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Adsorption and Diffusion of CH_4, N_2 and their Mixture in MIL-101(Cr): A Molecular Simulation Study

Yimin Shao
Supervised by
Dr. Wei Li

Content

1. Background
2. Results and Discussion
3. Conclusion
4. Ongoing Work

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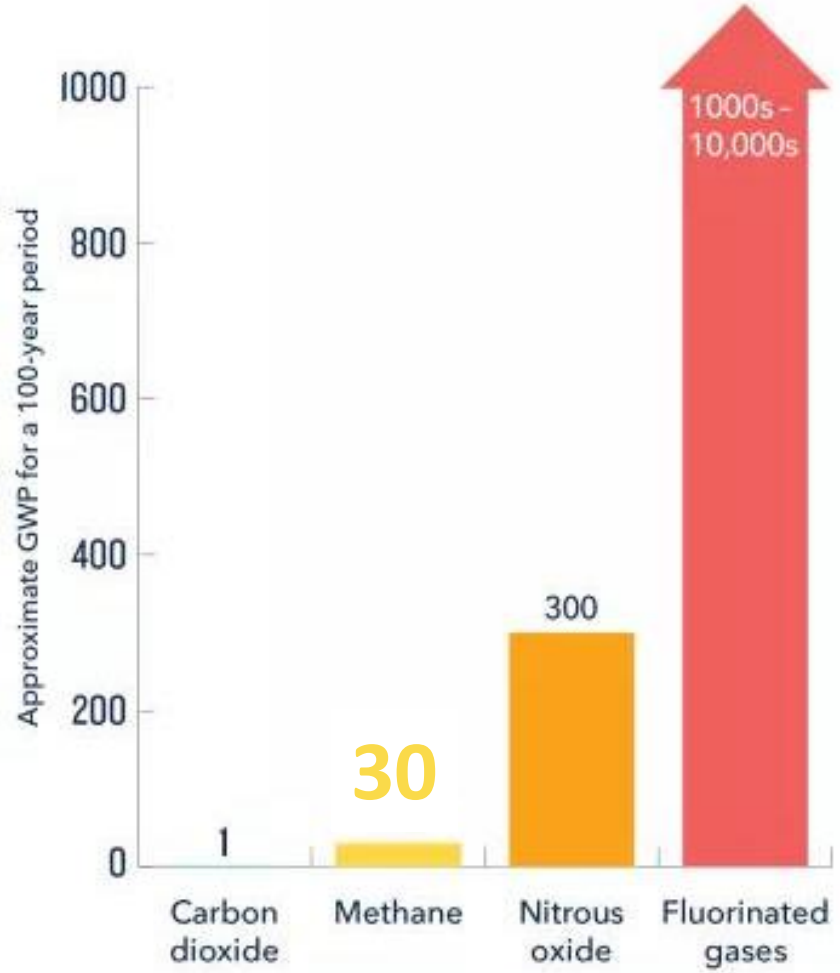
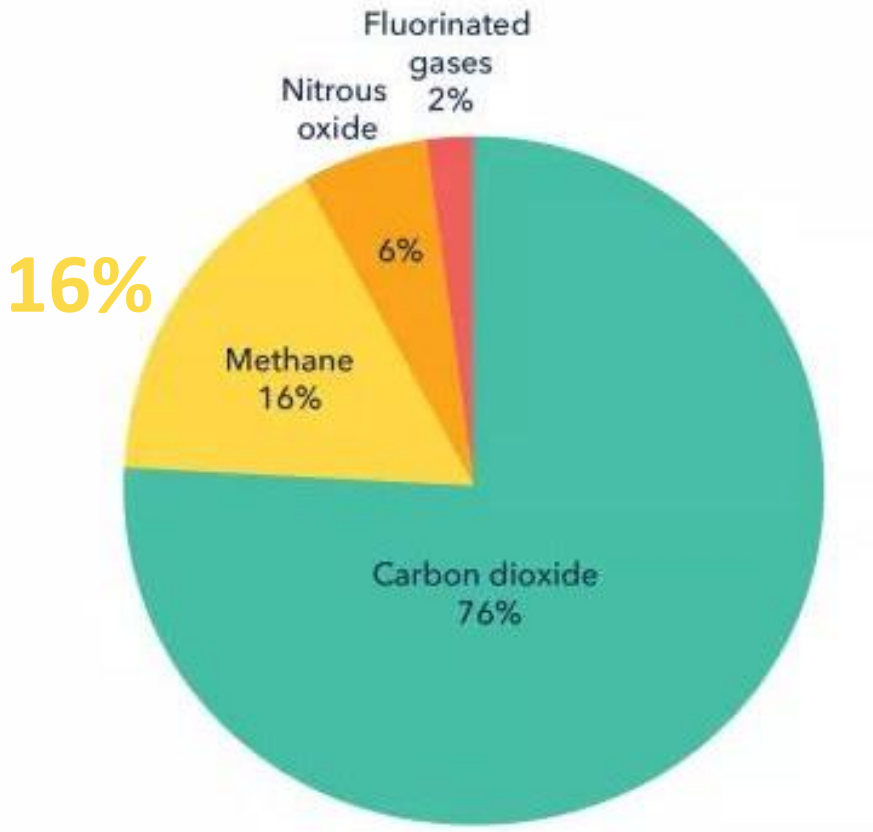
1. Background

1.1 Methane Facts



The global warming potential (GWP) of human-generated greenhouse gases is a measure of how much heat each gas traps in the atmosphere, relative to carbon dioxide.

Source: EPA



How much each human-caused greenhouse gas contributes to total emissions around the globe.

Source: IPCC (2014)

Sher, M. S. A. et al**.** ***Adv. Sci.*** **2020**, 7, 2001946.

