TECHNISCHE UNIVERSITÄT KAISERSLAUTERN

Japan Adsorption 2019

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Kinetic Separation of CO_2/CH_4 with MOF@Oxide Ceramic Core-Shell Composites

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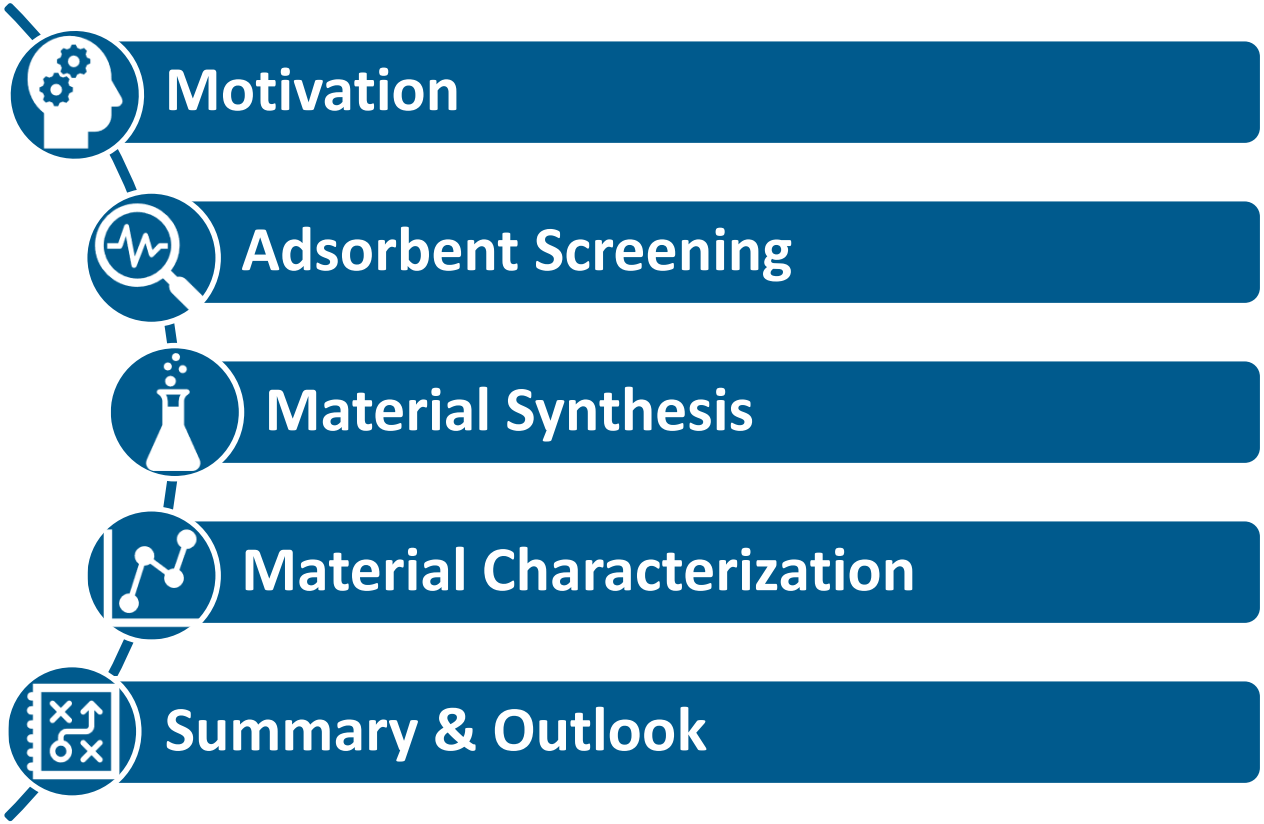
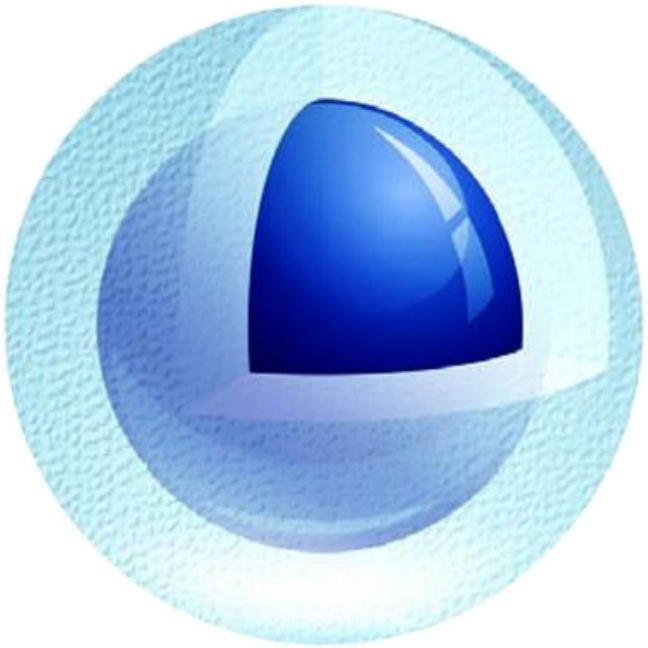
Agenda


Motivation
Adsorbent Screening
Material Synthesis
Material Characterization
Summary & Outlook

Motivation



Motivation

Desired benefits

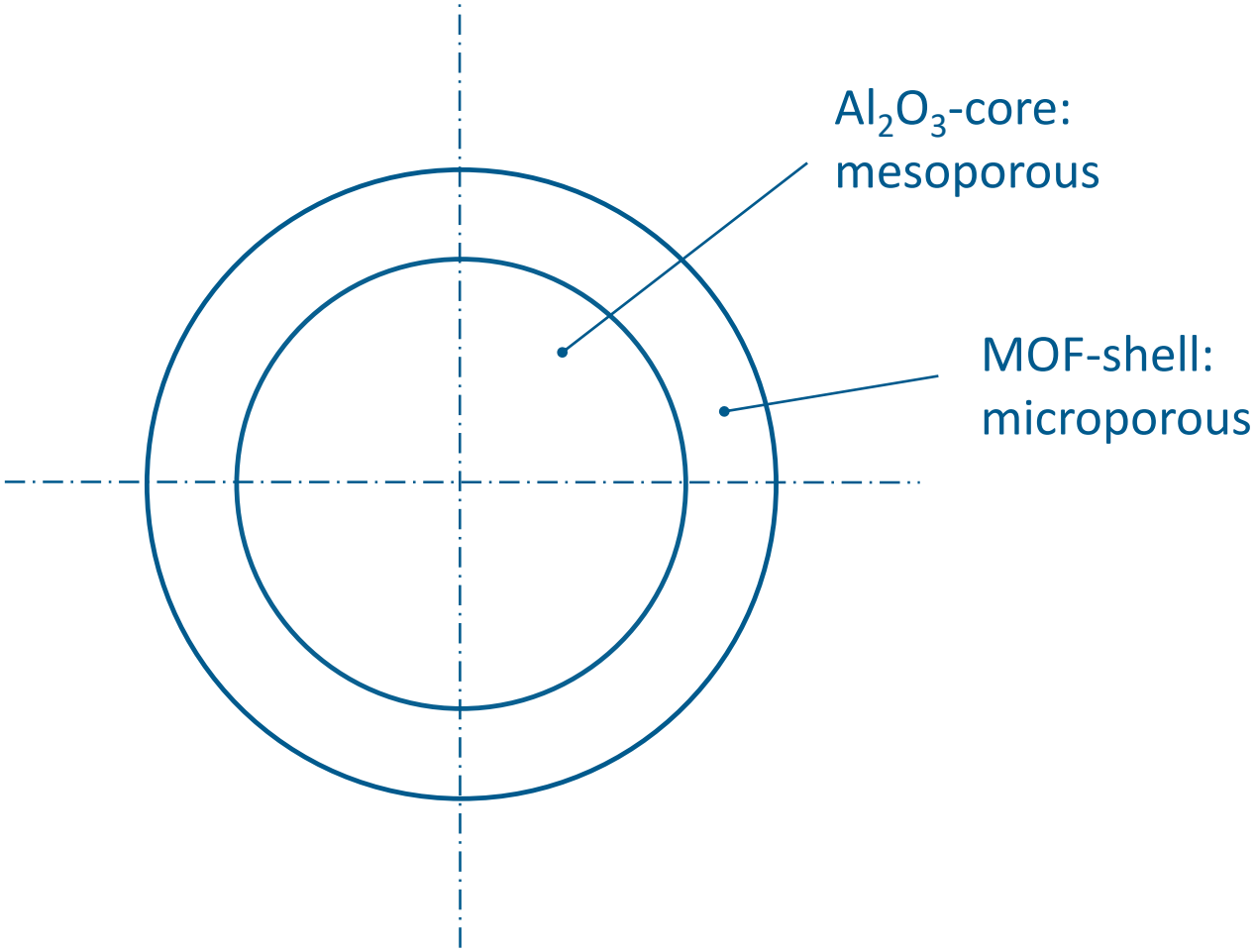
$$d_p \uparrow \rightarrow \Delta p \downarrow$$

Storage function
→ Porous Core

↓

Material savings and
Separation efficiency

Motivation



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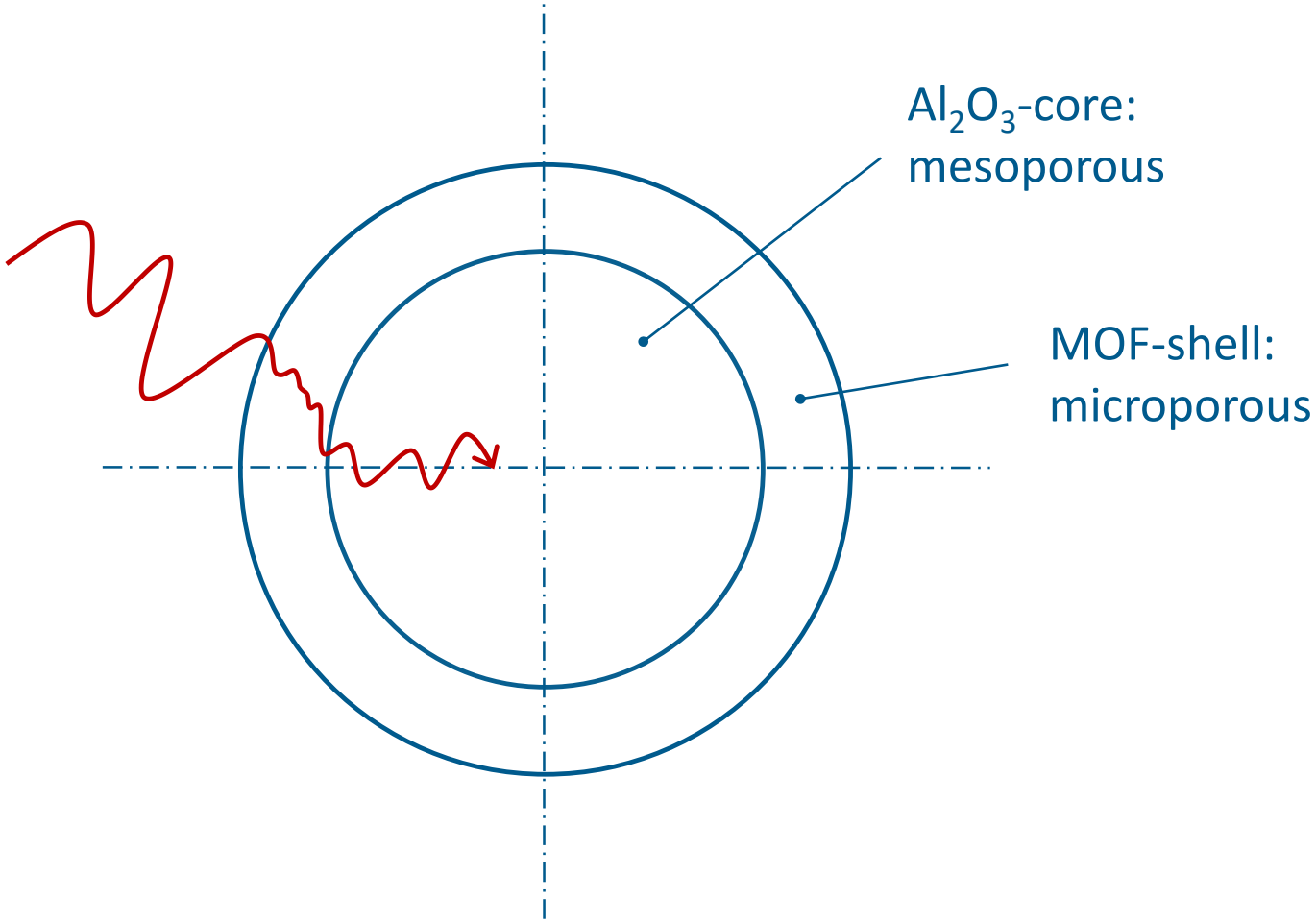

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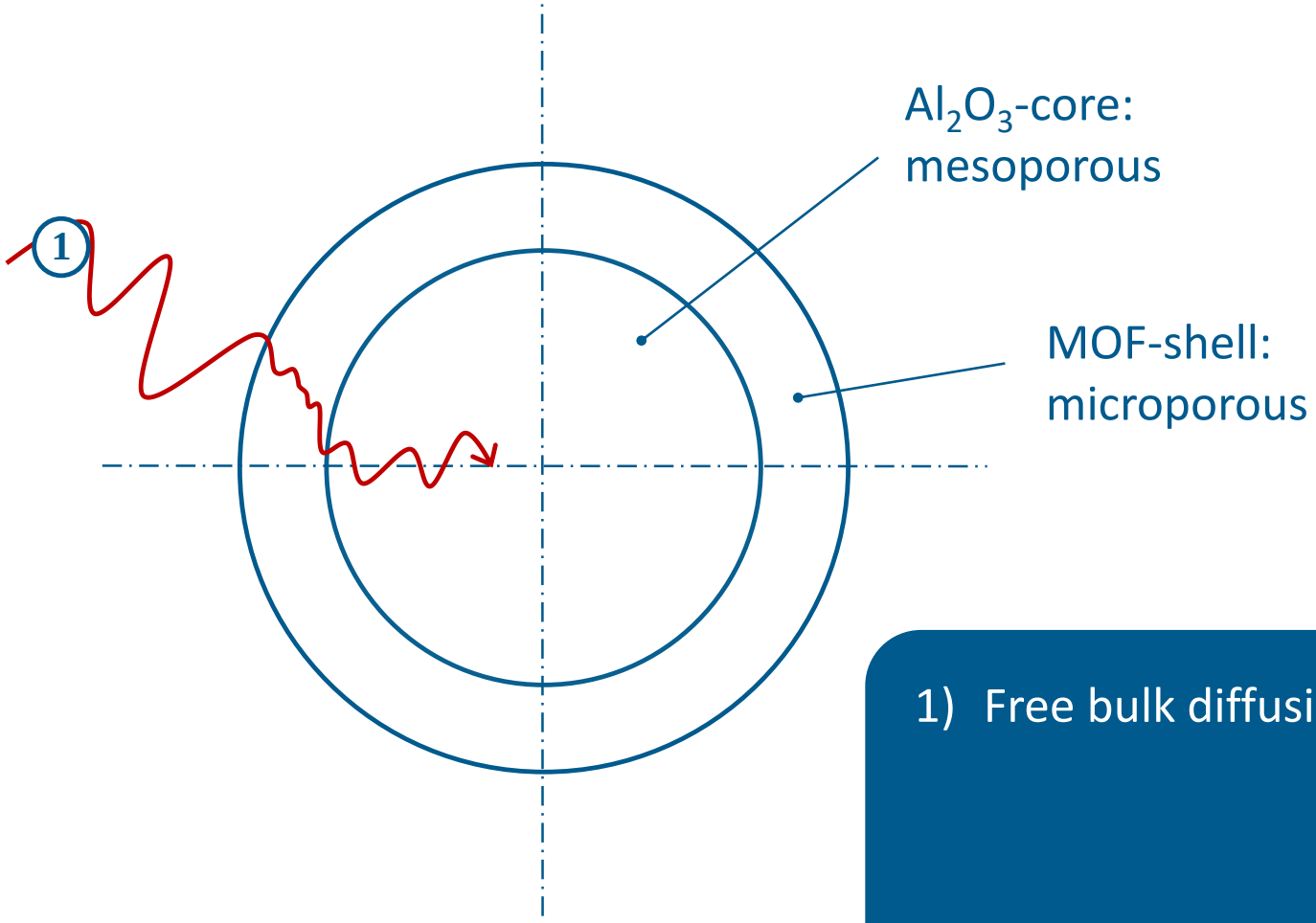
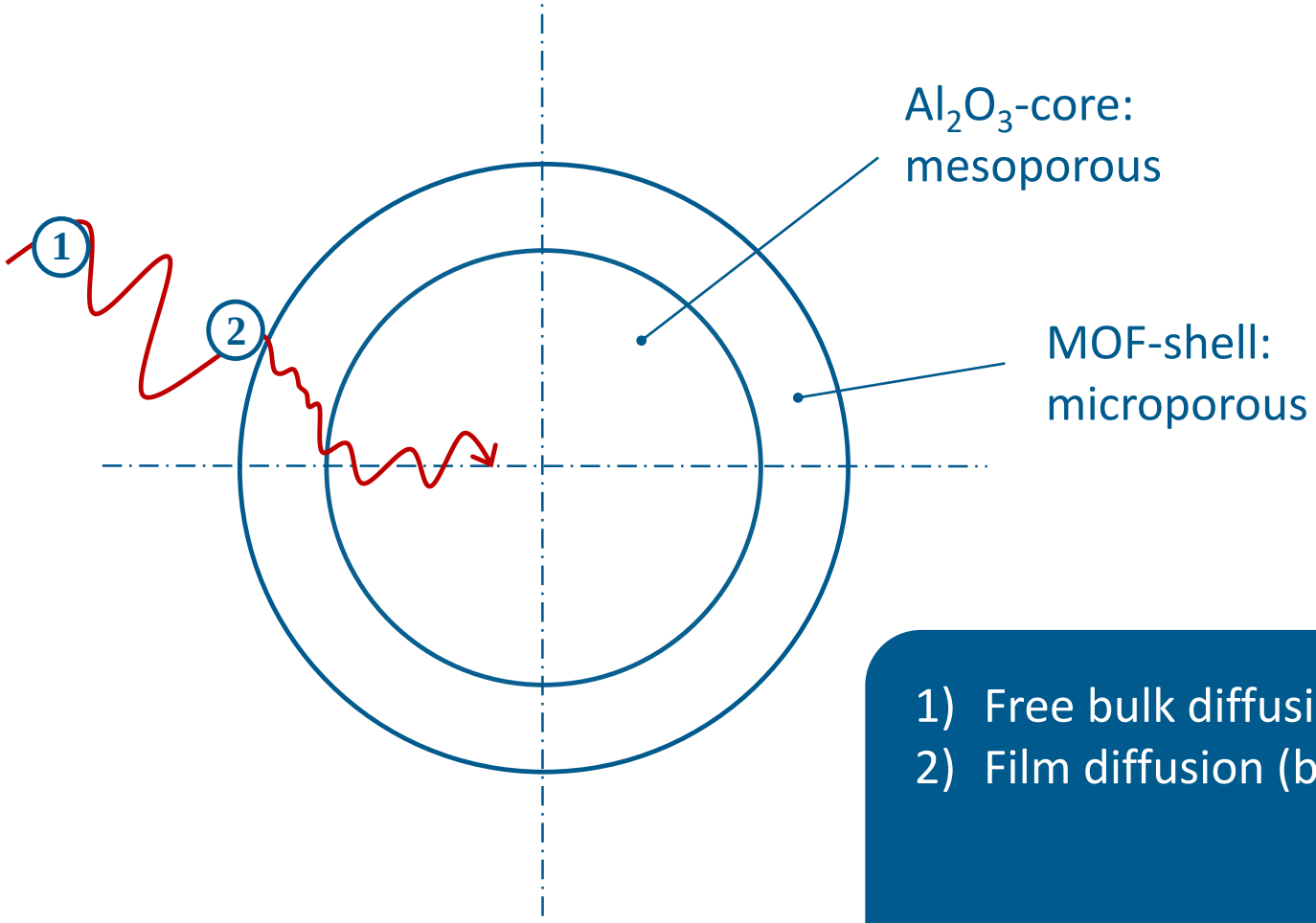


