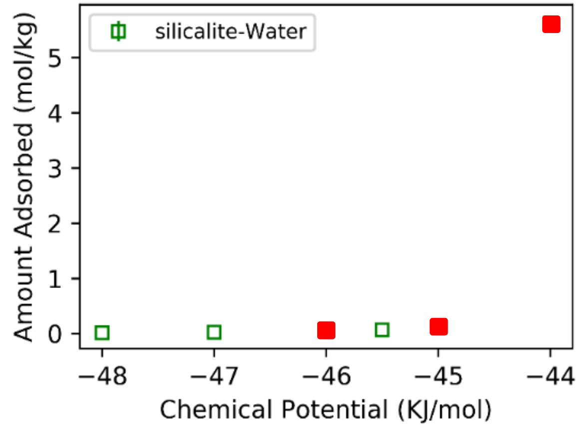
μ_{water}=-46kJ/mol, p~0.03 bar

μ_{water}=-45kJ/mol, p~216 bar

μ_{water}=-44kJ/mol, p~750 bar

Water

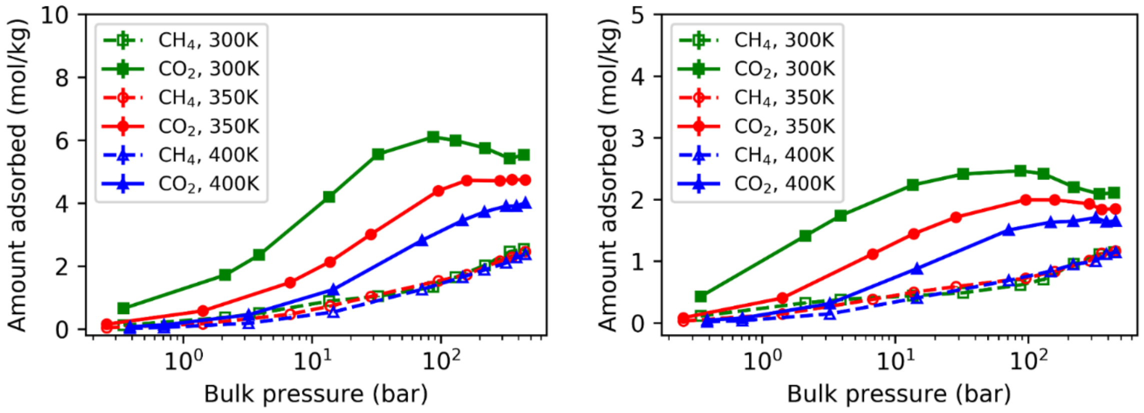




Results and discussion

- CO_2 & CH_4 competitive adsorption without water
  - 3 temperatures (300K, 350K, 400K) and 3 bulk-phase compositions (CH_4:CO_2 = 1:9, 1:1 and 9:1)
- Key findings
  - Both kerogen and silicalite preferentially adsorb CO_2 over CH_4
  - Adsorption of CH_4 is significantly suppressed in both adsorbents
  - CO_2 uptake increases with pressure till a maximum is reached, then, CH_4 molecules make their way into the nanopores