1.4 MIL-101 Adsorbent

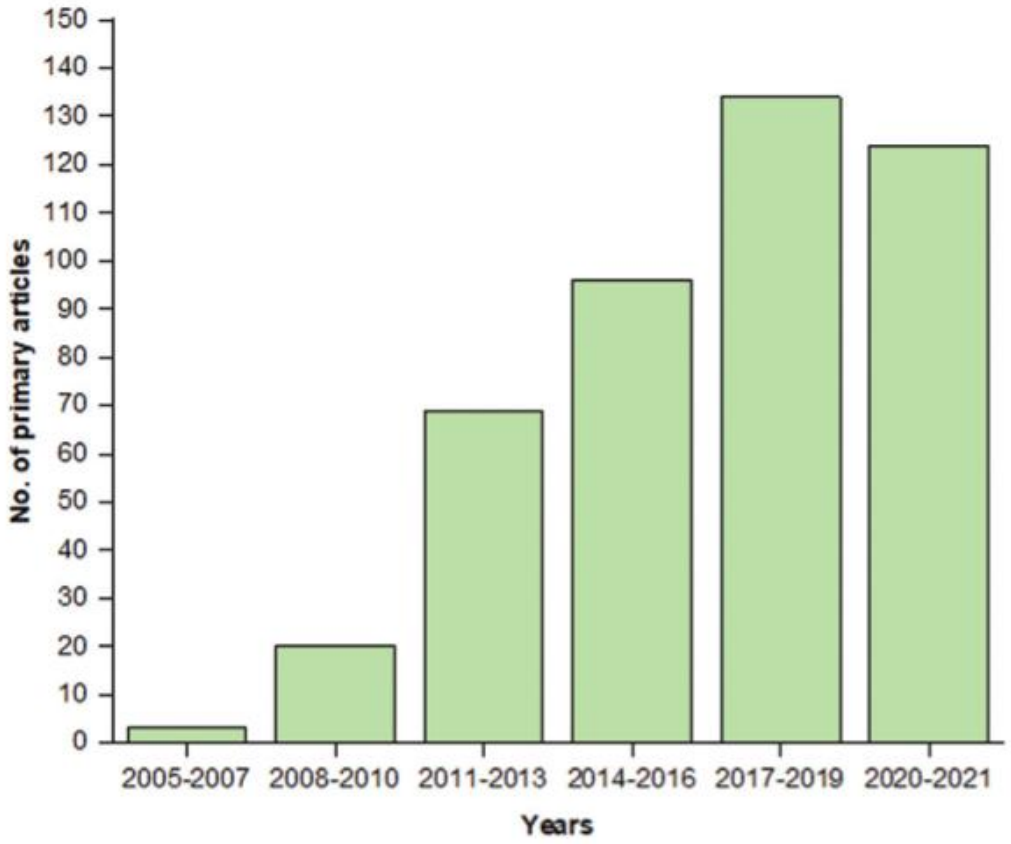


Figure 4. Publication trend across the 446 shortlisted primary research articles as of the end of March 2023.

1

High specific surface area

S_{BET} = 3000 – 4000 $m^2 g^{-1}$

2

Large pore size

V_{Pore} = 1 – 2 $cm^3 g^{-1}$

3

Ease of regeneration

4

High pore volume

5

Excellent thermal, chemical, and water stability

Wee, M.G.V., et al. ***Adv. Mater. Interfaces***, 10: 2300065.

1. How is the adsorption behavior of single-component CH_4 and N_2 in MIL-101?
2. How is the adsorption behavior of two-component CH_4 and N_2 in MIL-101?
3. Are the one-component and two-component adsorption behaviors related?

MIL-101 Adsorbent

Atoms

Pores

Topology

Research Gap

N_2

CH_4

Dipole Moment

Kinetic Diameter

Step 1
Analyze single N_2 and CH_4 Adsorption system

Step 2
Analyze mix N_2 and CH_4 Adsorption system

Step 3
Are the adsorption behaviors of **2** systems the same?

Theoretical Explanation

Challenge
Difficult to experimentally observe gas transport in pores

Aim
Explore adsorption mechanisms for future enhancements

Method
Molecular Simulation

LAMMPS

iRASPA Molecular Simulations

CH_4, N_2 Adsorption Sites

CH_4/N_2 Selectivity

CH_4

N_2

N_2

Adsorption Experimental Results

CH_4, N_2 Density Distribution

Density Plot

CH_4, N_2 Adsorption Capacity

CH4/MIL-101

N2/MIL-101

Gas Uptake

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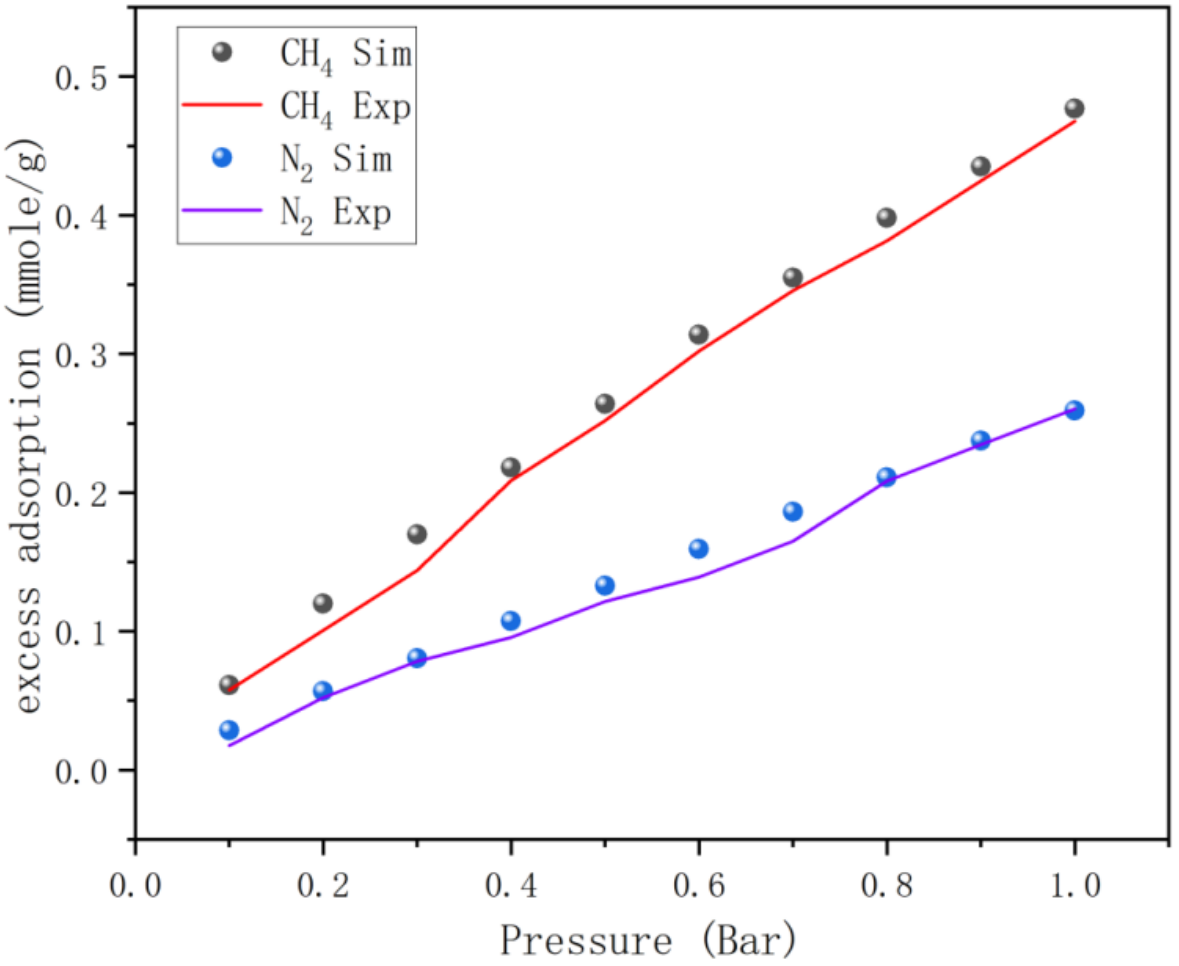
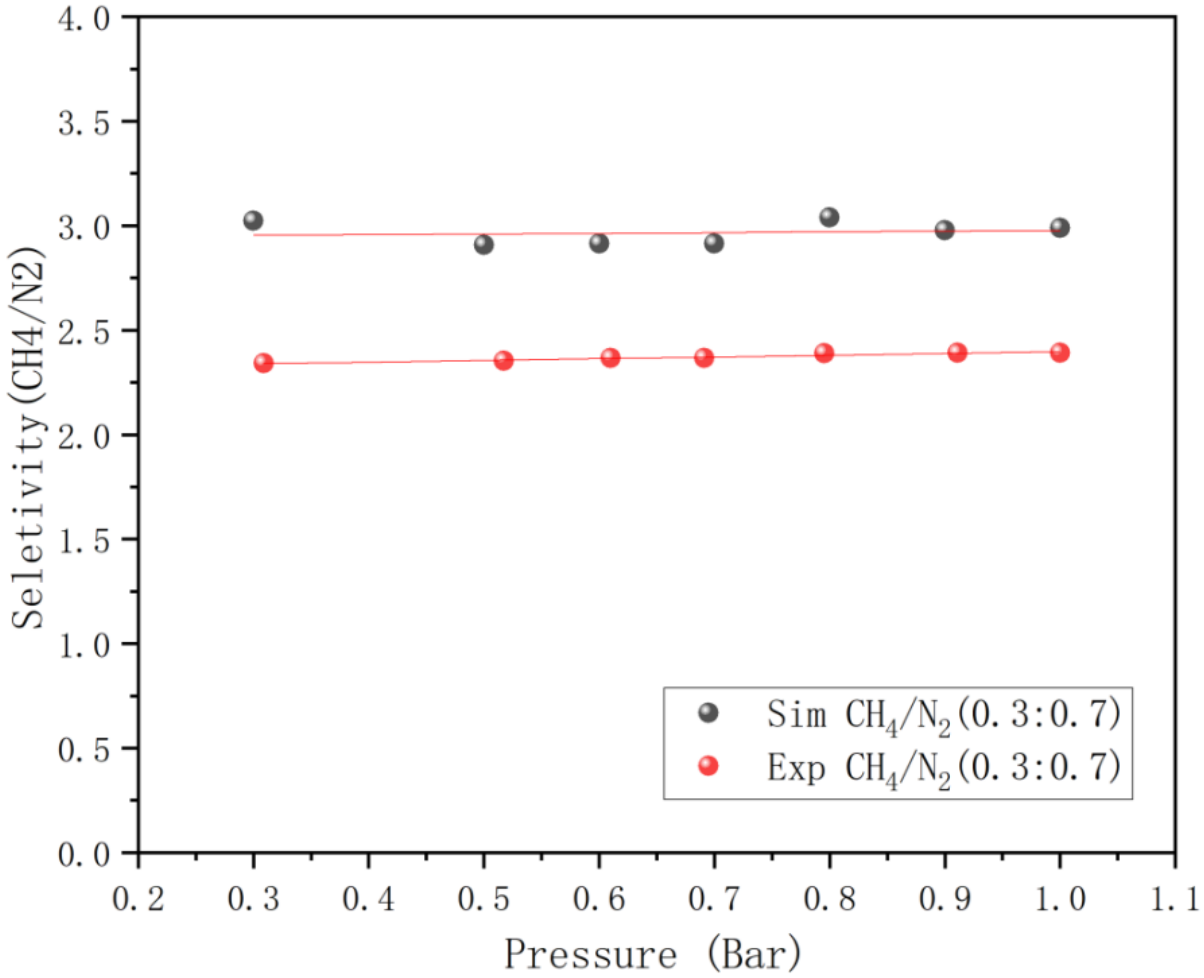
2. Results and Discussion