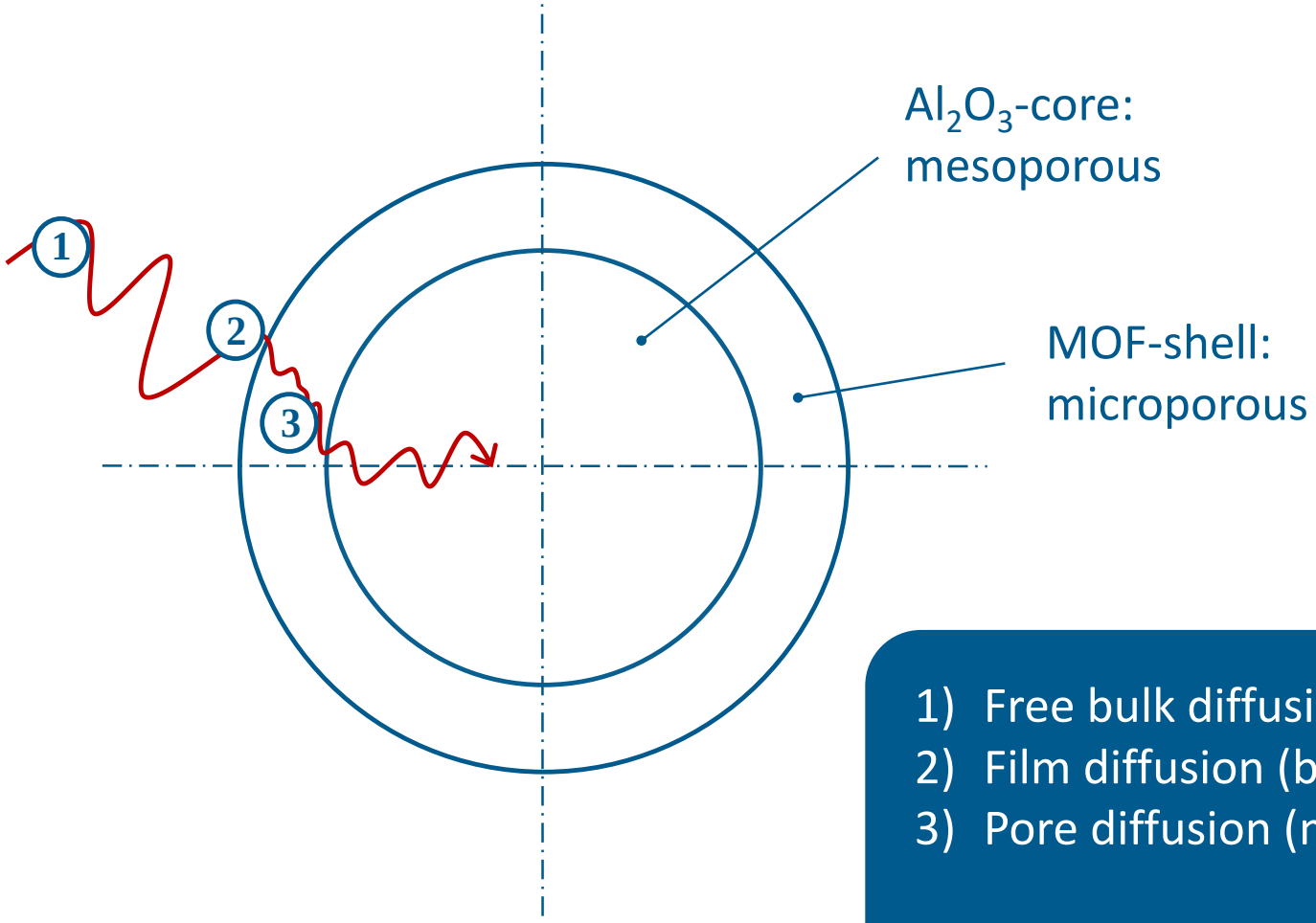
1) Free bulk diffusion

Motivation



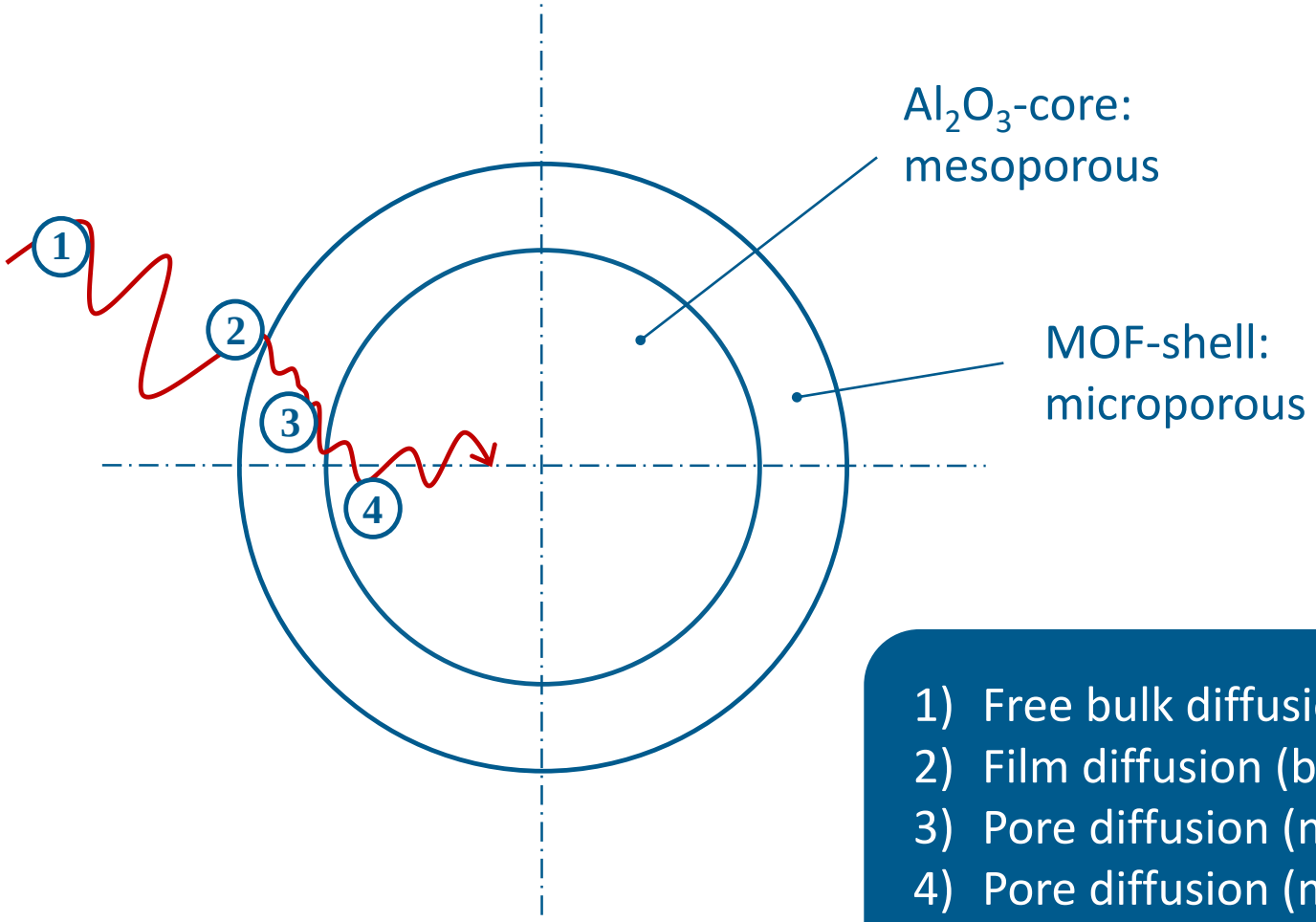
1) Free bulk diffusion
2) Film diffusion (bulk → shell)

Motivation



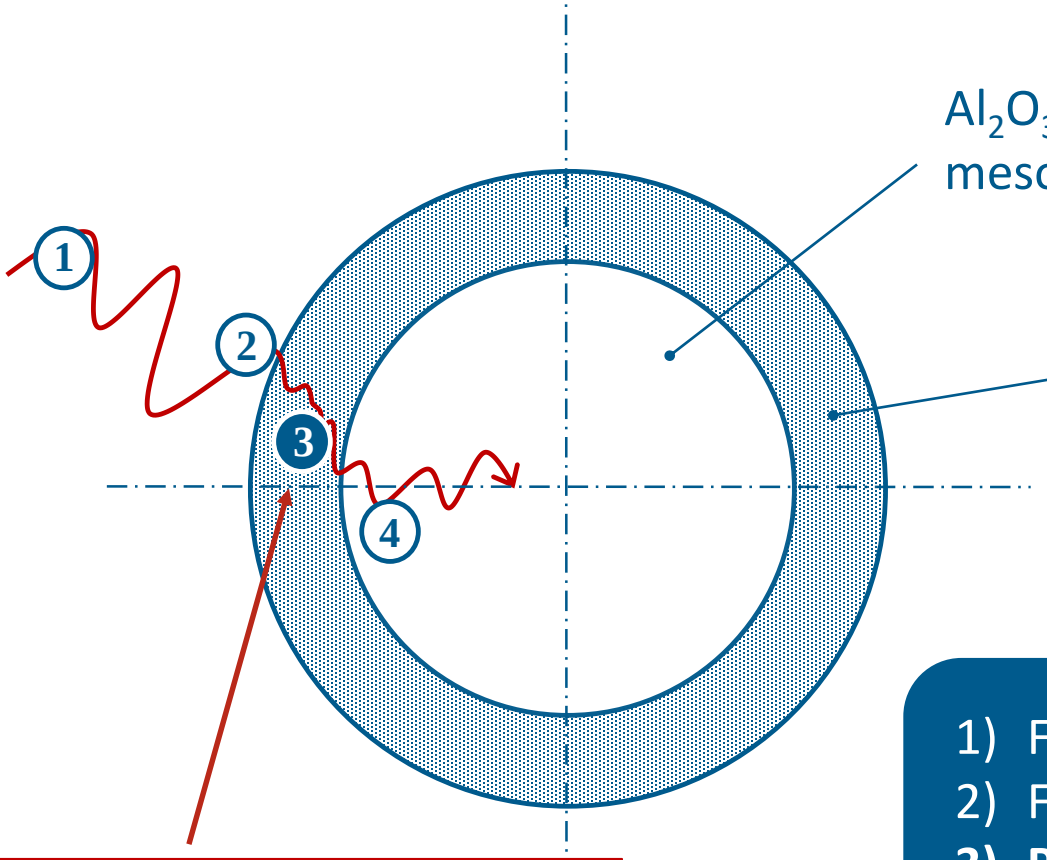
1) Free bulk diffusion
2) Film diffusion (bulk → shell)
3) Pore diffusion (micropores)

Motivation



1) Free bulk diffusion
2) Film diffusion (bulk → shell)
3) Pore diffusion (micropores)
4) Pore diffusion (mesopores)

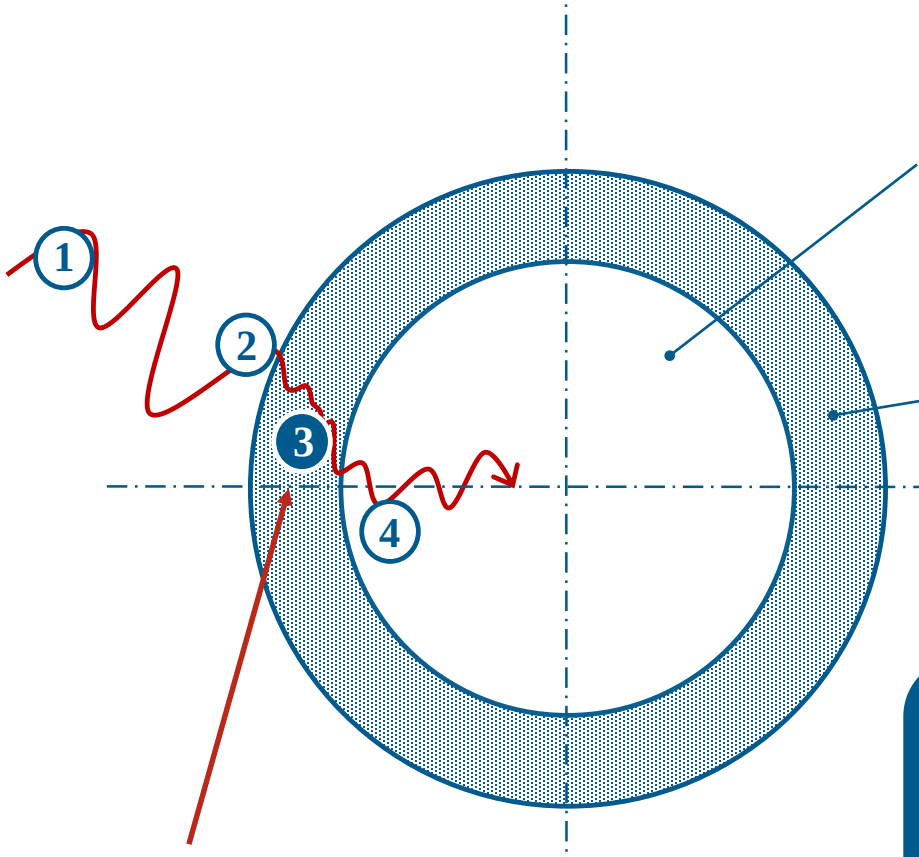
Motivation



Rate determining step

1) Free bulk diffusion
2) Film diffusion (bulk → shell)
3) **Pore diffusion (micropores)**
4) Pore diffusion (mesopores)

Motivation



Al_2O_3-core:
mesoporous

MOF-shell:
microporous

Rate determining step

1) Free bulk diffusion
2) Film diffusion (bulk → shell)
3) **Pore diffusion (micropores)**
4) Pore diffusion (mesopores)

