

# Post-Combustion Capture of CO<sub>2</sub>

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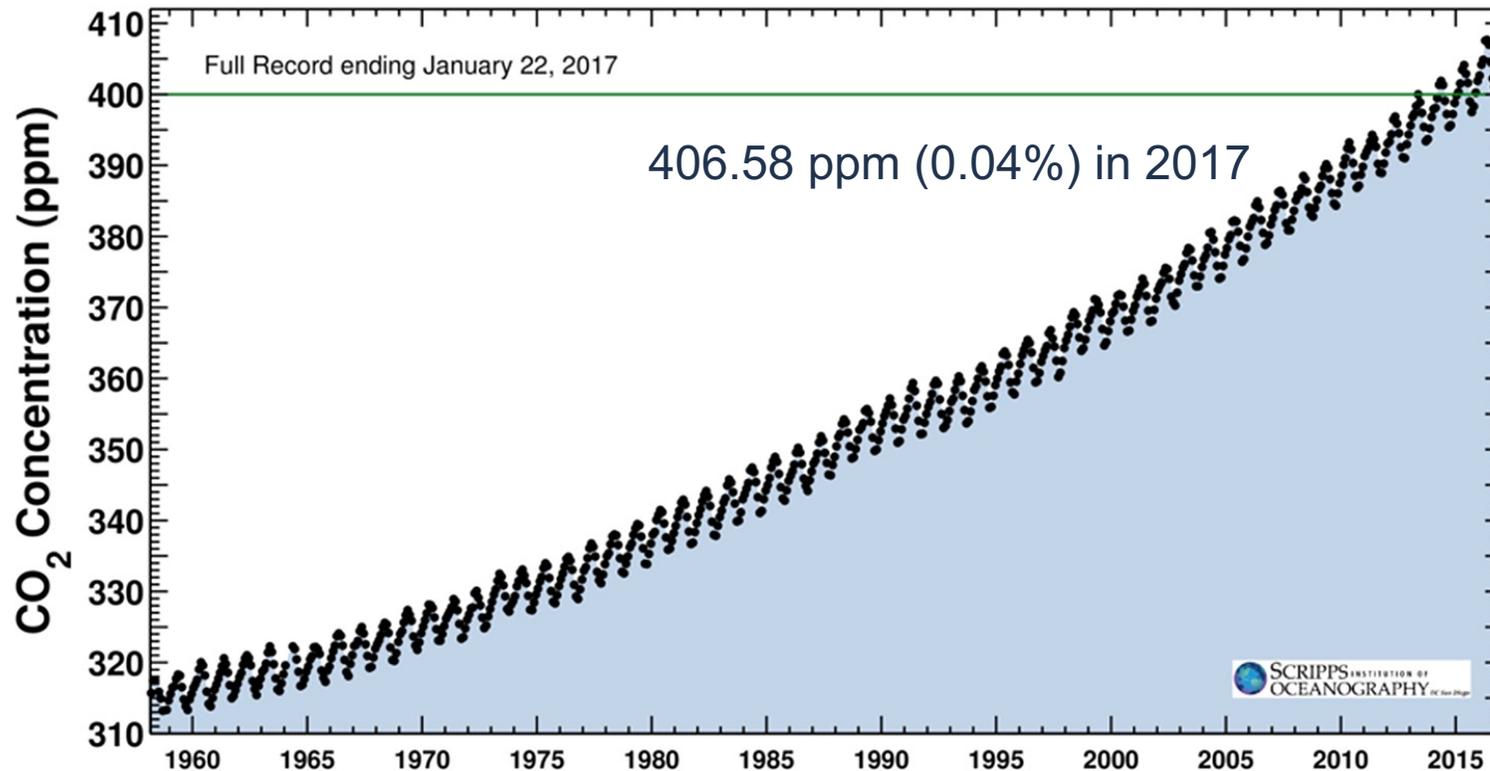
Prof. Mike McGuirk

Prof. Ryan Richards

Department of Chemistry

Colorado School of Mines

# Atmospheric [CO<sub>2</sub>], a GHG, is on the Rise



- GHGs absorb outgoing infrared radiation, warming the atmosphere

Image adapted from: <https://e360.yale.edu/features/how-the-world-passed-a-carbon-threshold-400ppm-and-why-it-matters>