2.1 Simulation Validation

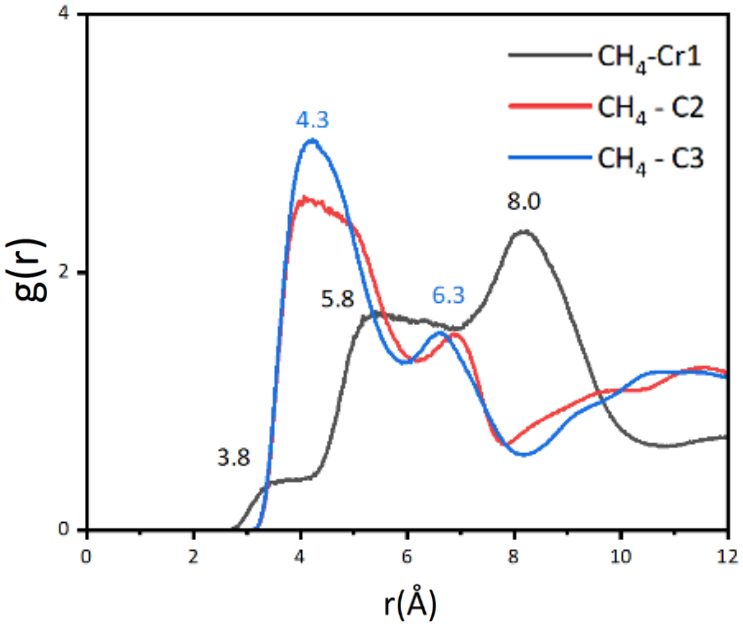
- Pure gases

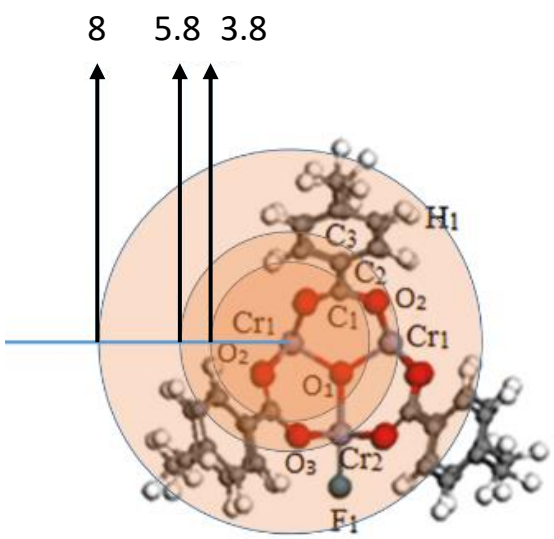


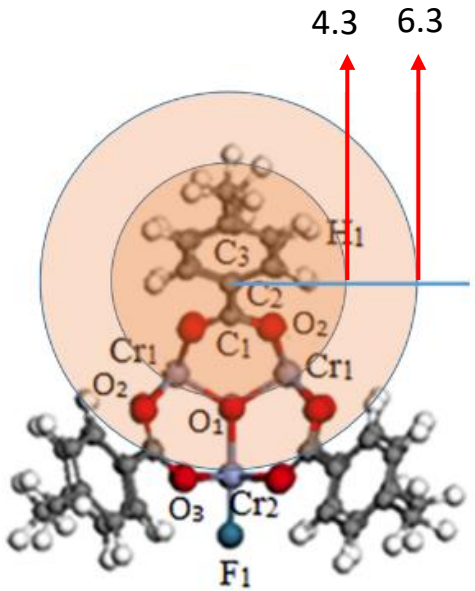
- Binary Mixture

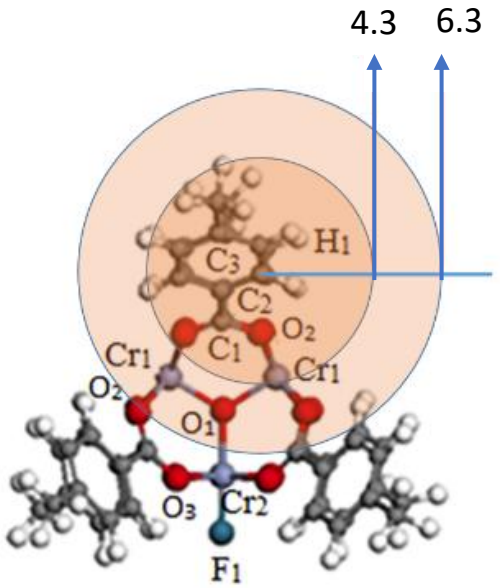


2.2 CH_4 RDF







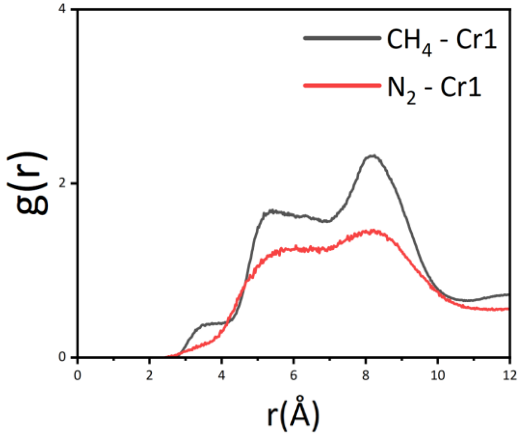


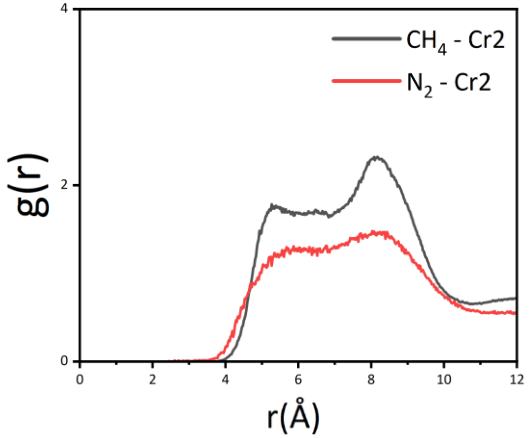
- C=C double bond in MIL-101 plays a dominant role in the adsorption of CH_4.
- Cr and O atoms have obvious adsorption effects on CH_4.

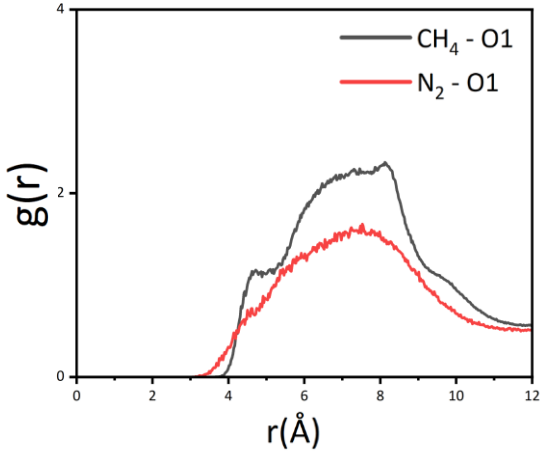
ACS Applied Materials & Interfaces, 14 (40) (2022) 45444-45450

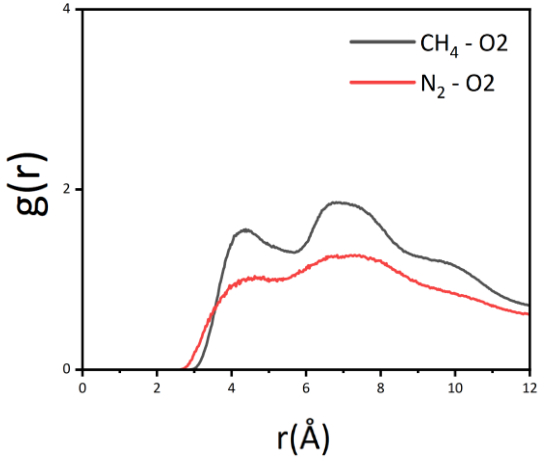
2.2 N_2 RDF

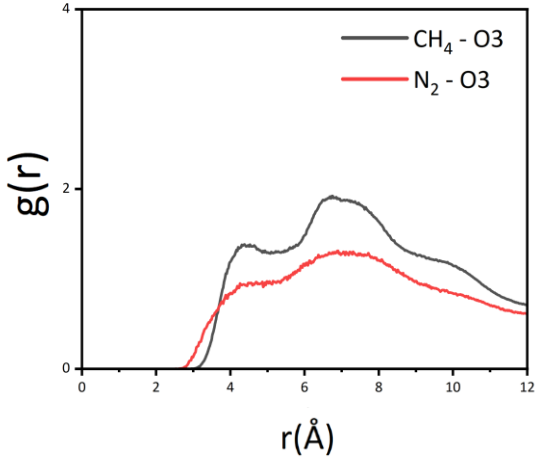
- RDF spectra of Cr, O, C and F for N_2 are very similar to that for CH_4.
- This suggests that the adsorption behavior of N_2 and CH_4 is influenced by similar atomic sites within the MIL-101.
- The peaks of each atom for CH_4 are higher than those for N_2.