Adsorbent Screening

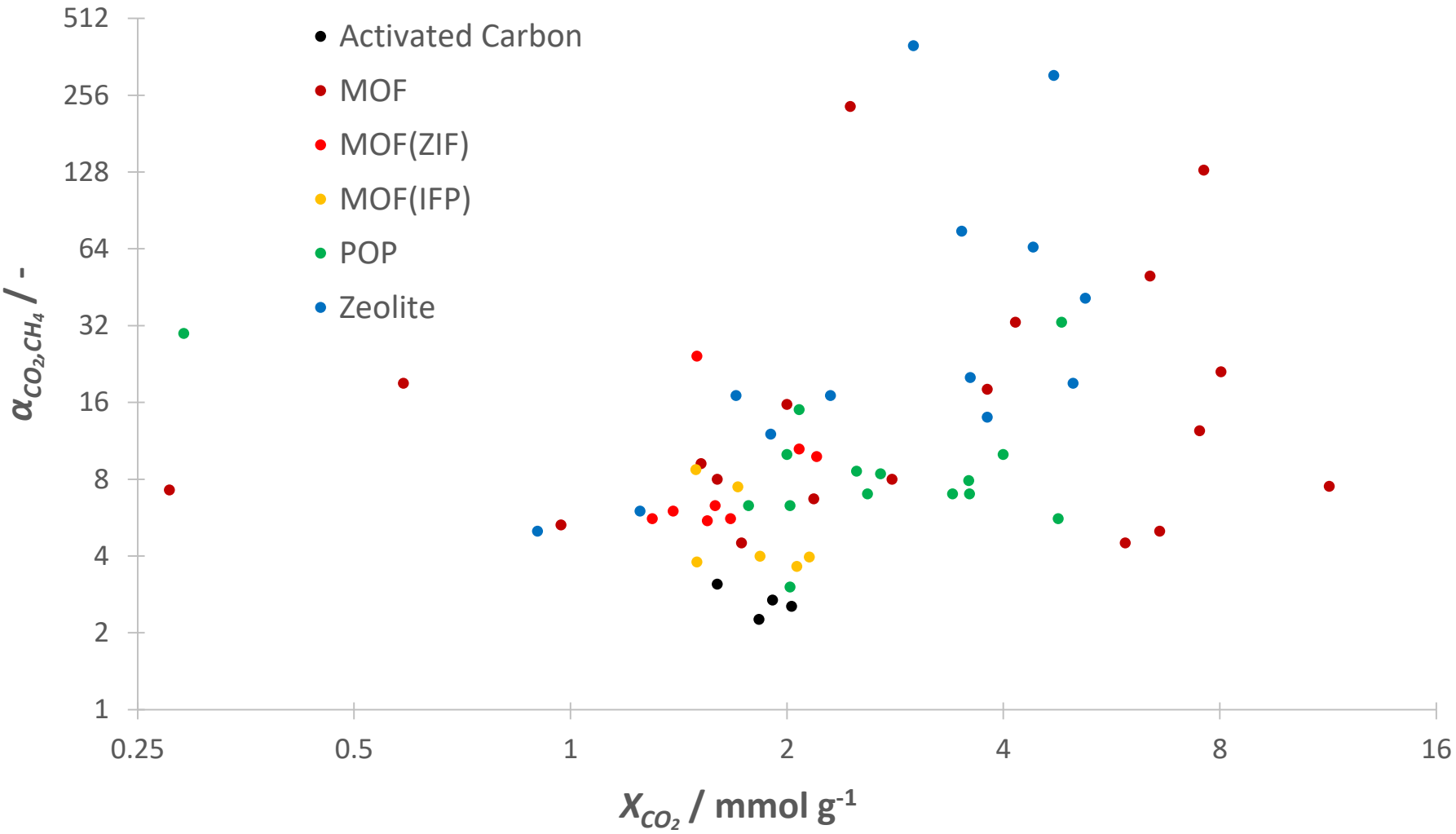


Fig. 1: Equilibrium uptake and selectivity of different adsorbents at STP

Adsorbent Screening

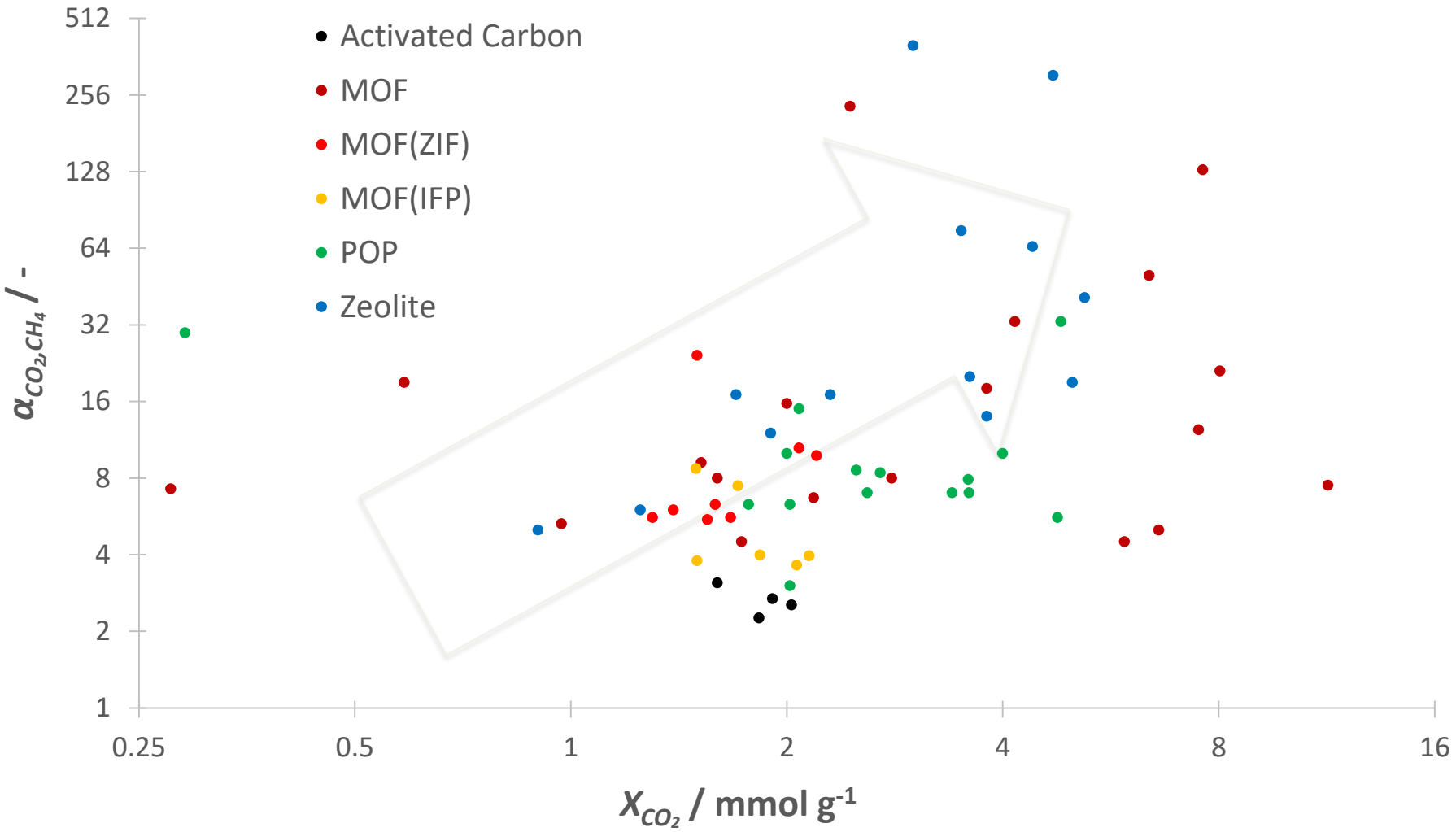


Fig. 1: Equilibrium uptake and selectivity of different adsorbents at STP

Adsorbent Screening

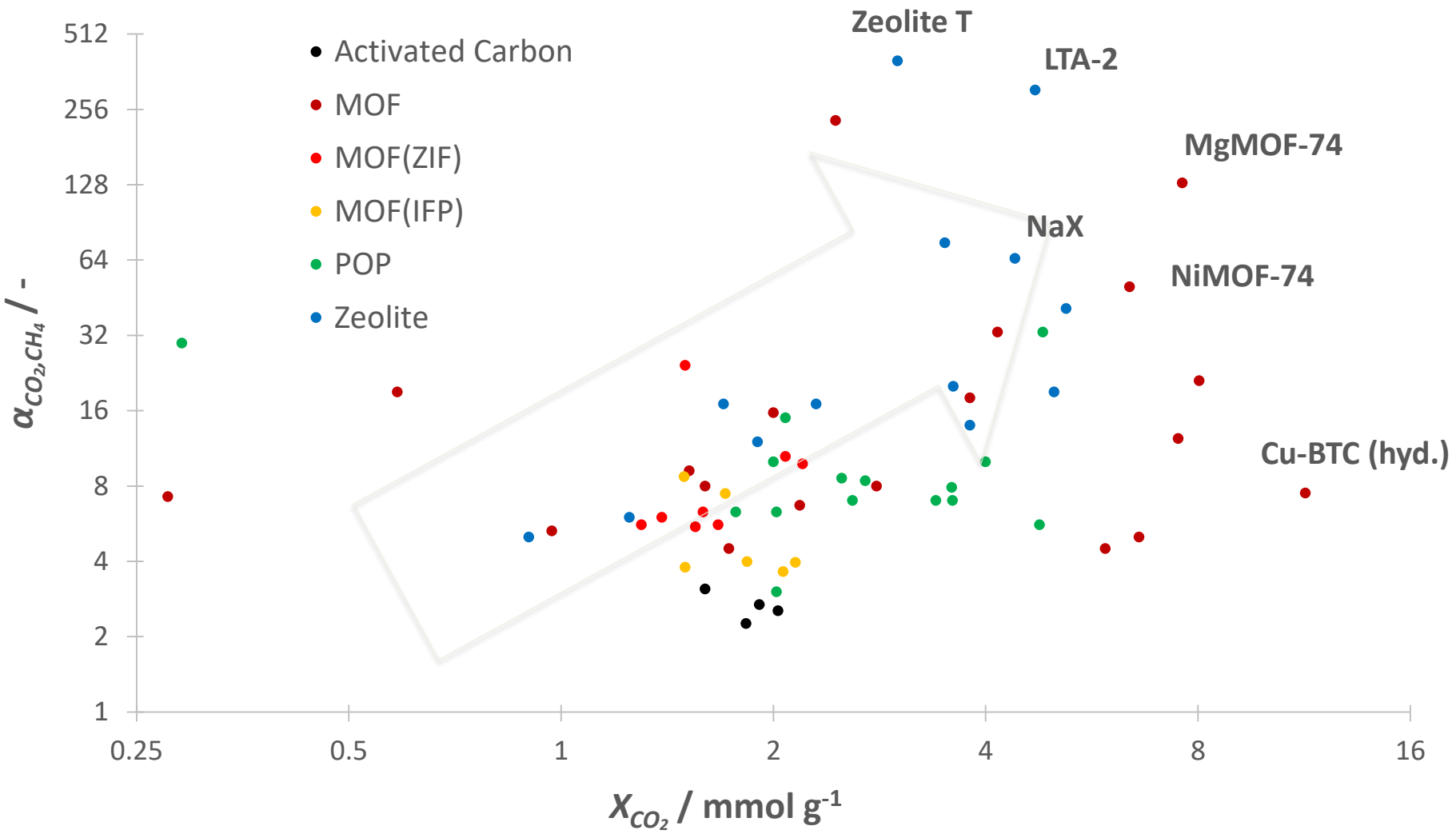


Fig. 1: Equilibrium uptake and selectivity of different adsorbents at STP

Adsorbent Screening

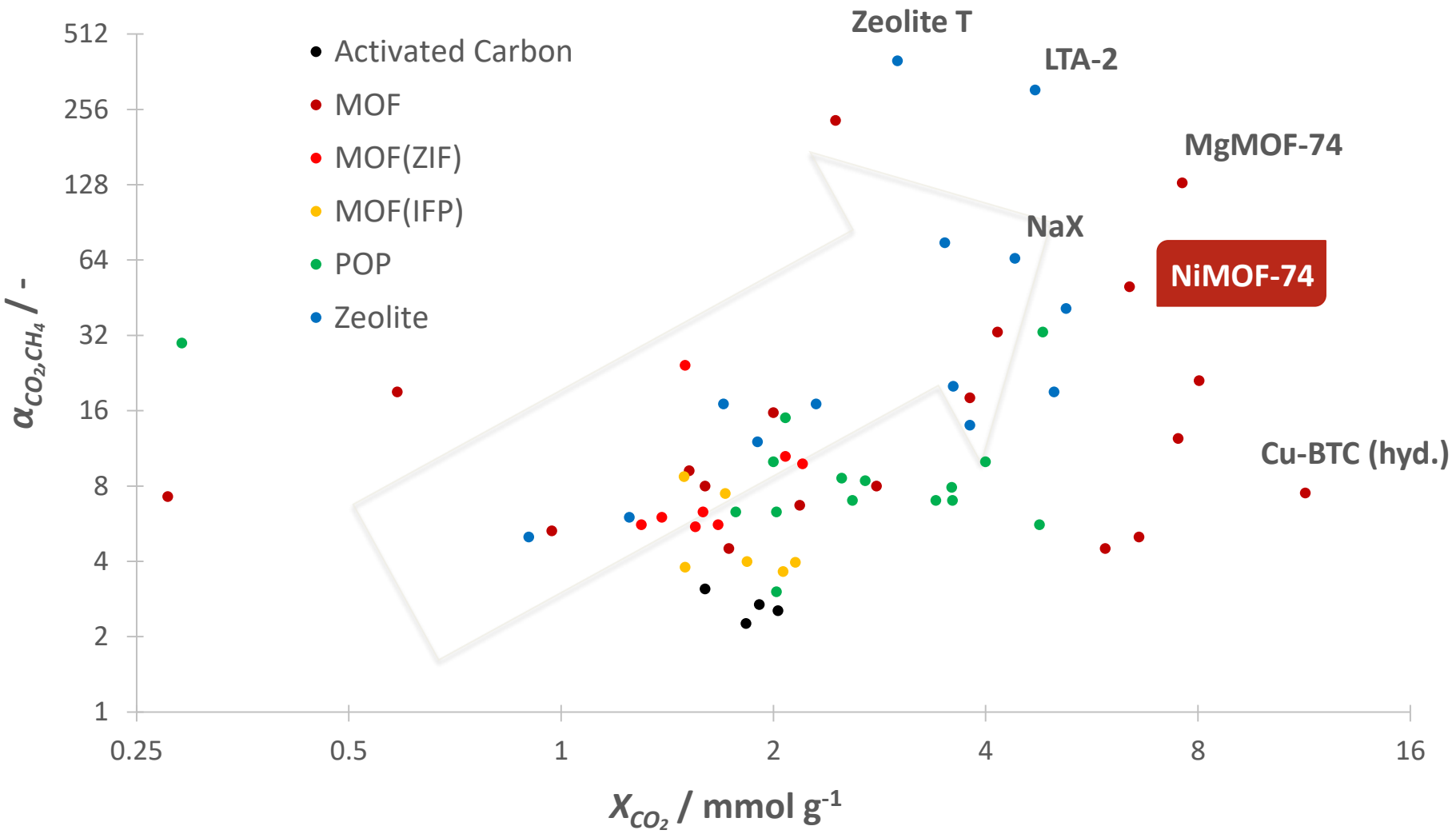
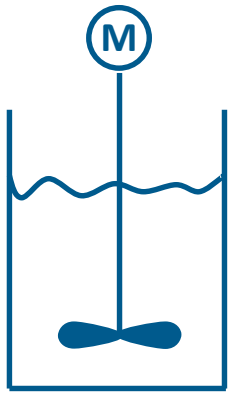
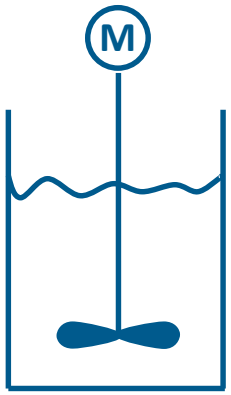