Equimolar (1:1) mixture of CO_2 and CH_4

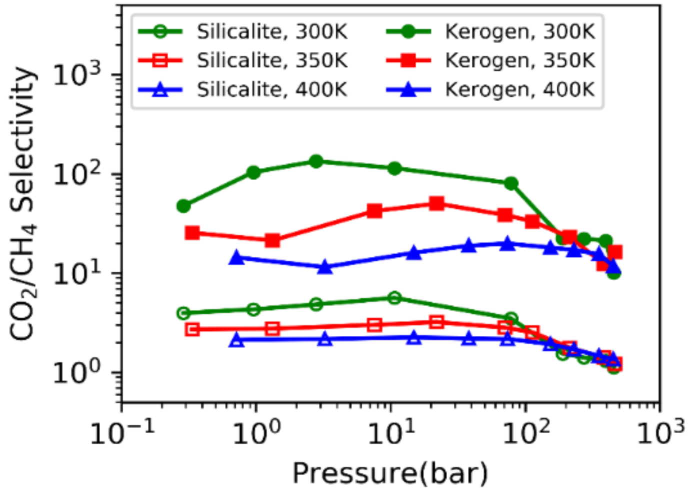


Kerogen

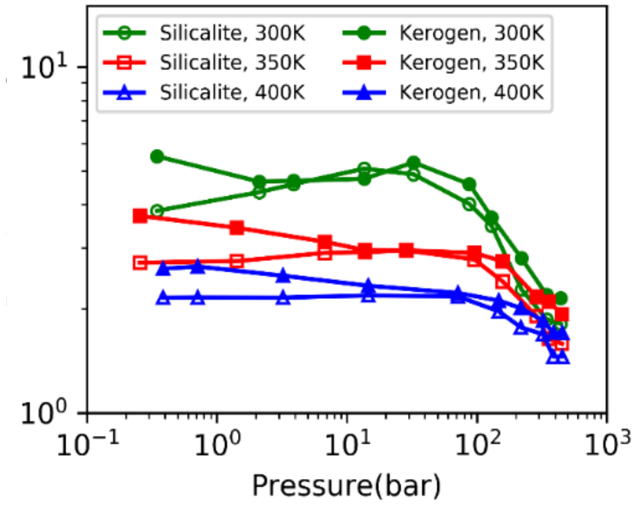
Silicalite

Results and discussion

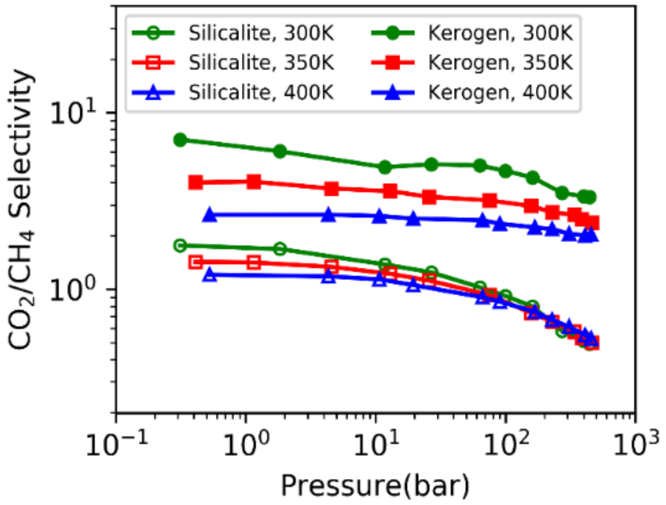
- CO_2/CH_4 selectivity without water
  - 3 temperatures (300K, 350K, 400K) and 3 bulk-phase compositions ($CH_4:CO_2$ = 1:9, 1:1 and 9:1)
- Key findings
  - Both kerogen and silicalite preferentially adsorb CO_2 over CH_4 under most conditions
  - Kerogen always has a higher CO_2/CH_4 selectivity than silicalite
  - Selectivity decreases with increasing CH_4 molar fraction in bulk phase