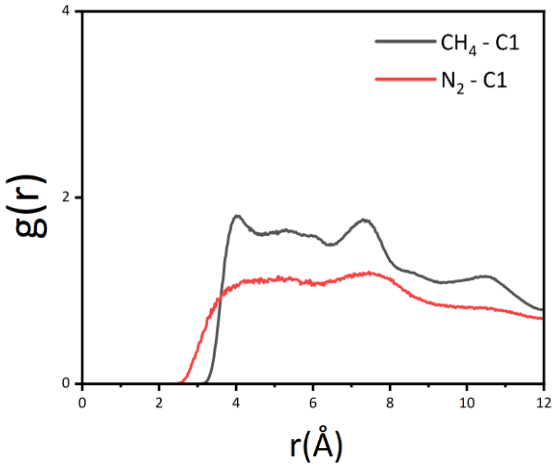


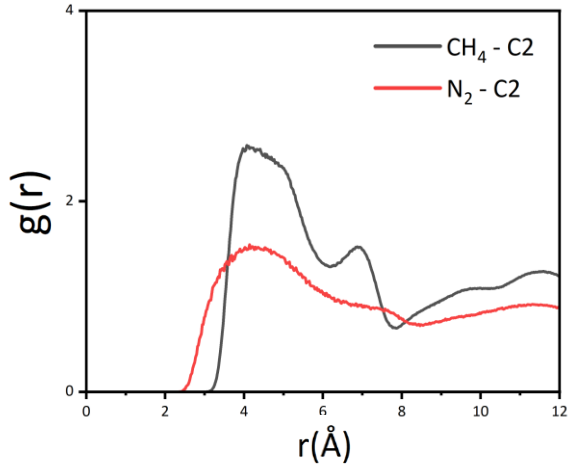


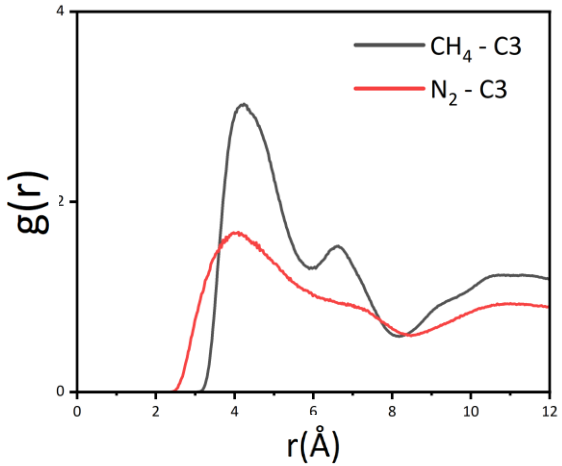




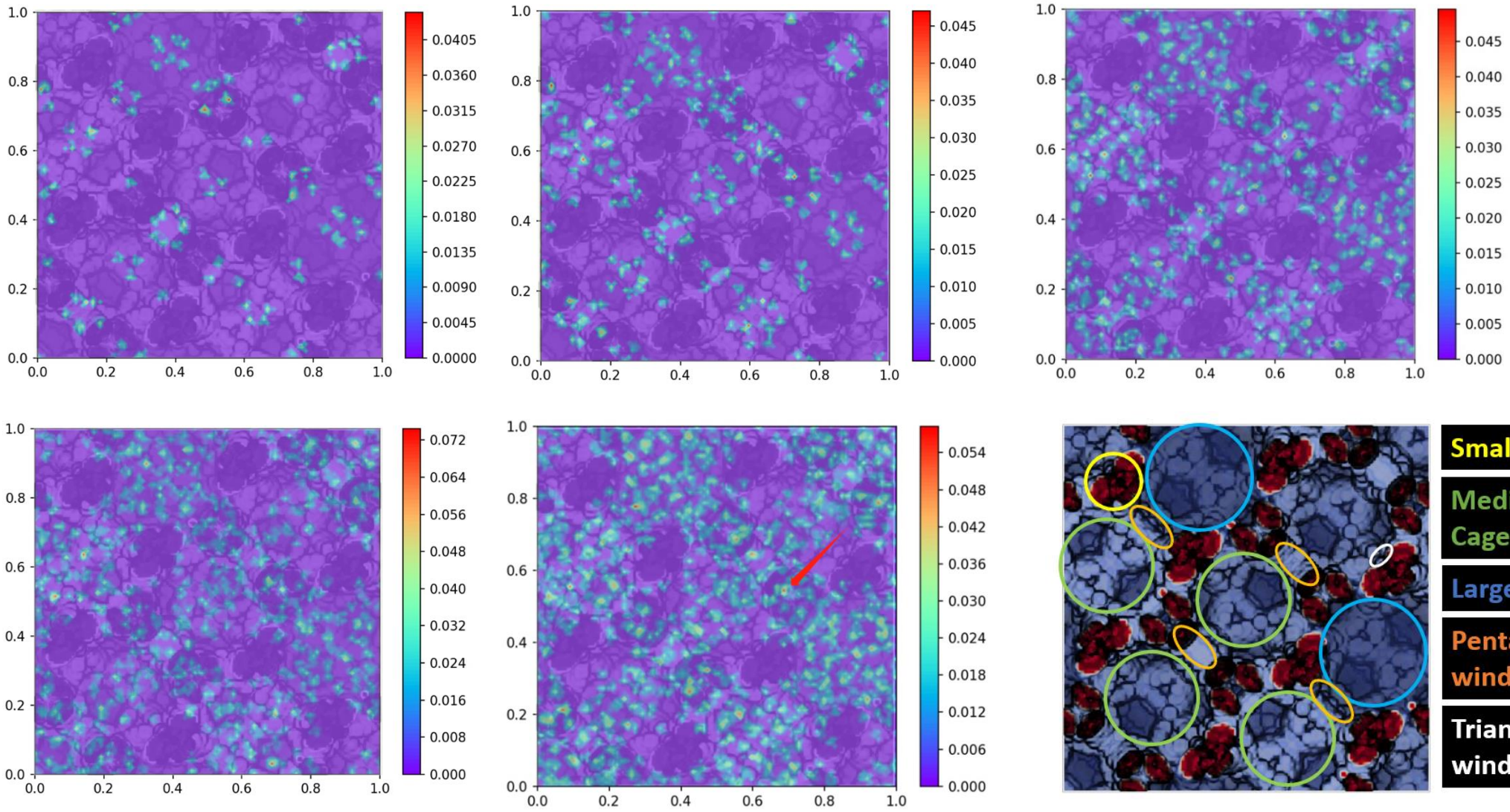






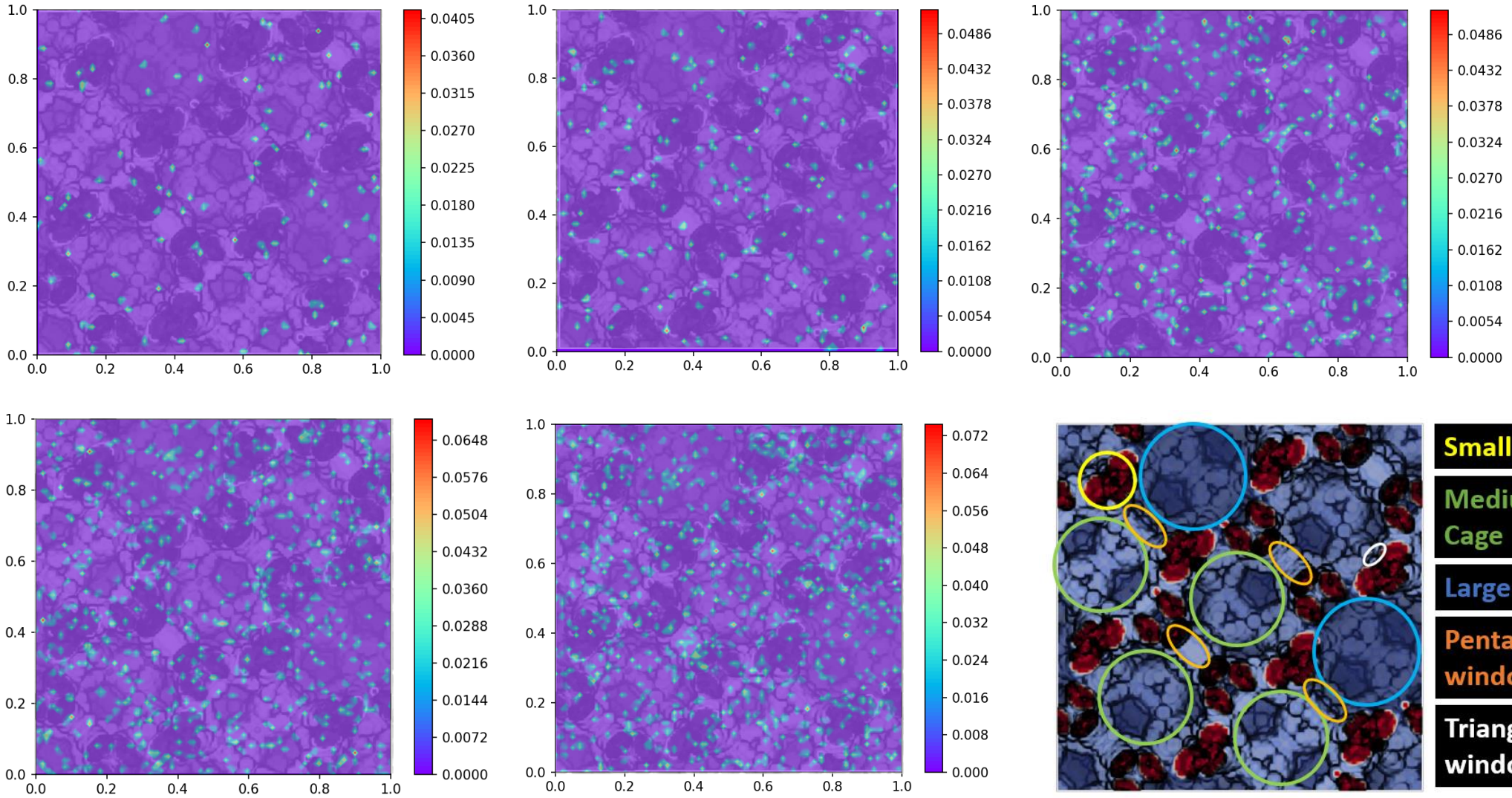


2.3 2D Density Distribution Profile (CH_4)