Fig. 1: Equilibrium uptake and selectivity of different adsorbents at STP

Material Synthesis

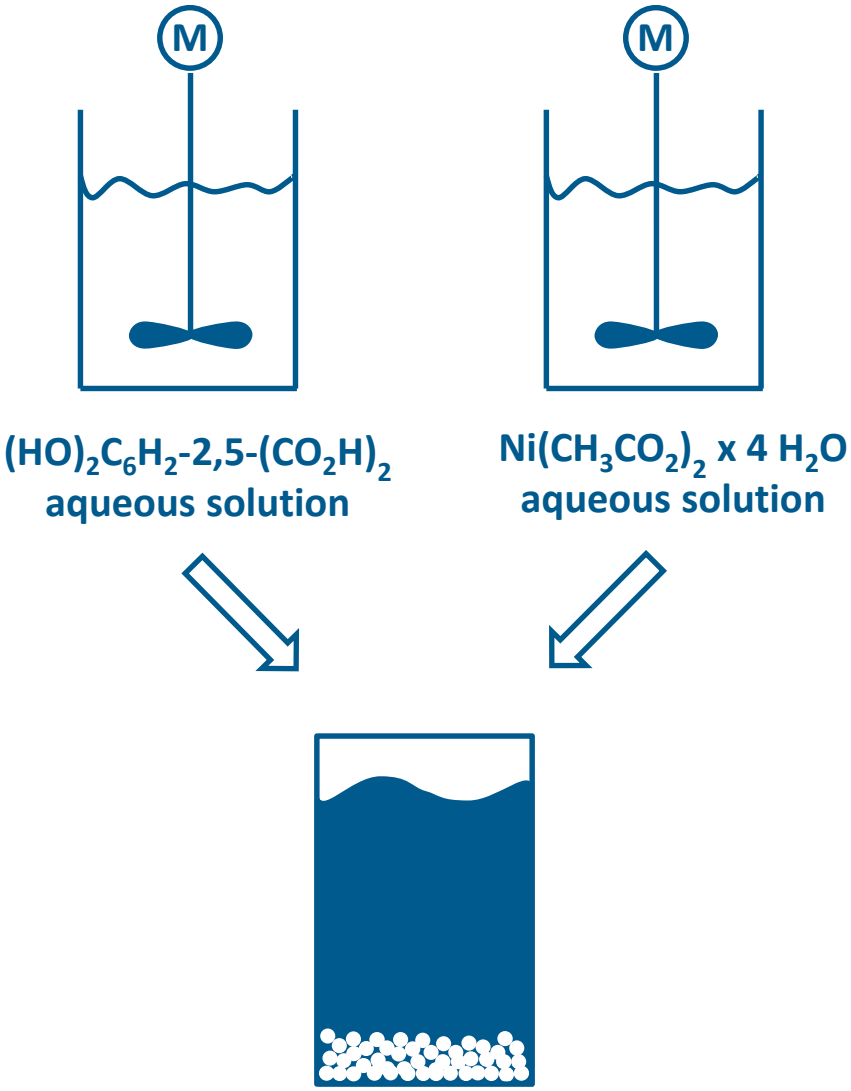


$(HO)_2C_6H_2$-2,5-$(CO_2H)_2$
aqueous solution

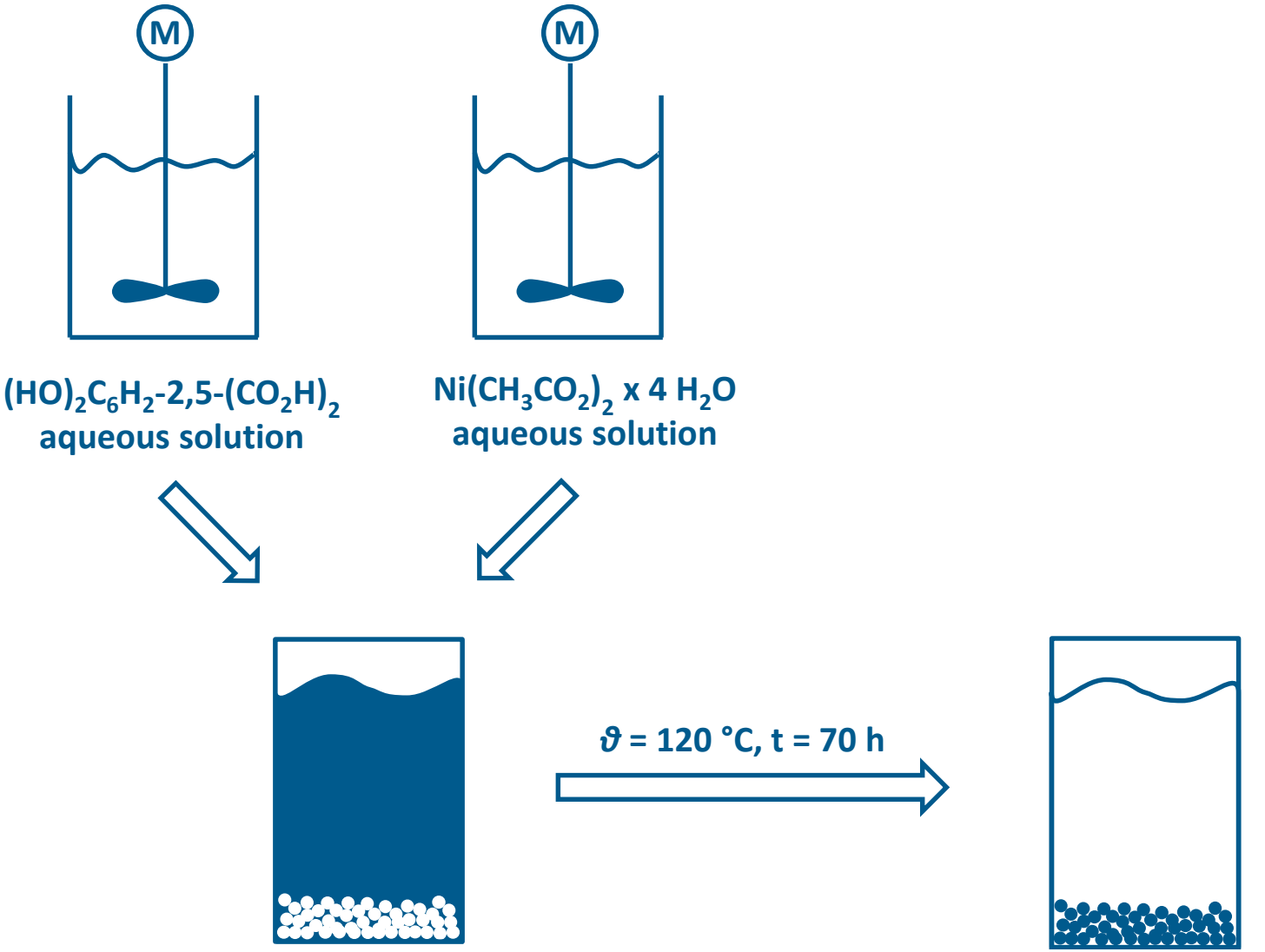


$Ni(CH_3CO_2)_2$ x 4 H_2O
aqueous solution

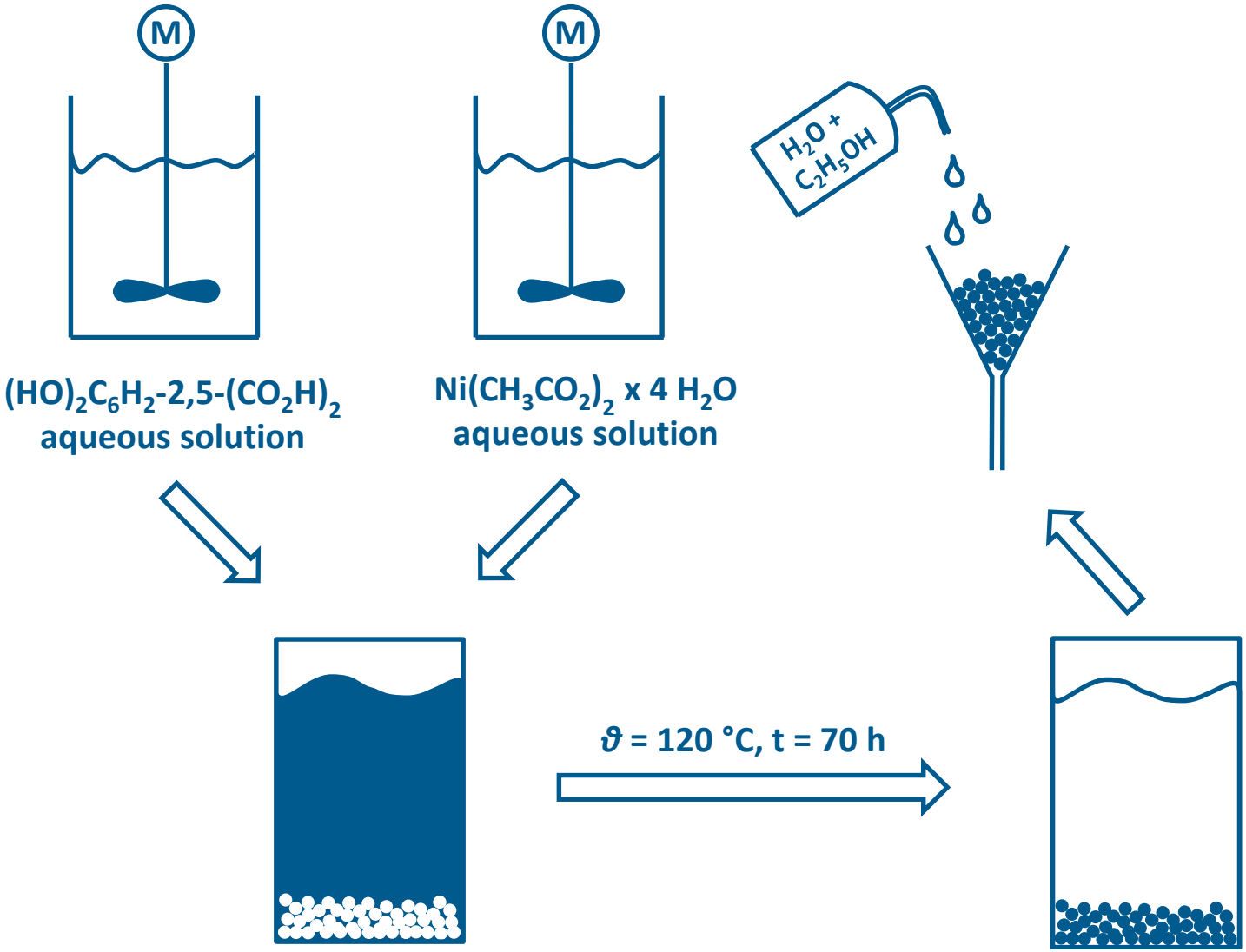
Material Synthesis



Material Synthesis



Material Synthesis



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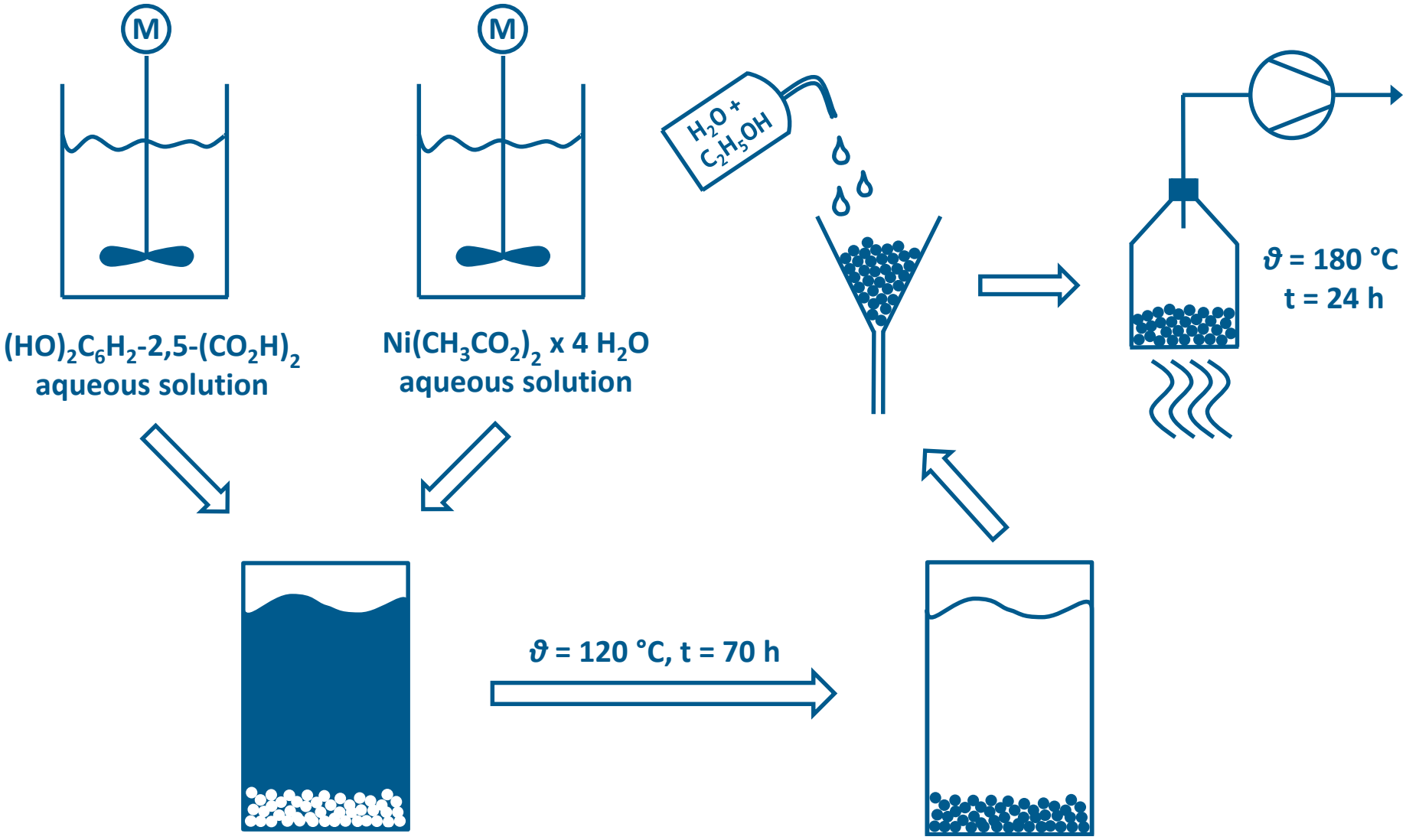
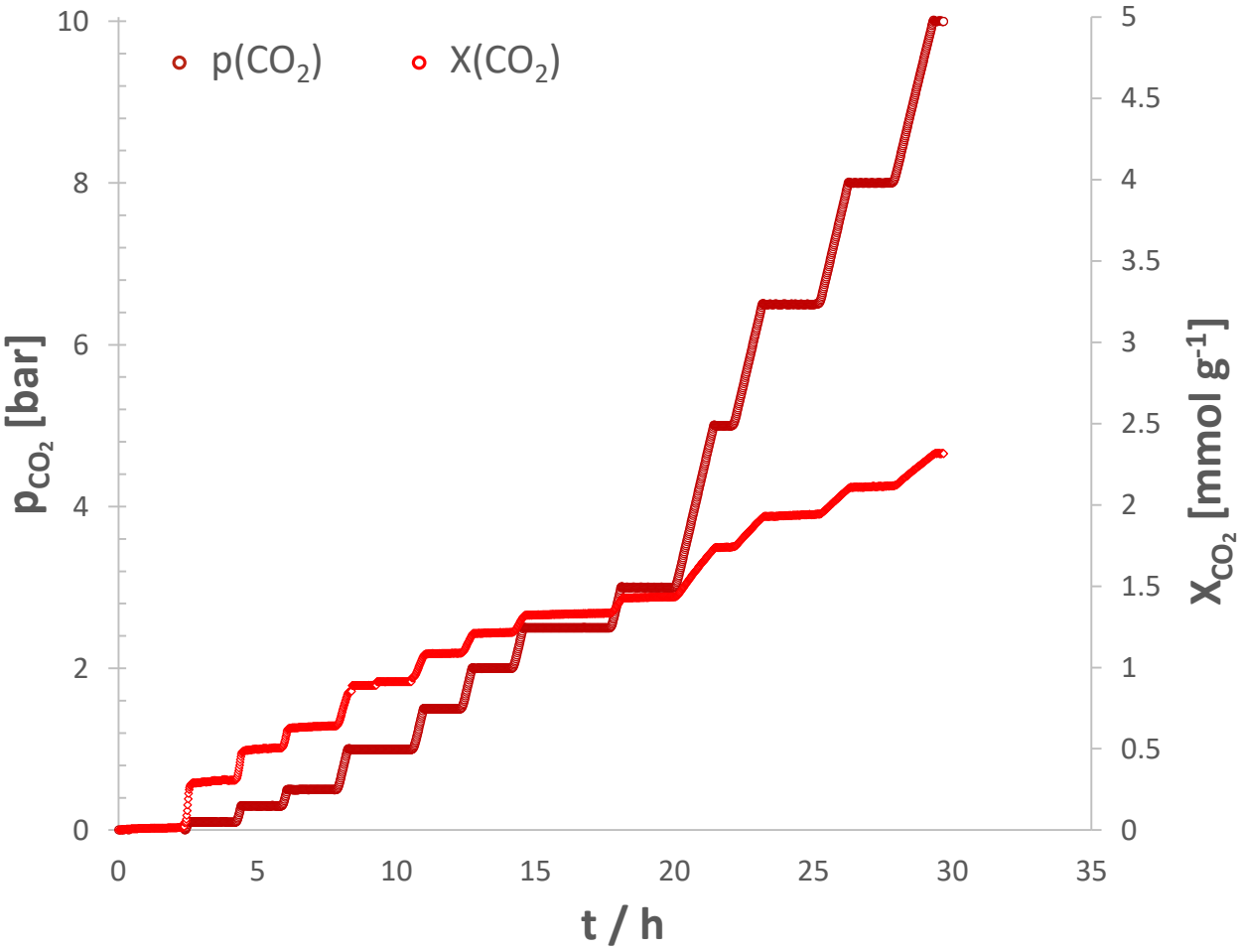