$CH_4:CO_2$ = 1:9



$CH_4:CO_2$ = 1:1



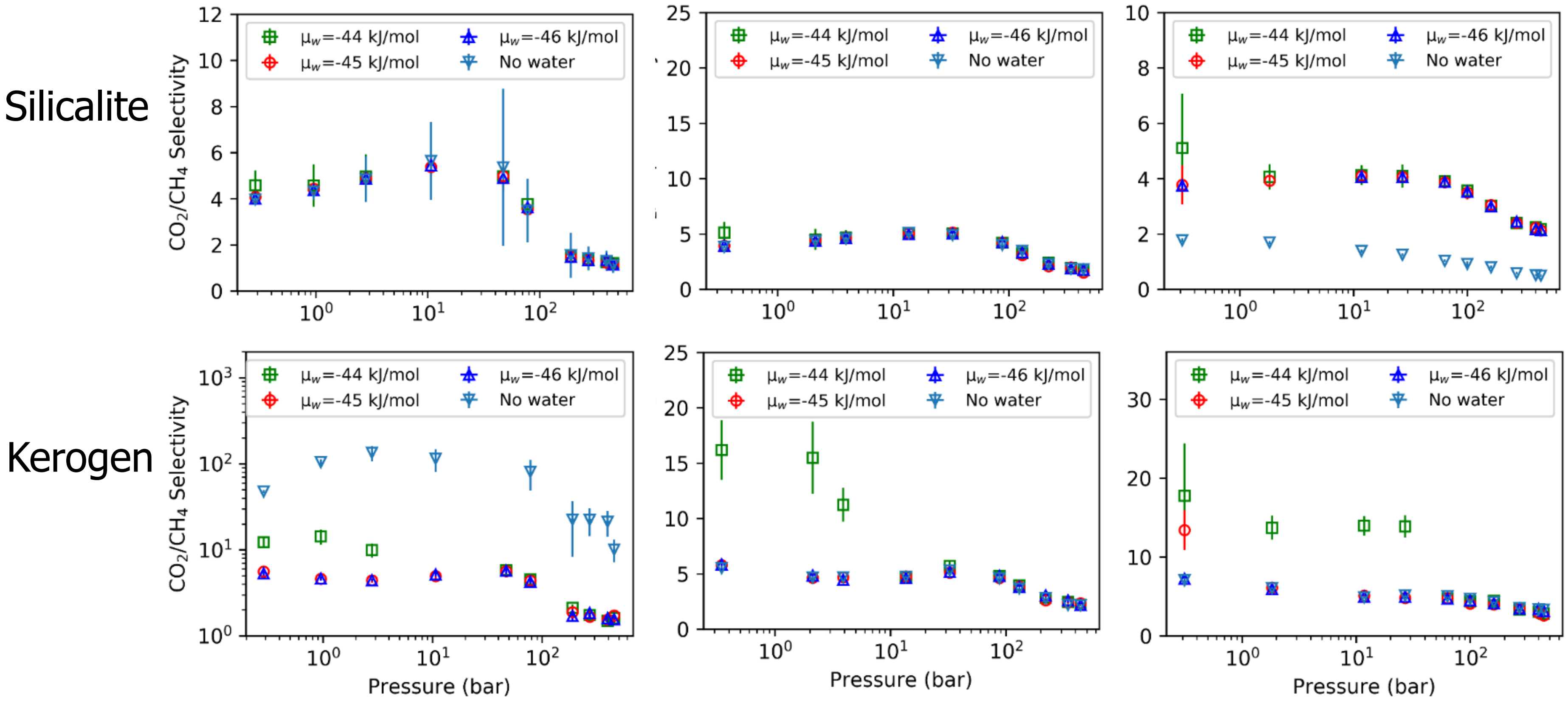
$CH_4:CO_2$ = 9:1

UNIVERSITY of HOUSTON | PETRO

Results and discussion

- CO_2/CH_4 selectivity with water
  - 3 gas-phase compositions ($CH_4:CO_2$ = 1:9, 1:1 and 9:1) and 3 water chemical potentials (μ_{water}=-46, -45 and -44 kJ/mol)

$CH_4:CO_2$ = 1:9 $CH_4:CO_2$ = 1:1 $CH_4:CO_2$ = 9:1



Conclusion and future work

- Both kerogen and silicalite selectively adsorb CO_2 over CH_4 under most conditions
- Water can significantly alter gas adsorption behavior in both adsorbents
- Kerogen always has a higher CO_2/CH_4 selectivity than silicalite
- Future work
  - Screening of economically viable microporous materials with desirable chemical and mechanical properties
  - Extend current work to EOR application
  - The coupling process of proppant transport and gas adsorption/desorption

- Thanks!