- CH_4 is mainly distributed in pentagonal windows and the large and medium cages.
- The place with the highest density of CH_4 is on the edges of the pentagonal window connecting the large and medium cages.

2.3 2D Density Distribution Profile (N_2)

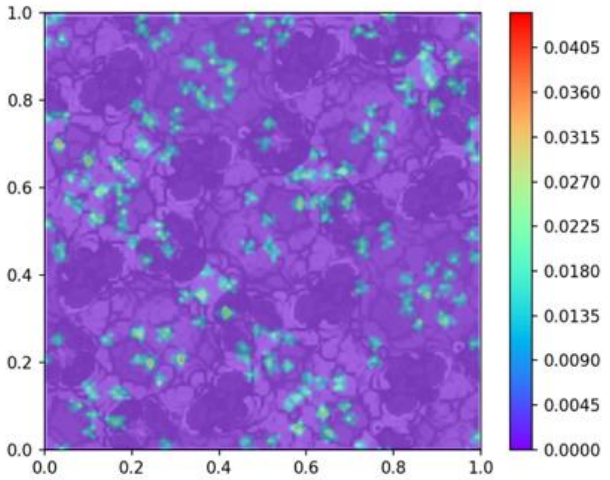


- N_2 molecules are relatively uniformly distributed on the edges of the pentagonal and triangle windows and the small cages of the tetrahedron.

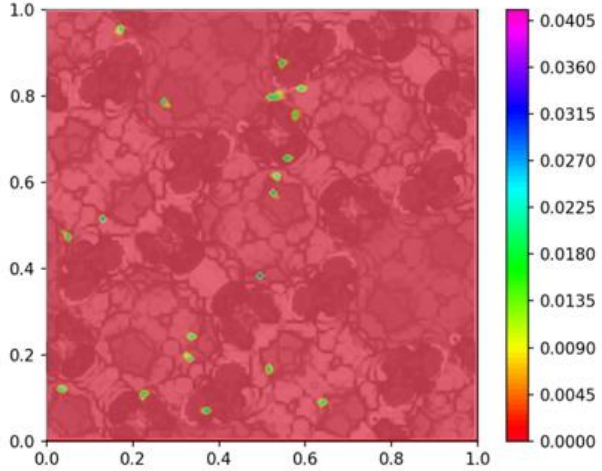
2.6 2D Density Distribution Profile (Binary Mixture)

(a)

200 CH_4 density Profile

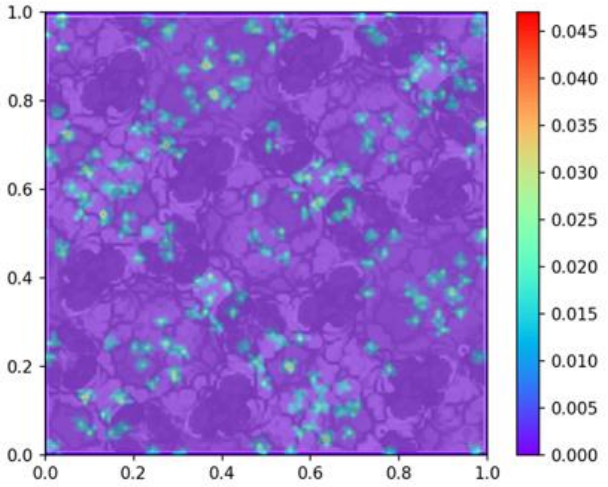


20 N_2 density Profile

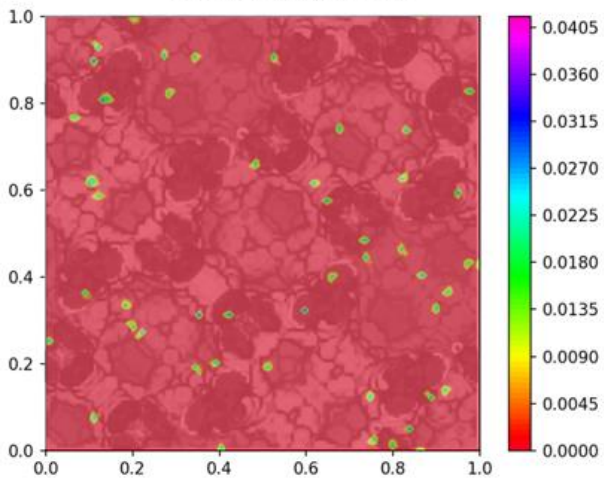


(b)

200 CH_4 density Profile

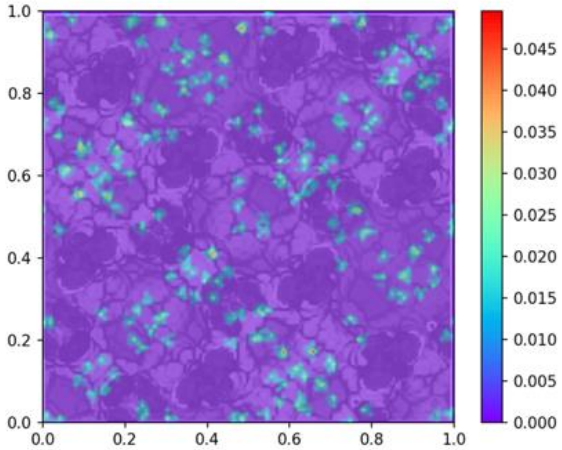


50 N_2 density Profile

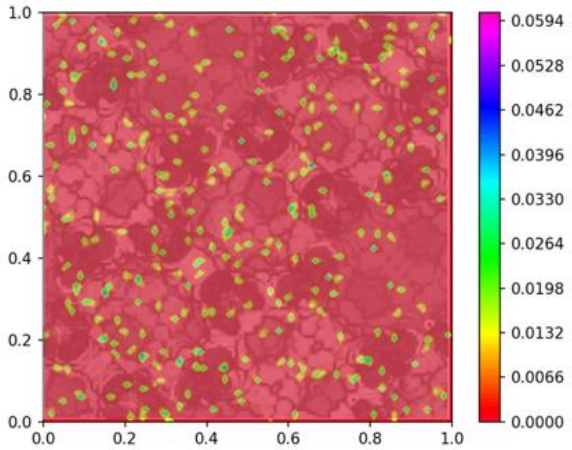


(d)