Material Characterization

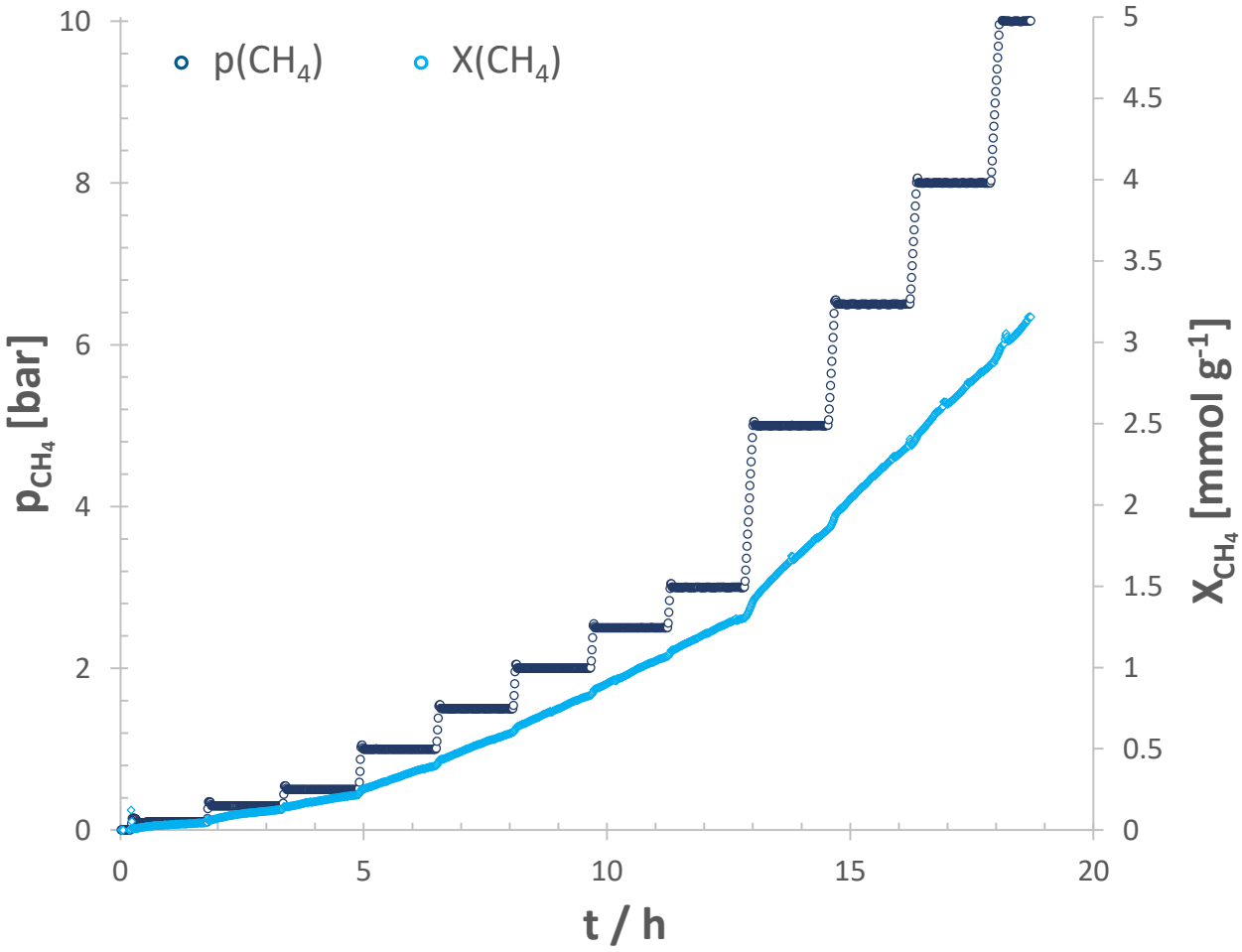


Adsorption kinetics

$$\frac{dX_{CO_2}}{dt} \rightarrow \infty$$

Fig. 2: Uptake kinetics of CO_2 on NiMOF-74@Al_2O_3 at ϑ = 15 °C

Material Characterization



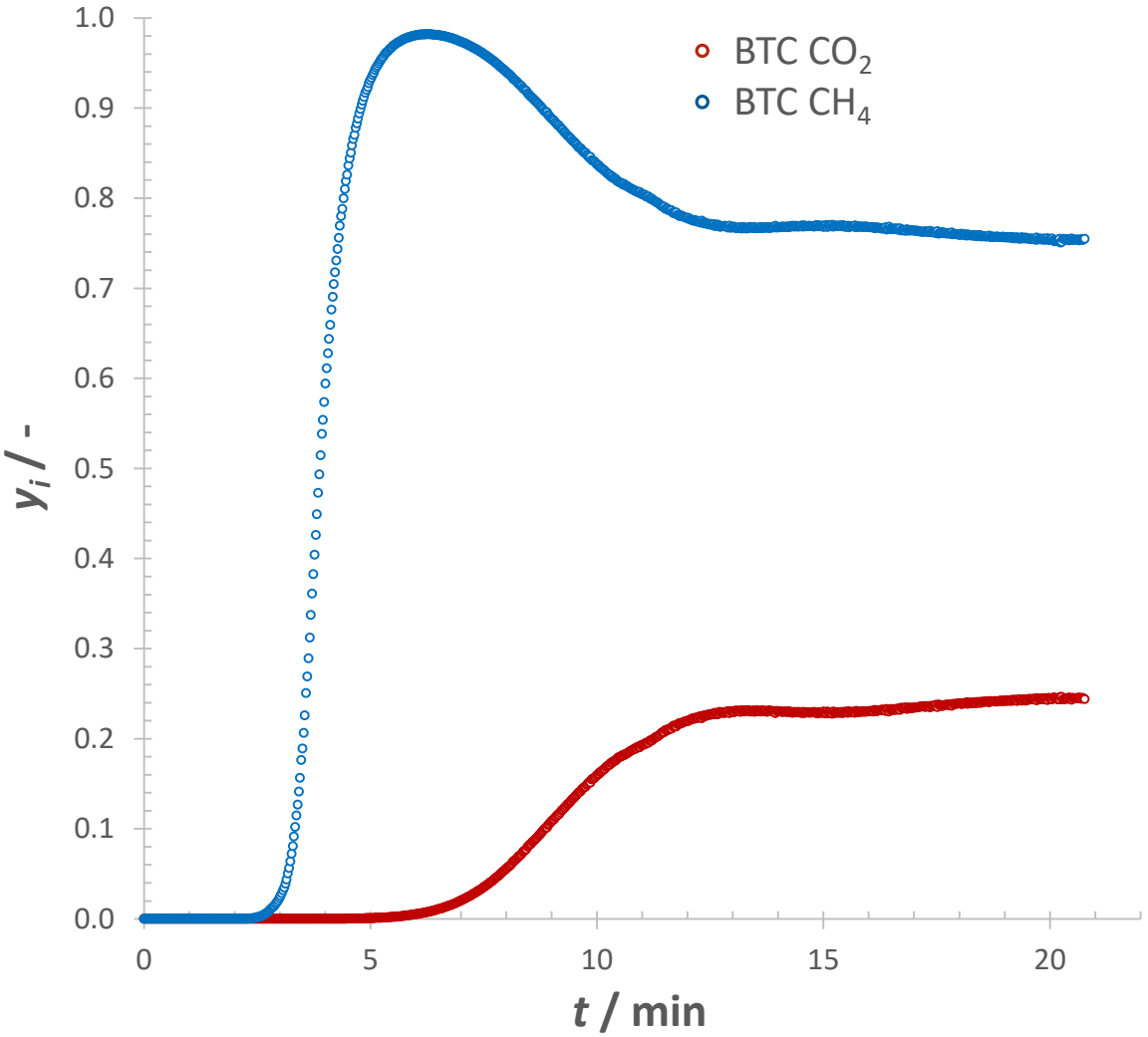
Adsorption kinetics

$$\frac{dX_{CO_2}}{dt} \rightarrow \infty$$

$$\frac{dX_{CH_4}}{dt} \rightarrow 0$$

Fig. 3: Uptake kinetics of CH_4 on NiMOF-74@Al_2O_3 at ϑ = 15 °C

Material Characterization



Breakthrough Experiments

Test conditions

$y_{CO_2} = 0.25$

$\dot{V} = 50\ \mathrm{Nml\ min^{-1}}$

$p = 5\ \mathrm{bar} \quad \vartheta = 30\ °\mathrm{C}$

Adsorber dimensions

$L = 14\ \mathrm{cm} \quad \mathrm{d} = 1.5\ \mathrm{cm}$

Fig. 5: Breakthrough of CO_2 and CH_4 on fixed bed of NiMOF-74@Al_2O_3

Material Characterization

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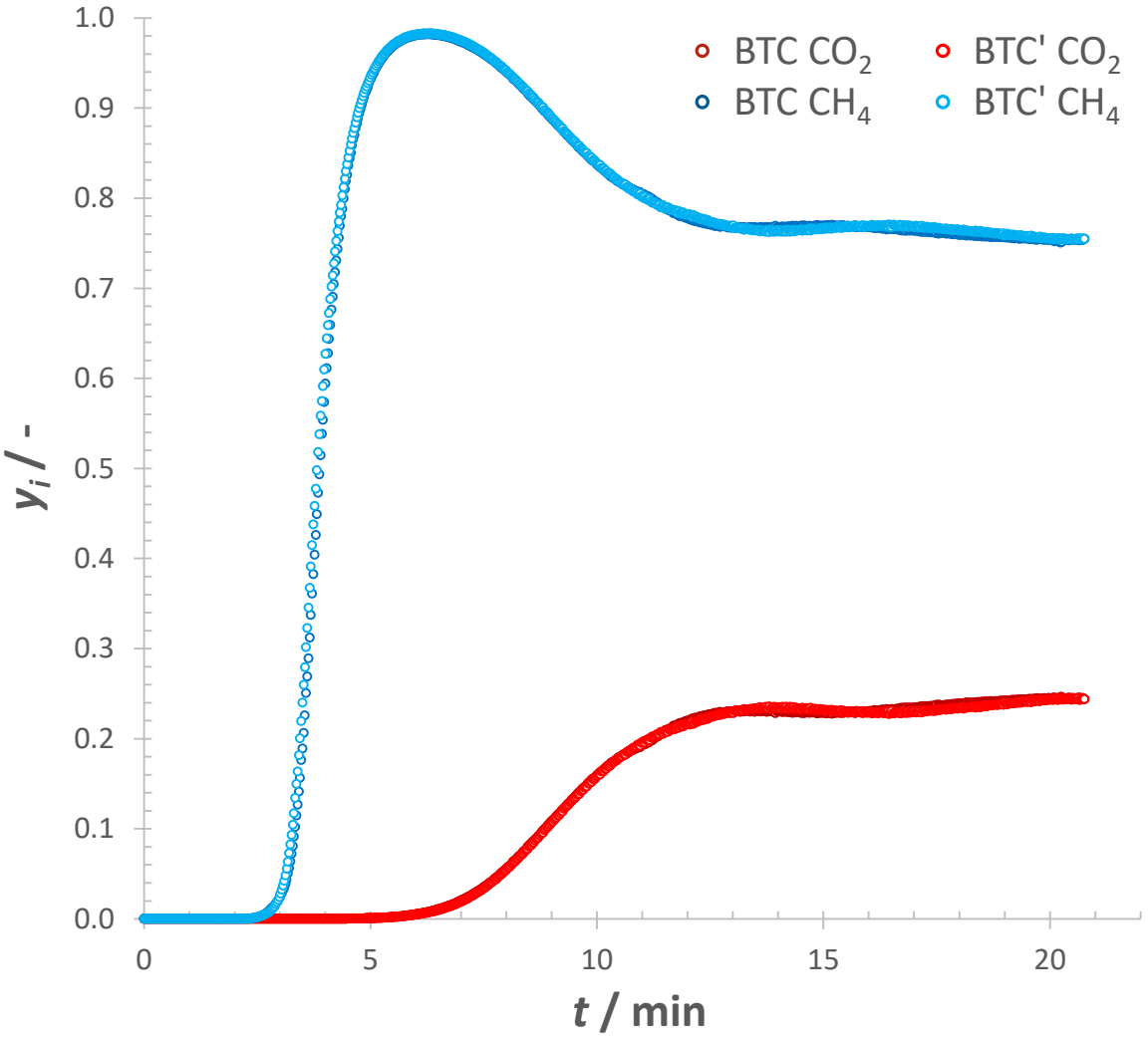

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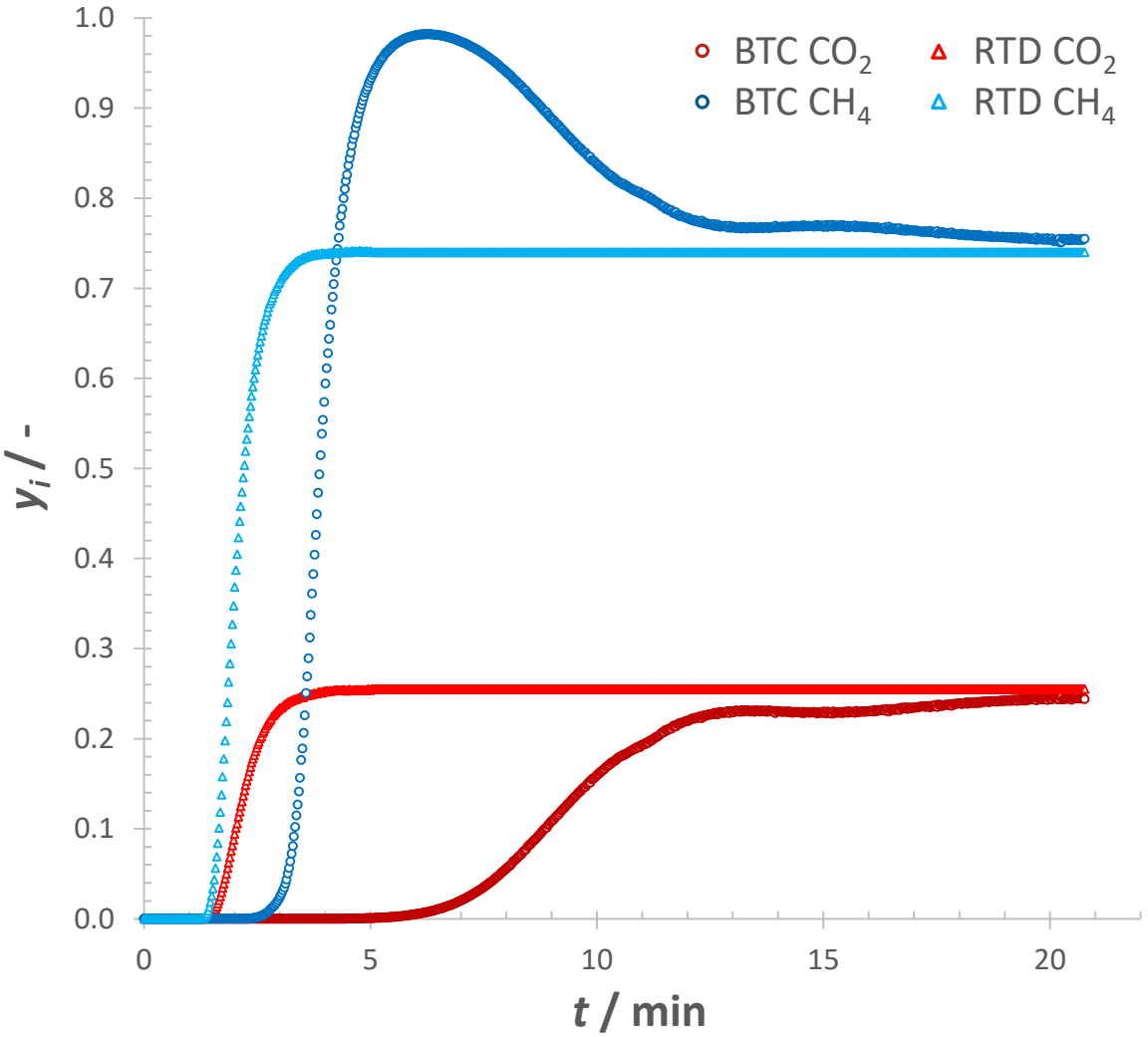
Reproducibility test ✓

Fig. 5: Breakthrough of CO_2 and CH_4 on fixed bed of NiMOF-74@Al_2O_3

Material Characterization



Integration of the BTC

$$X_{T,i} = \int_{t_0}^{t_\infty} \frac{\dot{V}_T(t) \cdot [c_{i,0} - c_{T,i}(t)]}{m_P} \, dt$$

$$= \int_{t_0}^{t_\infty} \frac{\dot{V}_T(t) \cdot [p_{i,0} - p_{T,i}(t)]}{m_P \cdot R \cdot T} \, dt$$

