Selective Adsorption of Small Hydrocarbons Using MOFs

1. Background

This *AMI Note* presents a study on the selective adsorption behavior of small molecule hydrocarbons—acetylene (C_2H_2), ethylene (C_2H_4), propane (C_3H_8), and propylene (C_3H_6)—on various metal-organic framework (MOF) materials. Using **AMI's Micro 300** for high-precision static adsorption isotherms, this work highlights the potential of MOFs in non-cryogenic, energy-efficient separation of light hydrocarbons. Although dynamic breakthrough testing was not performed in this study, **AMI's BTsorb 100** system is noted as an ideal platform for future validation under flow conditions.

In the petrochemical industry, C_2 hydrocarbons are foundational to the production of downstream products including polymers, rubbers, and specialty chemicals.[1] However, separating these components remains difficult due to their similar boiling points and molecular sizes.[2] Conventional cryogenic distillation is energy-intensive and cost-prohibitive, but porous materials offer a tunable framework for small molecule separation.

Recent studies have demonstrated that MOF materials—due to their tunable pore size and chemically functionalized internal surfaces—offer a promising solution for energy-efficient separation of these hydrocarbons. Examples include the SIFSIX series, known for acetylene/ethylene selectivity and flexible frameworks like sql-SIFSIX-bpe-Zn, which undergo reversible transformations in the presence of C_2H_2.[3,4] Additionally, MIL-142A, a cross-linked Fe-MOF, has shown remarkable capacity and selectivity for C_3H_8 over CH_4 under ambient conditions.[5]

2. Experiment

The **AMI Micro 300** was used to collect static adsorption isotherms of gases on MOF samples (MOF-1, MOF-2, MOF-3) at room temperature using pressures up to 100 kPa. The gases tested were C_2H_2, C_2H_4, C_3H_6, and C_3H_8.

3. Results

Adsorption isotherms recorded on the **Micro 300** revealed a distinct difference in uptake behavior between acetylene and ethylene. For MOF-1, acetylene displayed a steep increase in adsorption between 4–6 kPa, followed by saturation (Figure 1). Ethylene, by contrast, showed negligible adsorption across the tested pressure range.

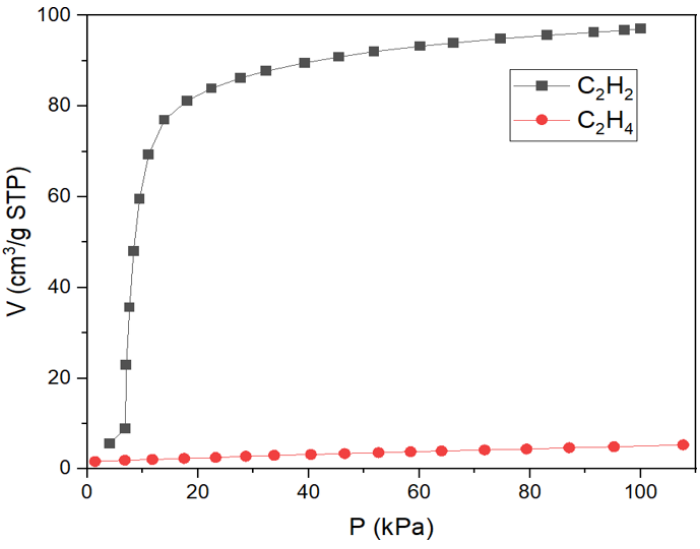


*Figure 1: Adsorption isotherms for C_2H_2 (black) and C_2H_4 (red) on MOF-1 using the **Micro 300***

These results are consistent with the known affinity of fluorinated MOFs for triple-bonded

hydrocarbons, likely due to π-H interactions with exposed SiF_6^{2-} groups.[6,7]

Further experiments evaluated the adsorption of propane and propylene on MOF-2 and MOF-3. Both materials exhibited strong uptake of propylene while showing no detectable adsorption of propane (Figure 2). The clear selectivity suggests that steric effects and kinetic diameter differences influence uptake behavior.