200 CH_4 density Profile

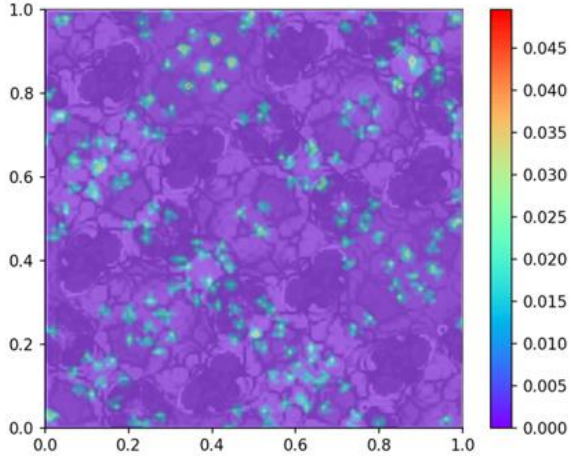


300 N_2 density Profile

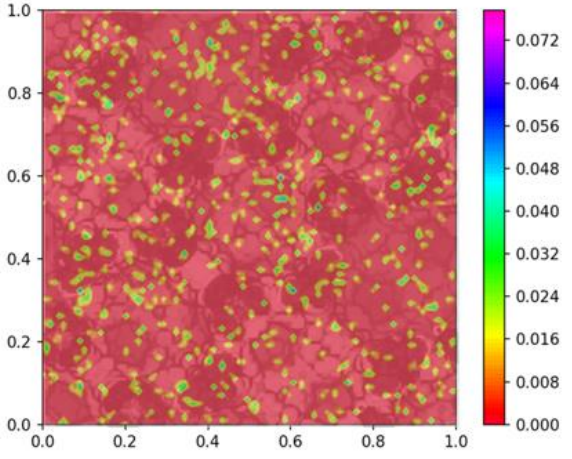


(e)