Fig. 5: Breakthrough of CO_2 and CH_4 on fixed bed of NiMOF-74@Al_2O_3

Material Characterization

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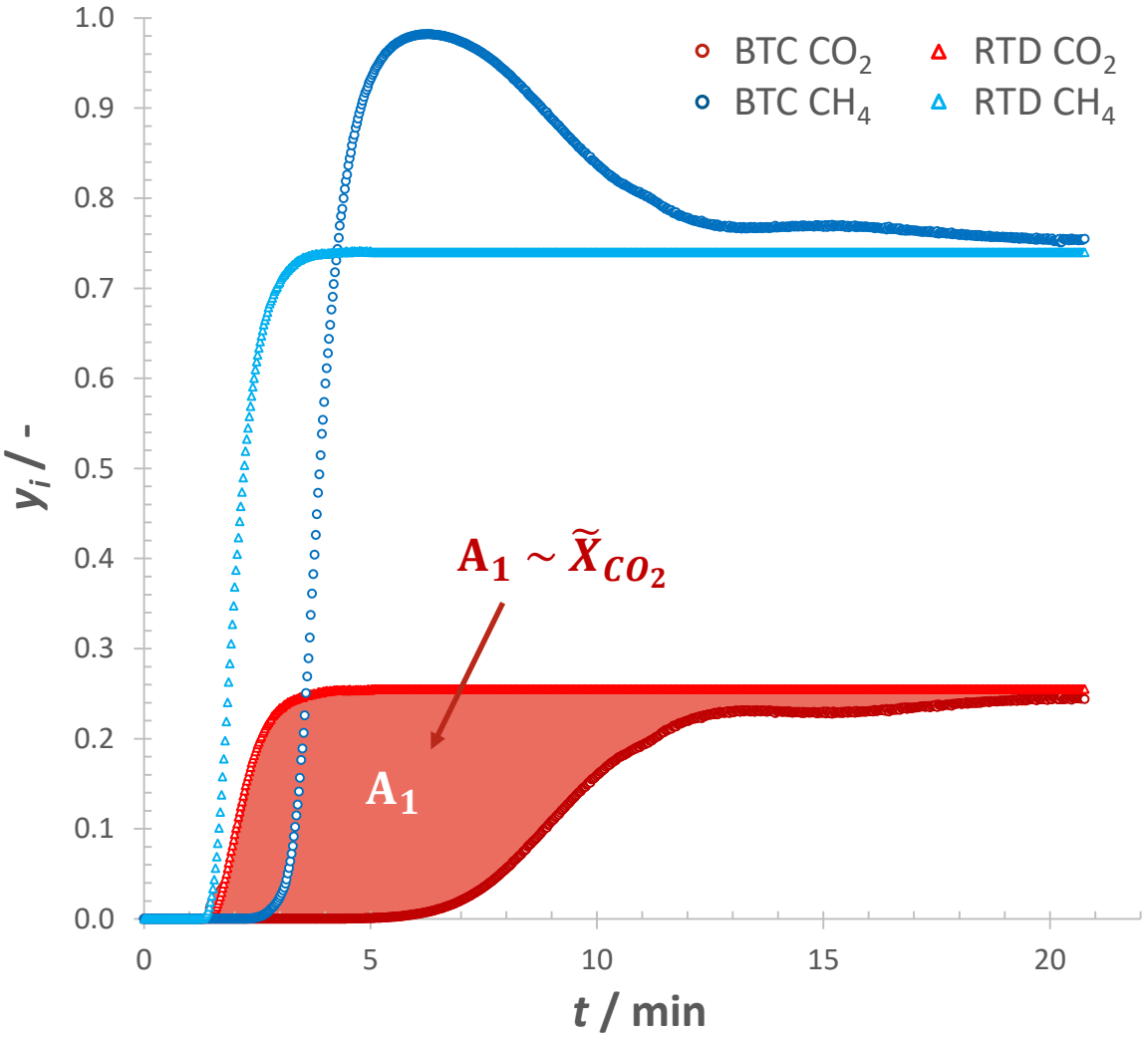

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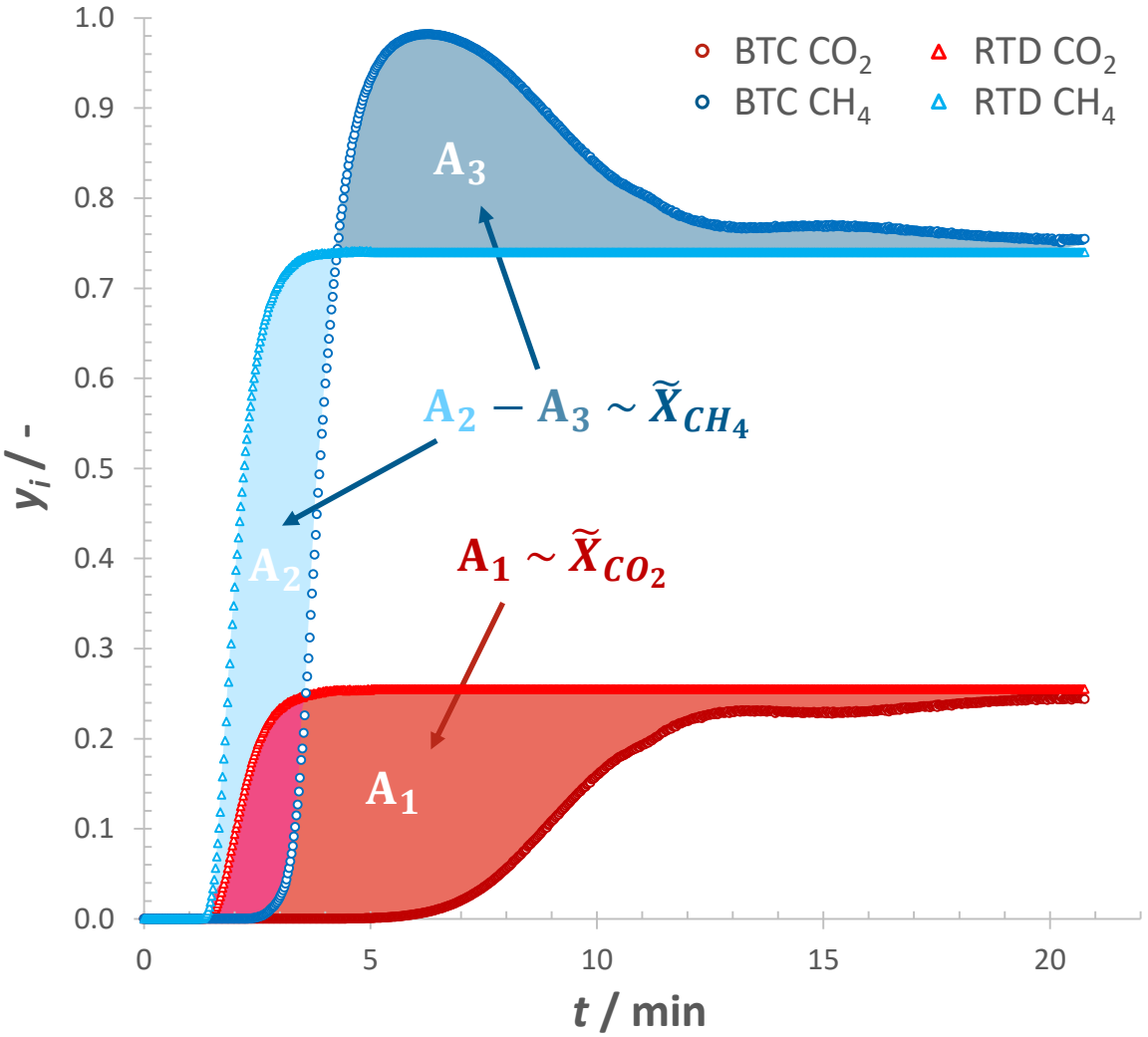
$$\tilde{X}_{CO_2} = 1.18 \, \frac{mmol}{g}$$

Fig. 5: Breakthrough of CO_2 and CH_4 on fixed bed of NiMOF-74@Al_2O_3

Material Characterization



Integration of the BTC

$$X_{T,i} = \int_{t_0}^{t_\infty} \frac{\dot{V}_T(t) \cdot [c_{i,0} - c_{T,i}(t)]}{m_P} \, dt$$

$$= \int_{t_0}^{t_\infty} \frac{\dot{V}_T(t) \cdot [p_{i,0} - p_{T,i}(t)]}{m_P \cdot R \cdot T} \, dt$$

$$\tilde{X}_{CO_2} = 1.18 \, \frac{mmol}{g}$$

$$\tilde{X}_{CH_4} \approx 0 \, \frac{mmol}{g}$$

Fig. 5: Breakthrough of CO_2 and CH_4 on fixed bed of NiMOF-74@Al_2O_3

Material Characterization

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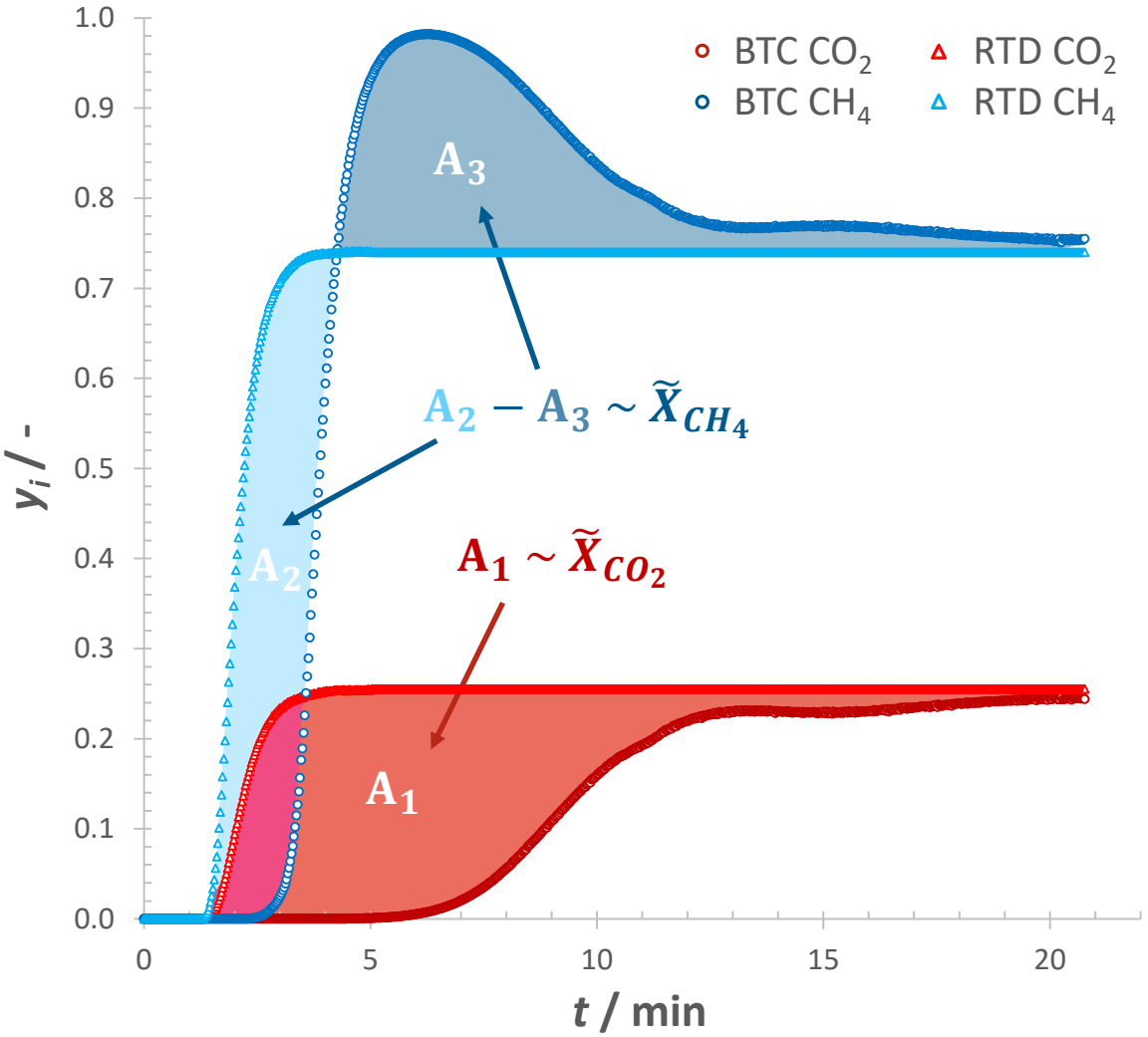

Integration of the BTC

$$X_{T,i} = \int_{t_0}^{t_\infty} \frac{\dot{V}_T(t) \cdot [c_{i,0} - c_{T,i}(t)]}{m_P} \, dt$$

$$= \int_{t_0}^{t_\infty} \frac{\dot{V}_T(t) \cdot [p_{i,0} - p_{T,i}(t)]}{m_P \cdot R \cdot T} \, dt$$

$$\tilde{X}_{CO_2,real} = 11.79 \, \frac{mmol}{g}$$

$$\tilde{X}_{CH_4,real} \approx 0 \, \frac{mmol}{g}$$

Fig. 5: Breakthrough of CO_2 and CH_4 on fixed bed of NiMOF-74@Al_2O_3

Material Characterization

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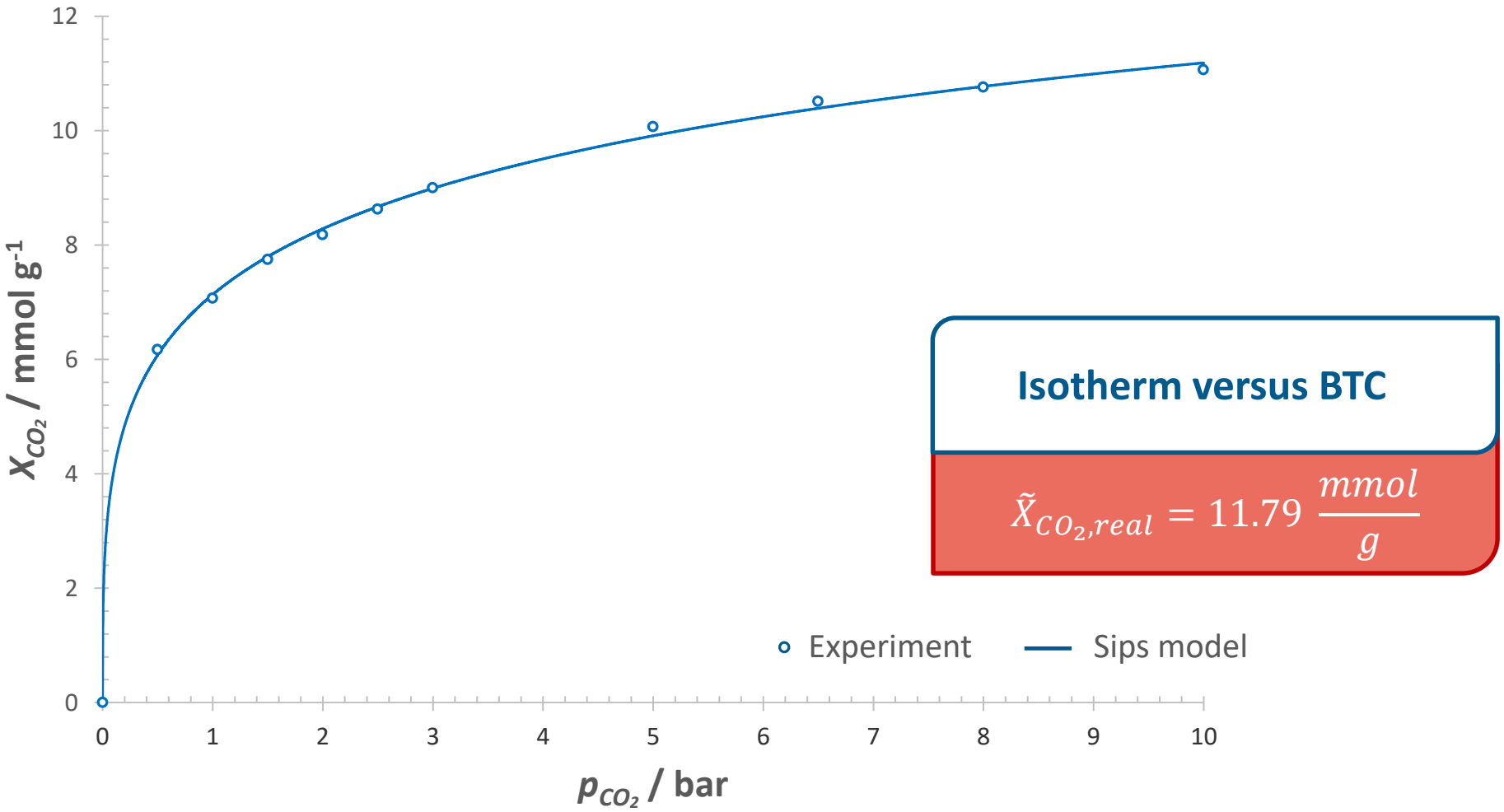