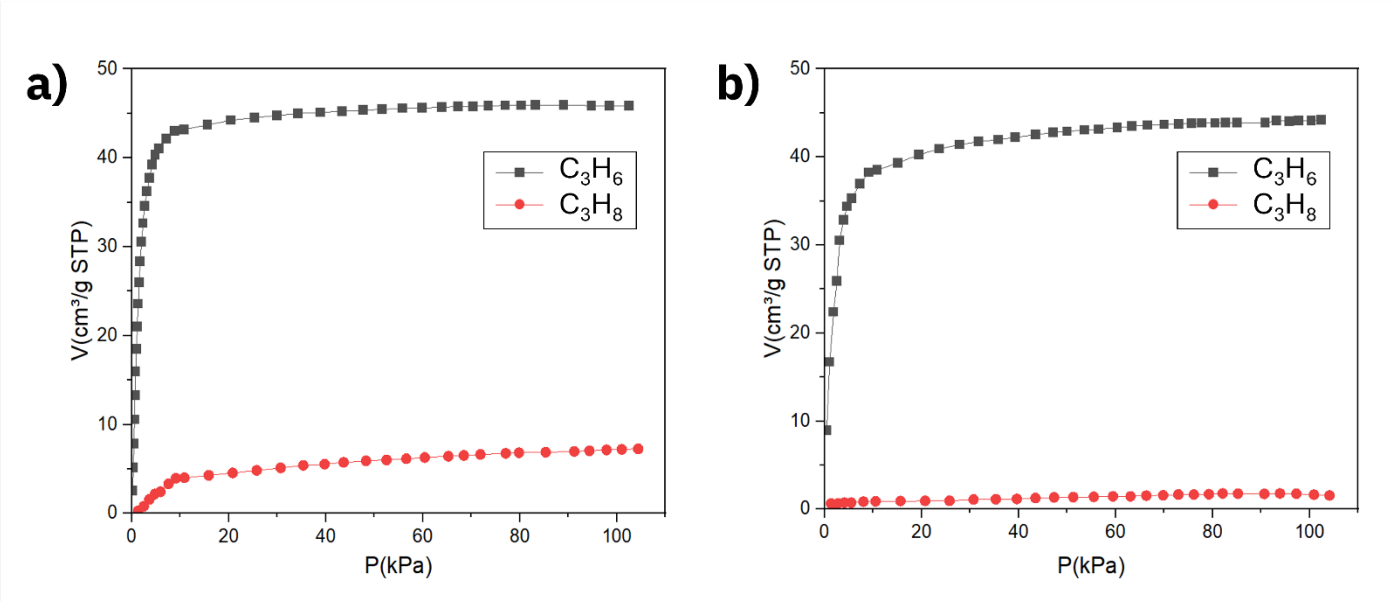


*Figure 2: Adsorption isotherms for C_3H_6 (black) and C_3H_8 (red) on a) MOF-2 and b) MOF-3 using the **Micro 300***

Although dynamic breakthrough testing was not conducted as part of this study, the **AMI BTsorb 100** is designed for such evaluations and remains a valuable tool for future studies aimed at simulating industrial gas separation scenarios.

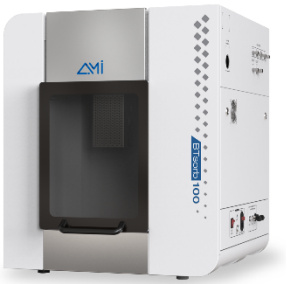
4. Conclusions

These findings indicate that:

- ✓ MOF-1 is suited for trace acetylene removal from ethylene streams in polymer production.
- ✓ MOF-2 and MOF-3 can selectively capture propylene, ideal for propylene recovery or purification from LPG mixtures.

Micro 300

- ✓ High precision physisorption instrument designed for:
  - ✓ Adsorption-desorption isotherms
  - ✓ Specific surface area
  - ✓ Pore size analysis
- ✓ Three independently operating analysis ports for simultaneous experiments



BTsorb 100

- ✓ Versatile and comprehensive dynamic sorption analyzer designed for:
  - ✓ Breakthrough curve analysis
  - ✓ Competitive adsorption
  - ✓ Kinetic analysis
- ✓ Ideal for adsorption and separation analysis of porous materials like MOFs and zeolites

*Figure 3: Highlighted features of **Micro 300** and **BTSorb 100** by **AMI***

By pairing the **AMI Micro 300** for equilibrium data and the **BTsorb 100** for future dynamic testing, researchers can comprehensively assess adsorbent materials for industrial gas separation applications. The highlighted features of both instruments are shown in Figure 3.

This study underscores the promise of MOF-based adsorbents for targeted separation of light hydrocarbons at ambient conditions. While this work focused on static adsorption behavior, AMI's suite of instruments, especially the **Micro 300** and **BTsorb 100**, provides a scalable, versatile platform for future full-cycle evaluation from material screening to process development.

5. References

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