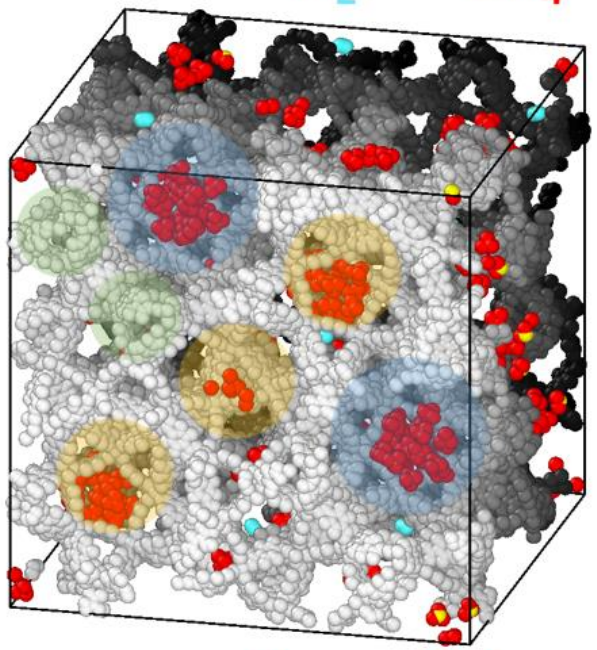
200 CH_4 density Profile



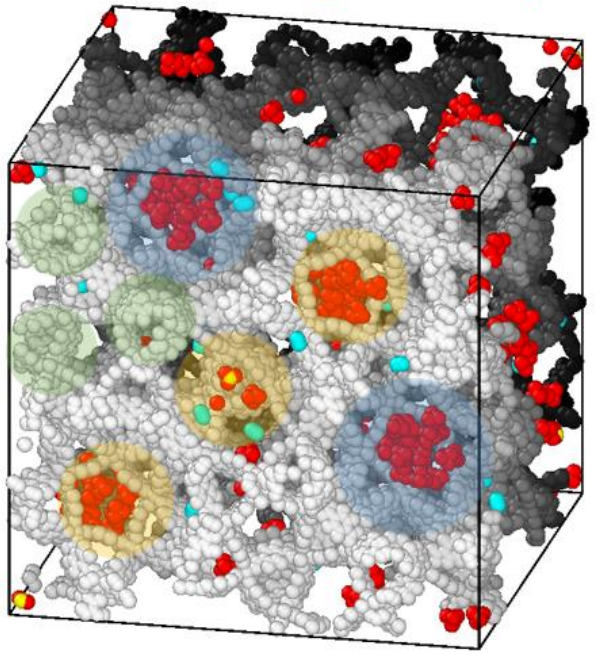
600 N_2 density Profile



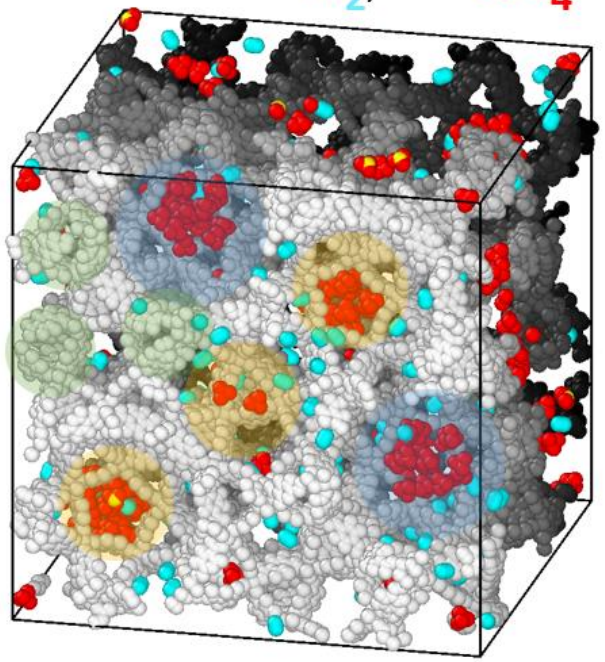
20 N_2, 200 CH_4



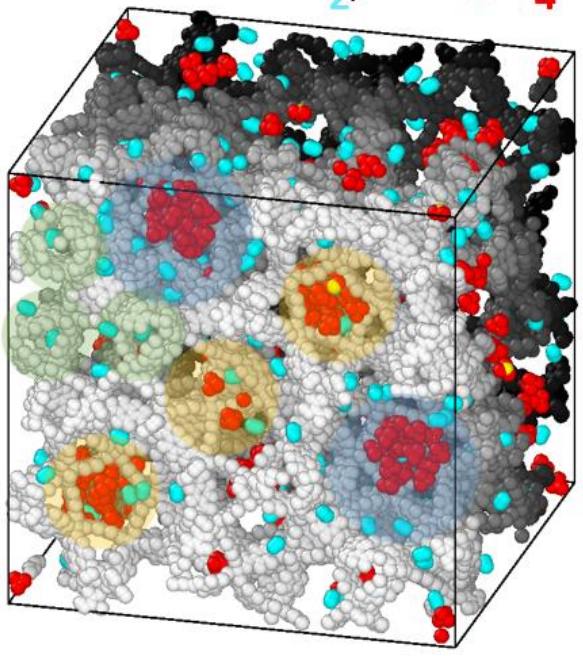
50 N_2, 200 CH_4



200 N_2, 200 CH_4



300 N_2, 200 CH_4

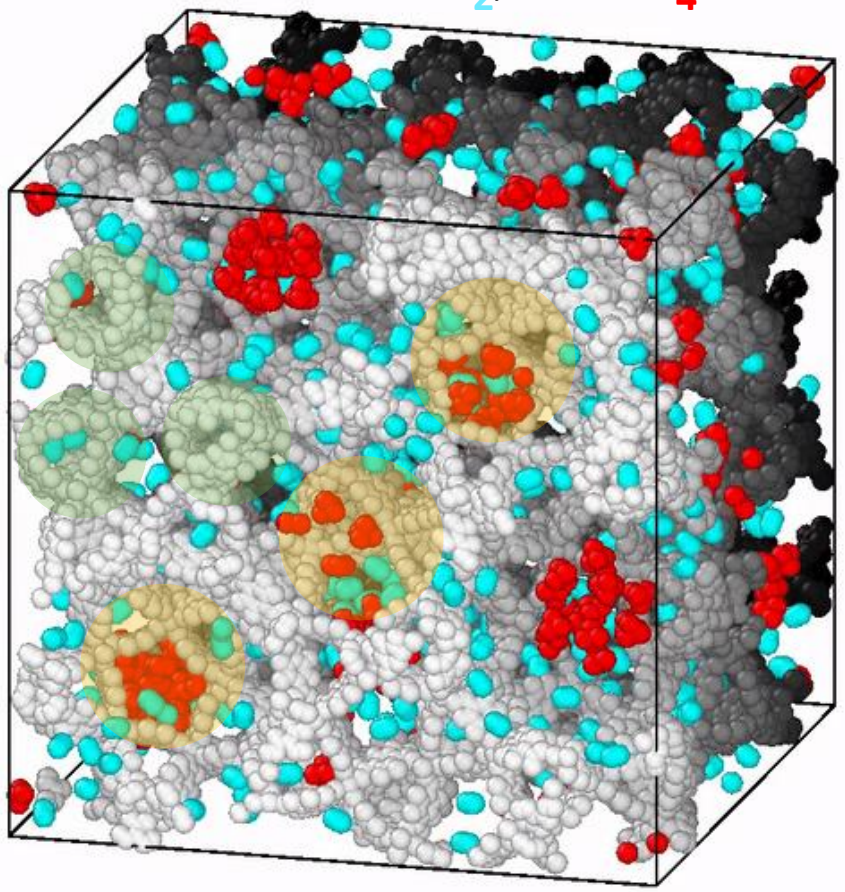


Small cage

Medium cage

Large cage

600 N_2, 200 CH_4



- The increase in N_2 molecules does not affect the distribution of CH_4 molecules.
- CH_4 molecules are agglomerated in large and medium-sized cages.