Isotherm versus BTC

$$\tilde{X}_{CO_2,real} = 11.79 \frac{mmol}{g}$$

Fig. 6: Adsorption equilibrium of CO_2 on pure NiMOF-74 at ϑ = 30 °C

Material Characterization

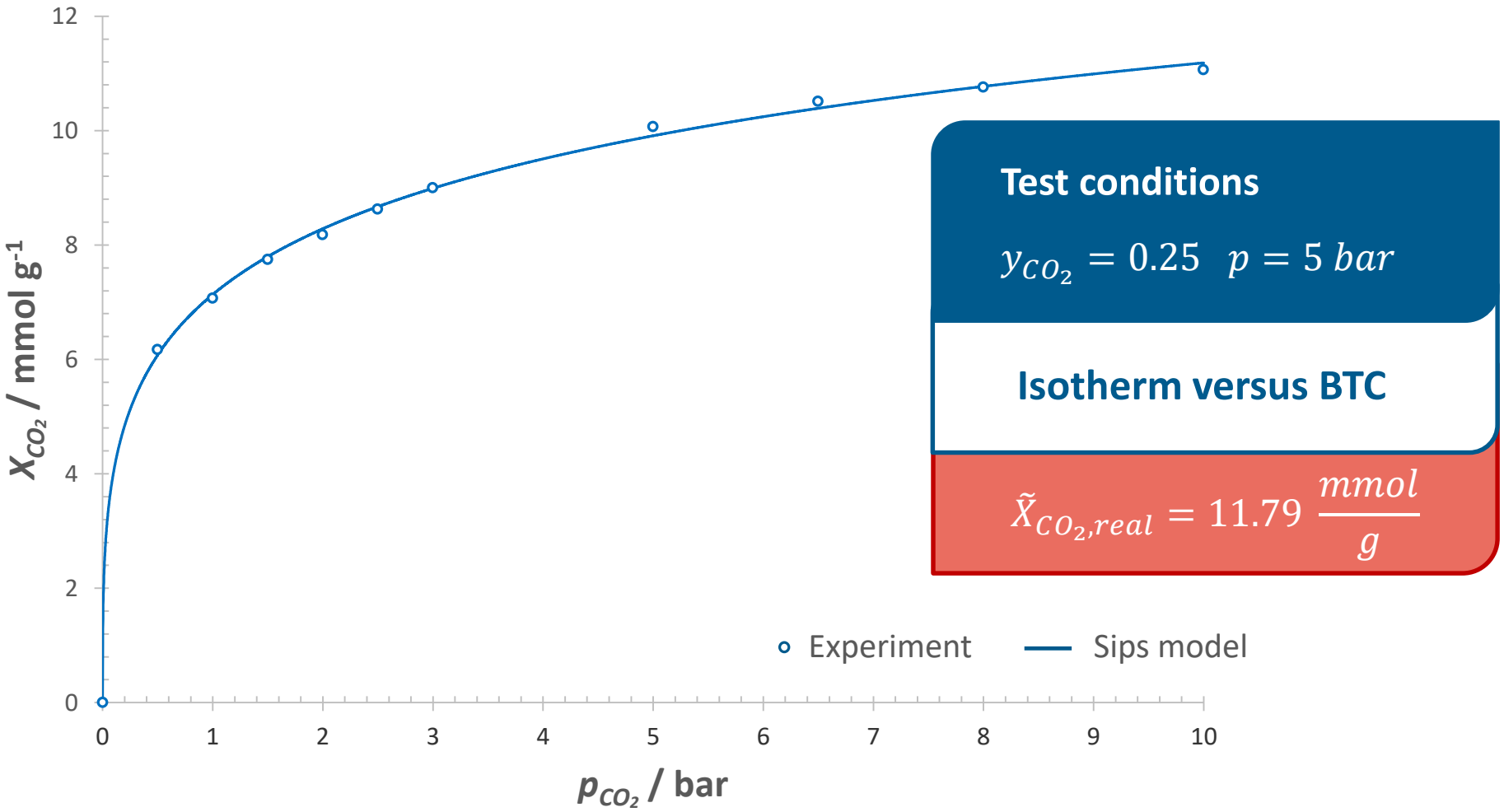

Fig. 6: Adsorption equilibrium of CO_2 on pure NiMOF-74 at ϑ = 30 °C

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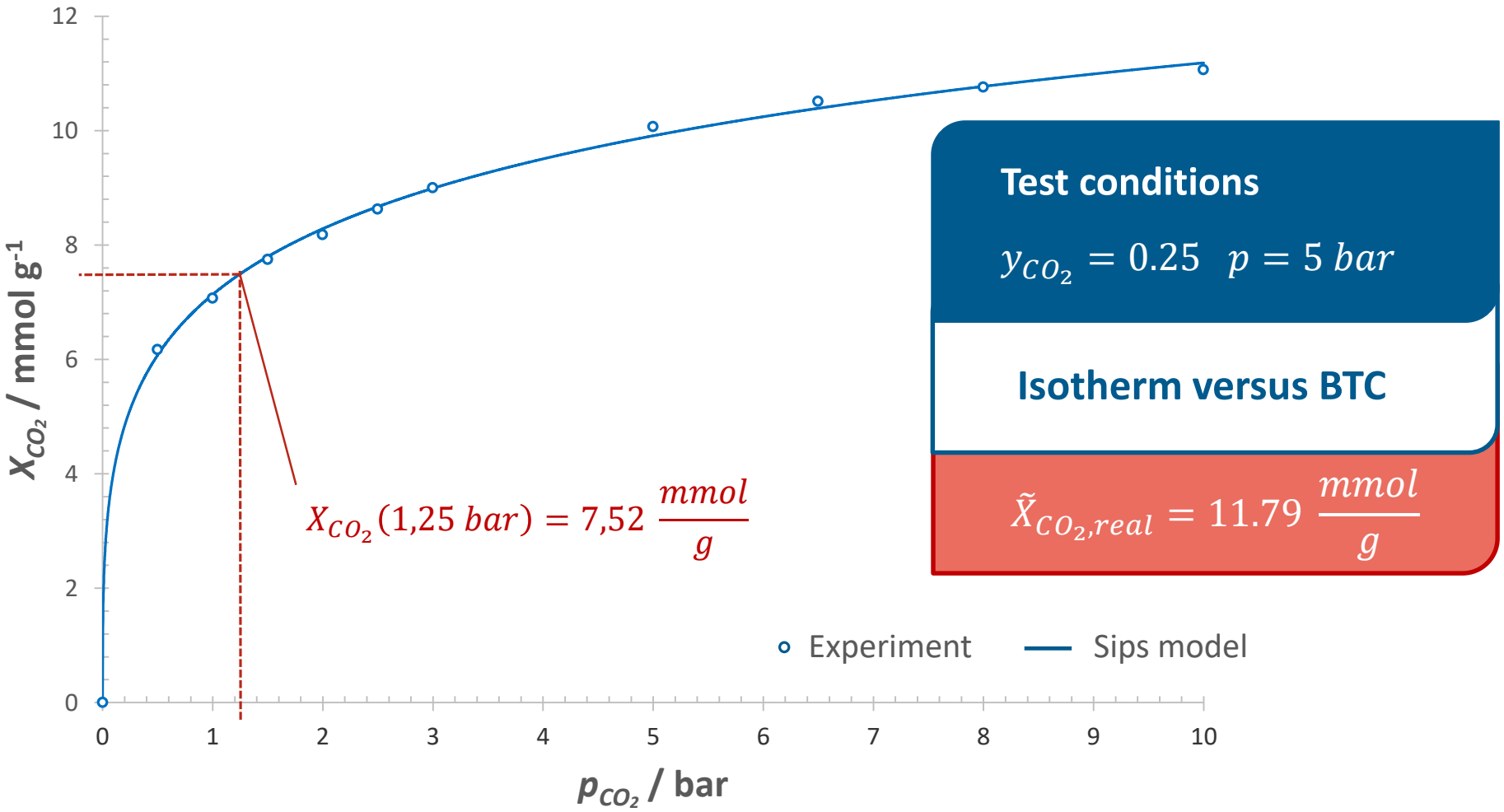

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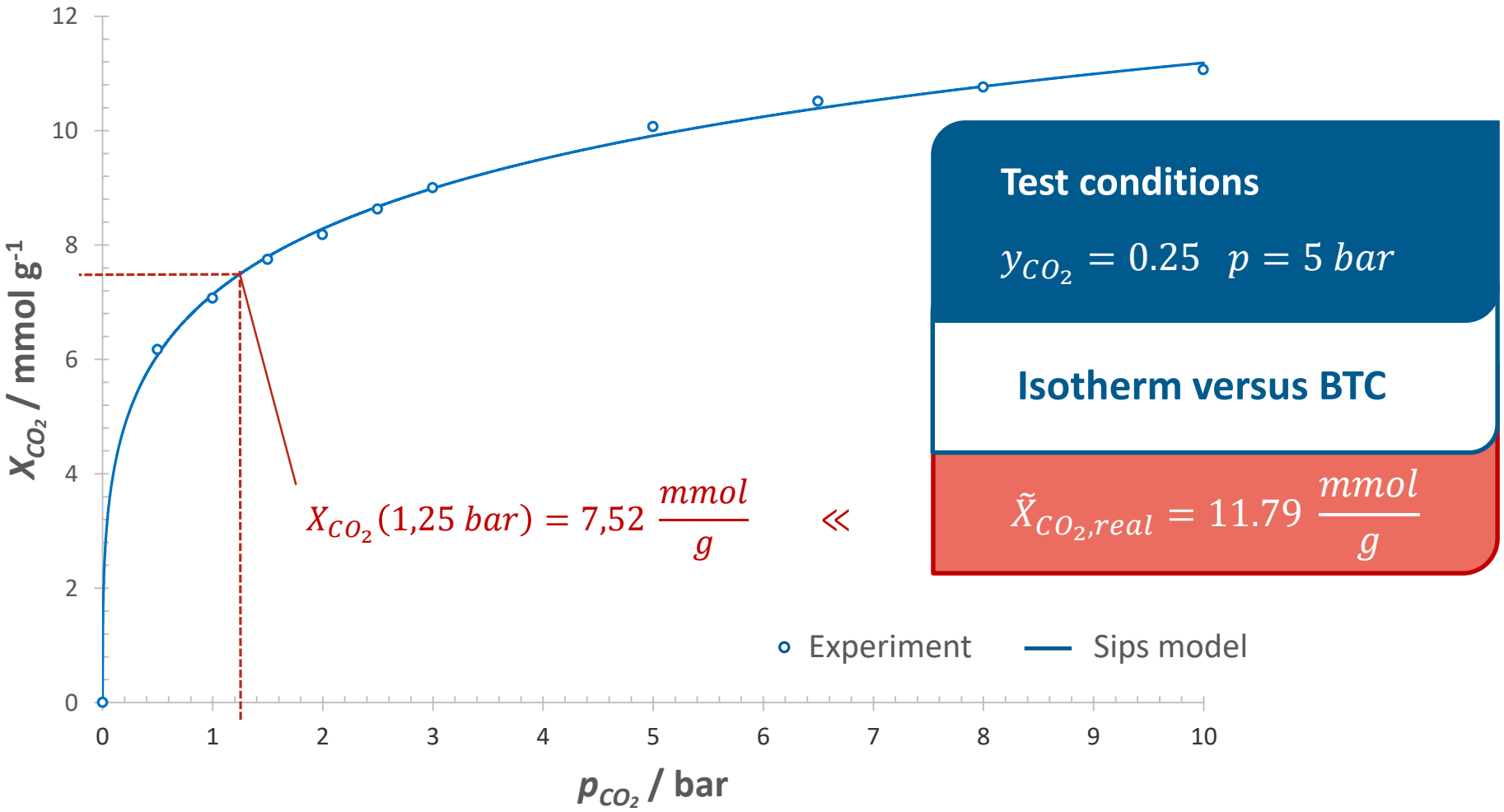

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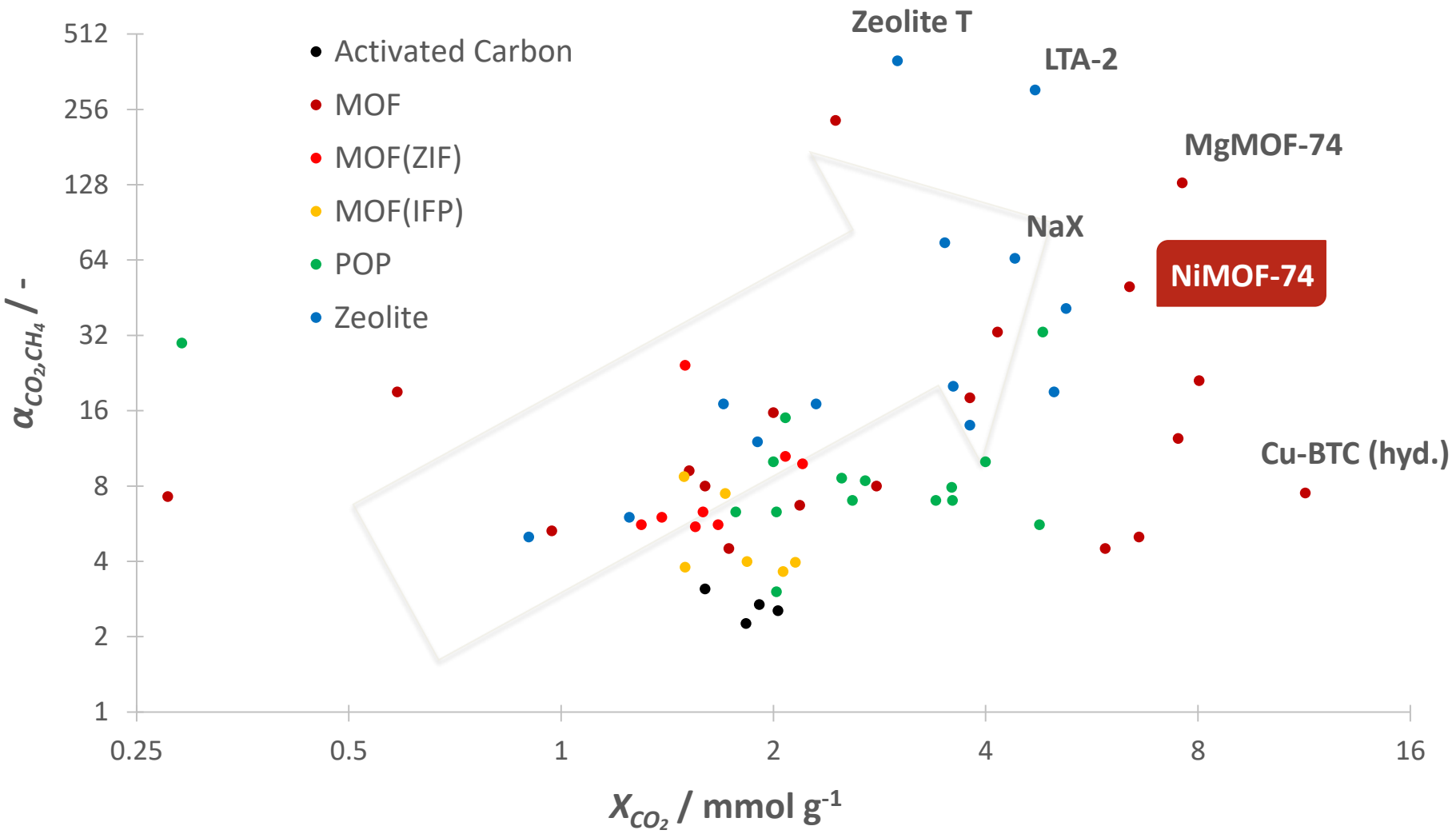

Fig. 1: Equilibrium uptake and selectivity of different adsorbents at STP

Material Characterization

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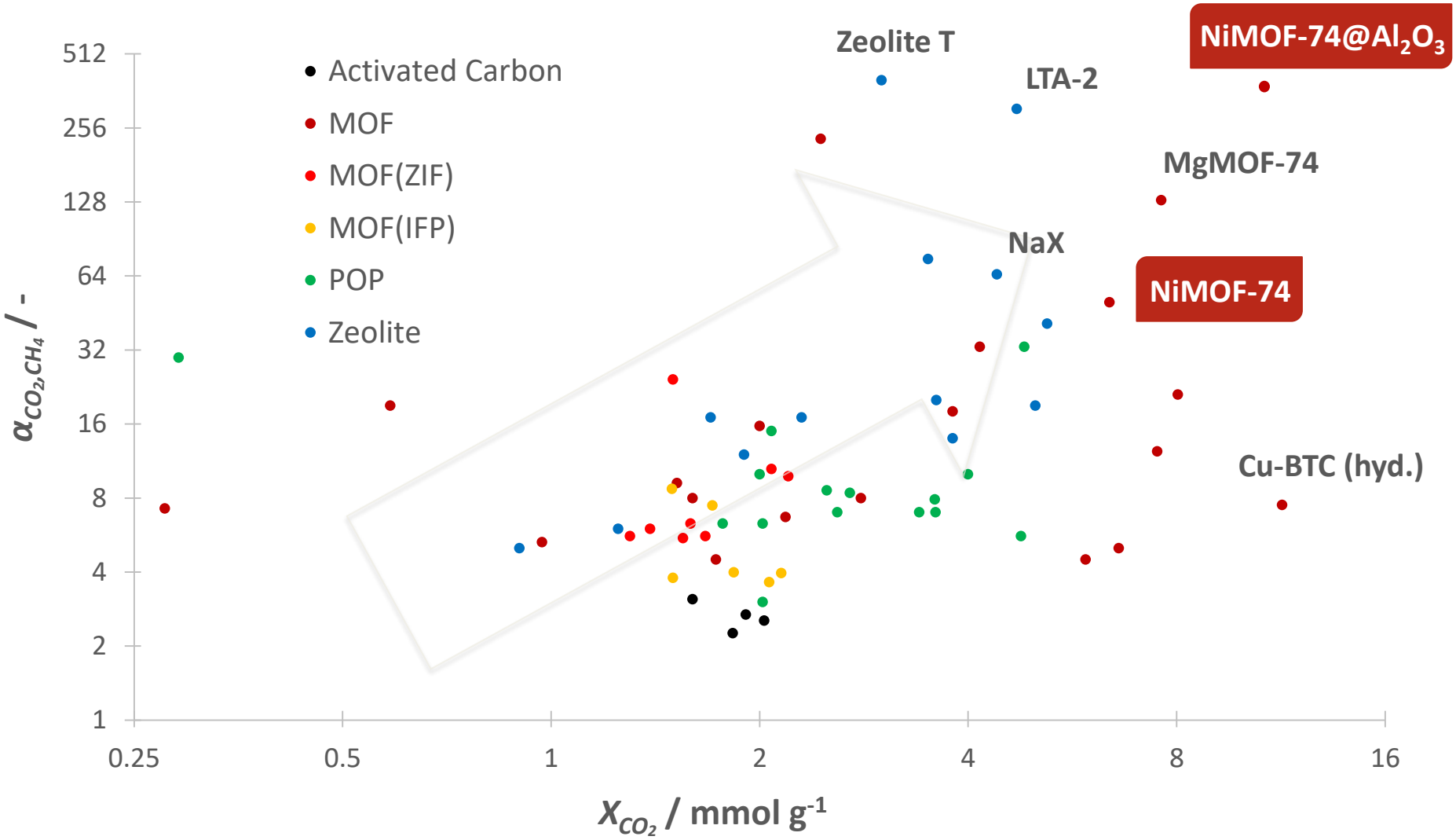

Fig. 1: Equilibrium uptake and selectivity of different adsorbents at STP

Summary and Outlook

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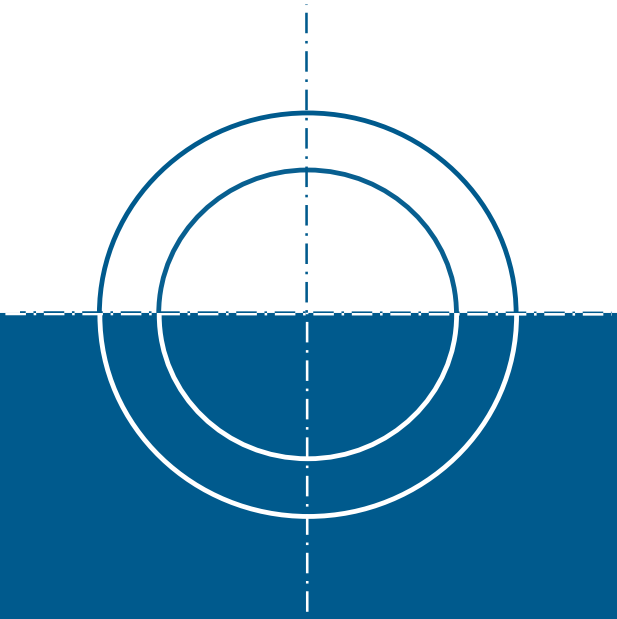
NiMOF-74@Al_2O_3 core shell composites are a very promising approach:

- **Kinetic separation proven**
- **Enhanced „quasi equilibrium“ uptake of CO_2**
  - **→ Storage function of the core**
- **Enhanced selectivity towards CO_2**



Launching a funded project:

- **Improve synthesis**
- **Raise more data for validation**
- **More detailed kinetic studies**
  - **→ Mathematical modelling of BTC**
- **Looking for interested people for a joined project**

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Thank you for your attention!

Special thanks to:

3P INSTRUMENTS

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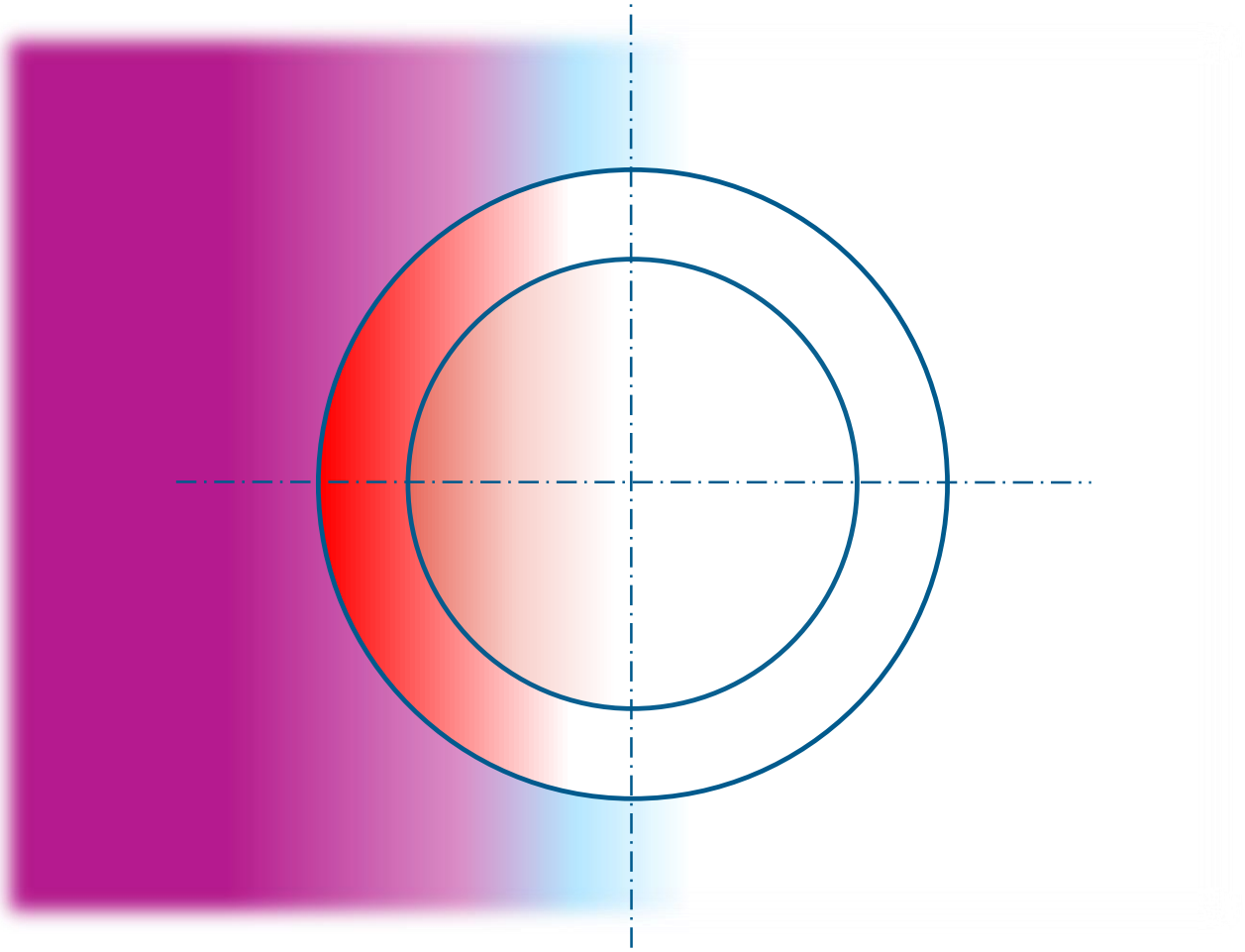
Prof. Dipl.-Ing. Dr. techn. H.-J. Bart
Phone: +49 (0) 631 205 2117
http://www.mv.uni-kl.de/tvt/

Motivation



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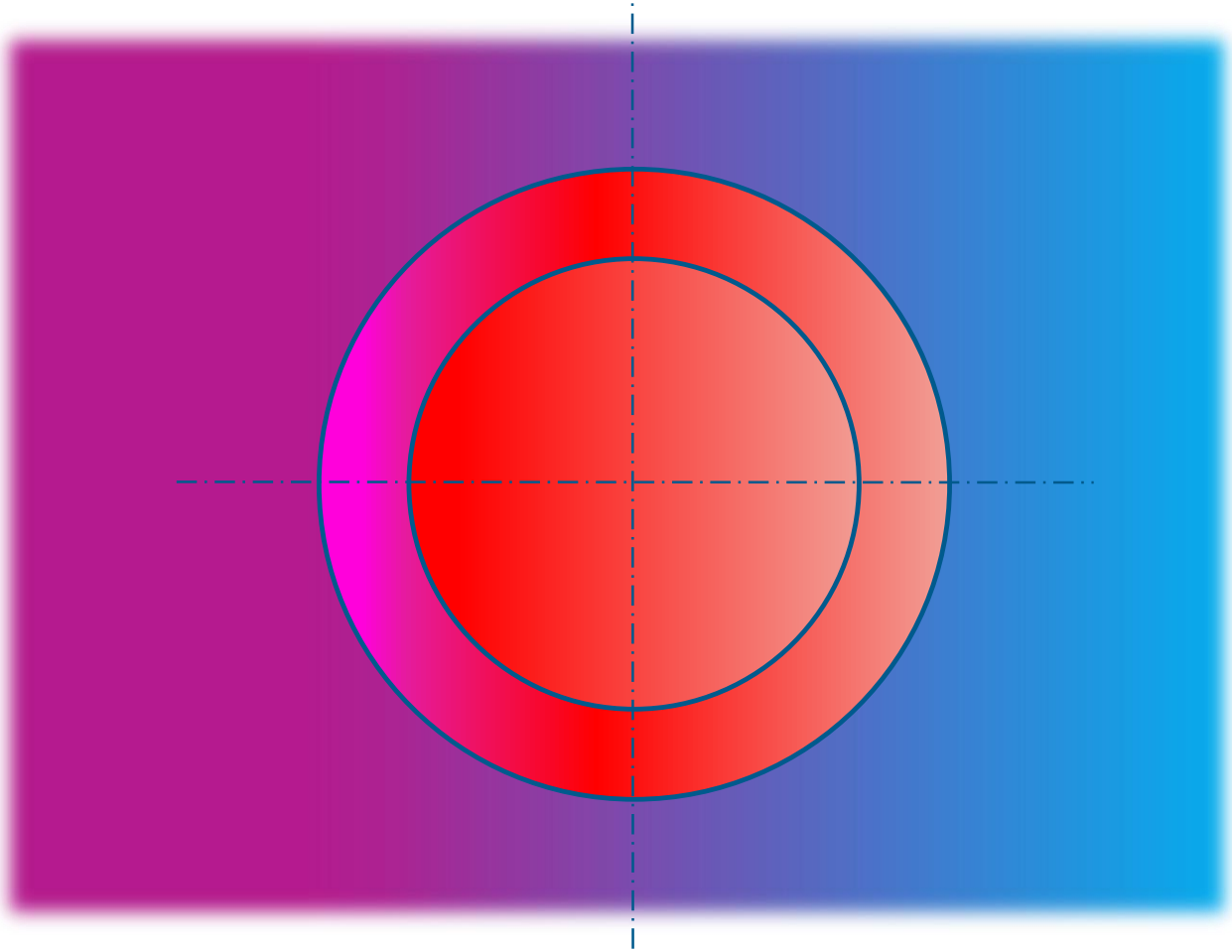
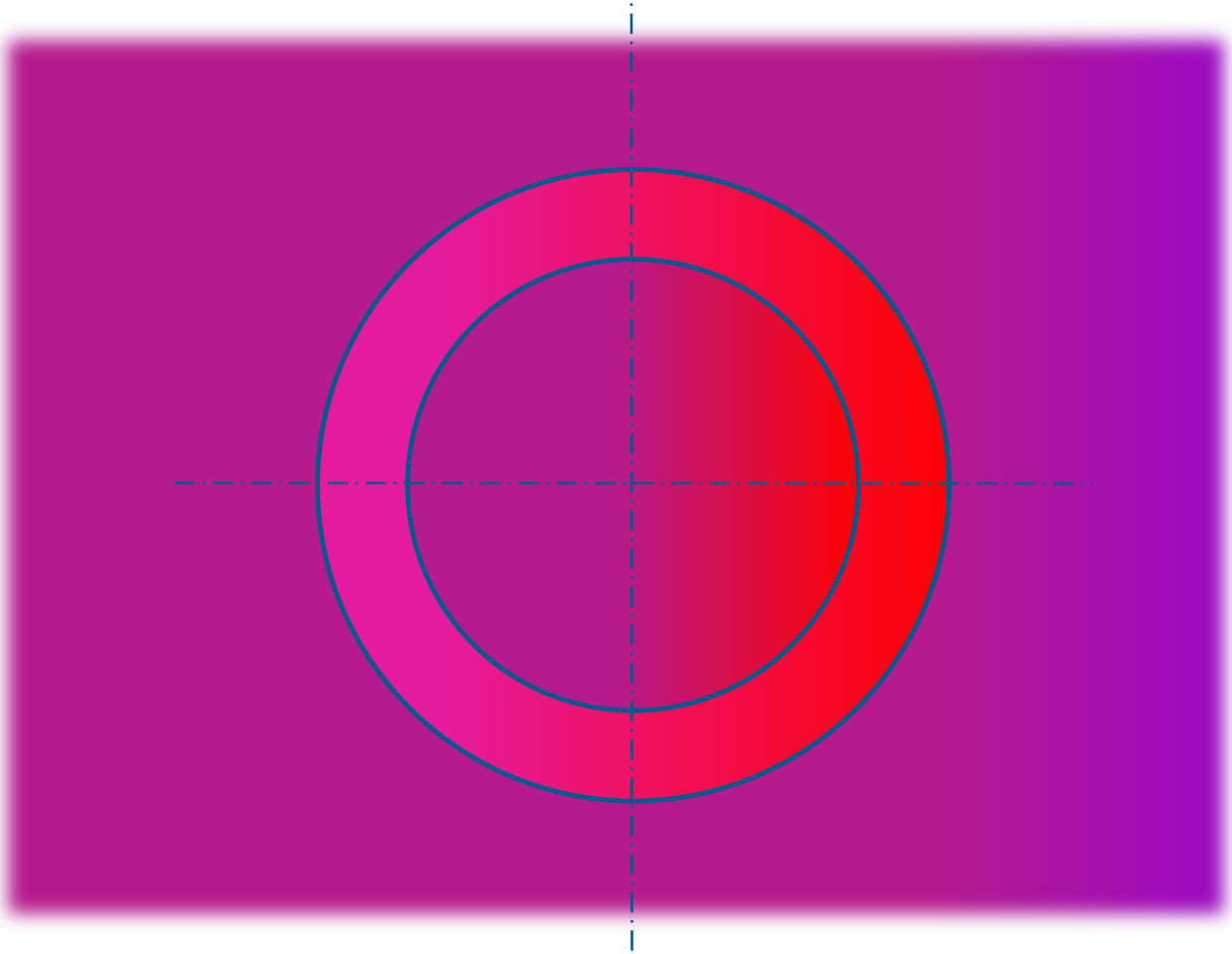
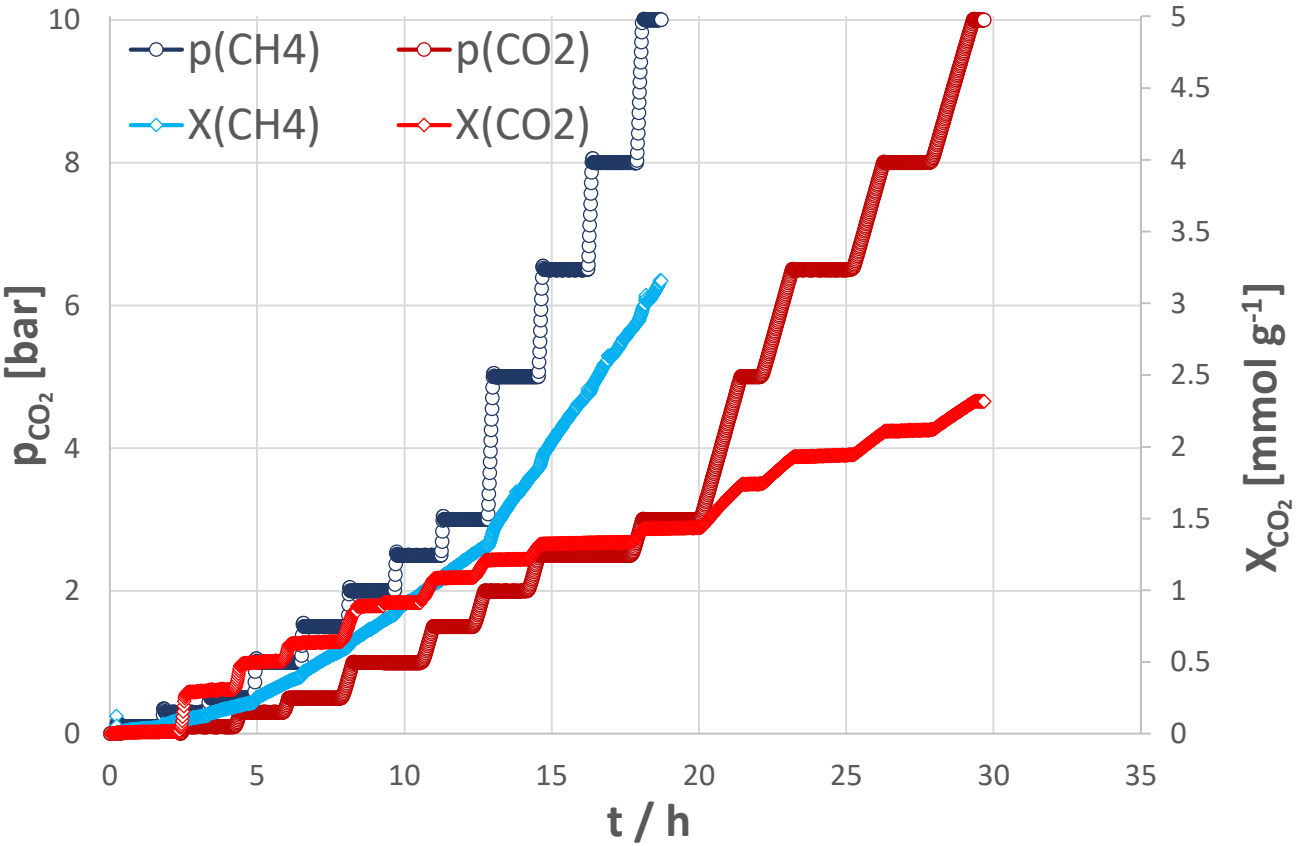


Motivation




p(CH4)
p(CO2)
X(CH4)
X(CO2)
p_{CO_2} [bar]
X_{CO_2} [mmol g^{-1}]
t / h
0
2
4
6
8
10
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0
5
10
15
20
25
30
35