- N_2 molecules tend to distribute on the edges of large and medium-sized cages and windows, and also appear in the small cavity.

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3. Conclusion

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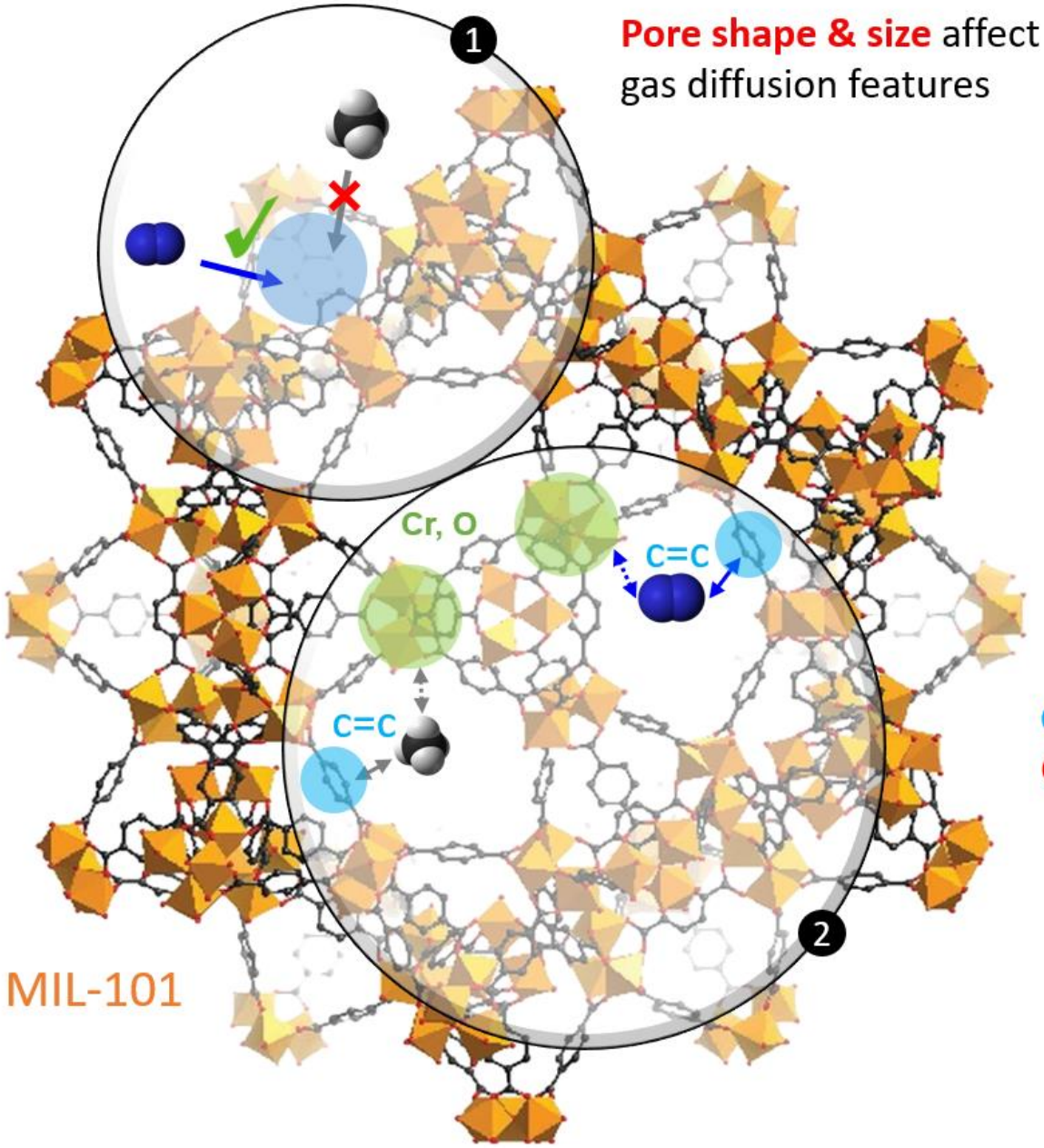
CH_4 and N_2 Adsorption Mechanism



Ongoing Work

1 Simulation

CO_2 & CH_4 Binary System

2 Simulation

CO_2 & CH_4 & N_2 Ternary system

3 Simulation

Machine Learning Predictions

4 Experiment

In-Situ FTIR

Thank you

Yimin Shao
Y.Shao-20@sms.ed.ac.uk
Project PI: Dr Wei Li
wei.li@ed.ac.uk

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