# Need the Big Picture to Truly Appreciate our Impact

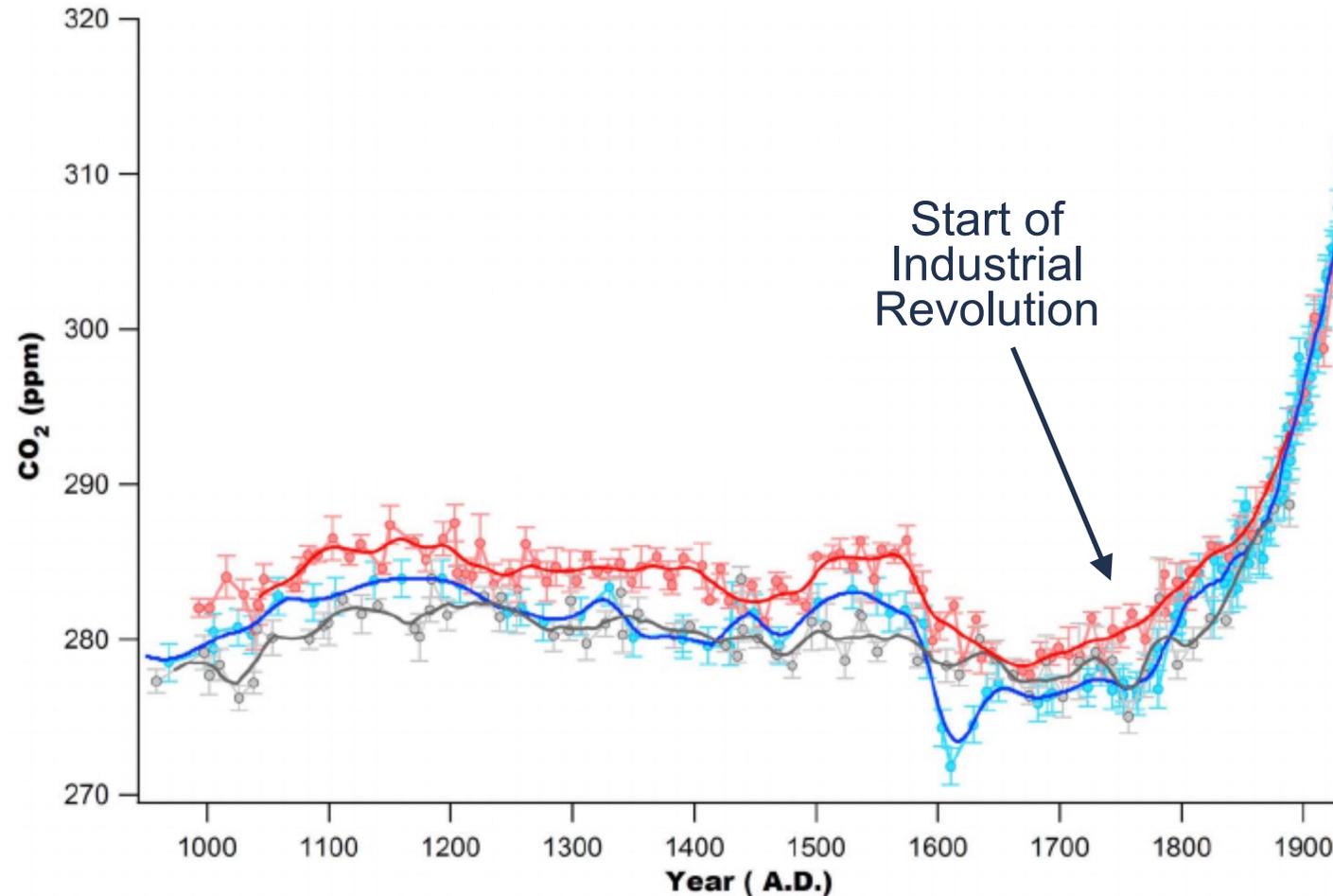


Image adapted from: Ahn, J.; Brook, E. J.; Mitchell, L.; Rosen, J.; McConnell, J. R.; Taylor, K.; Etheridge, D.; Rubino, M. *Global Biogeochem. Cycles* **2012**, 26

# Part of the Solution: Carbon Capture, Utilization, and Storage

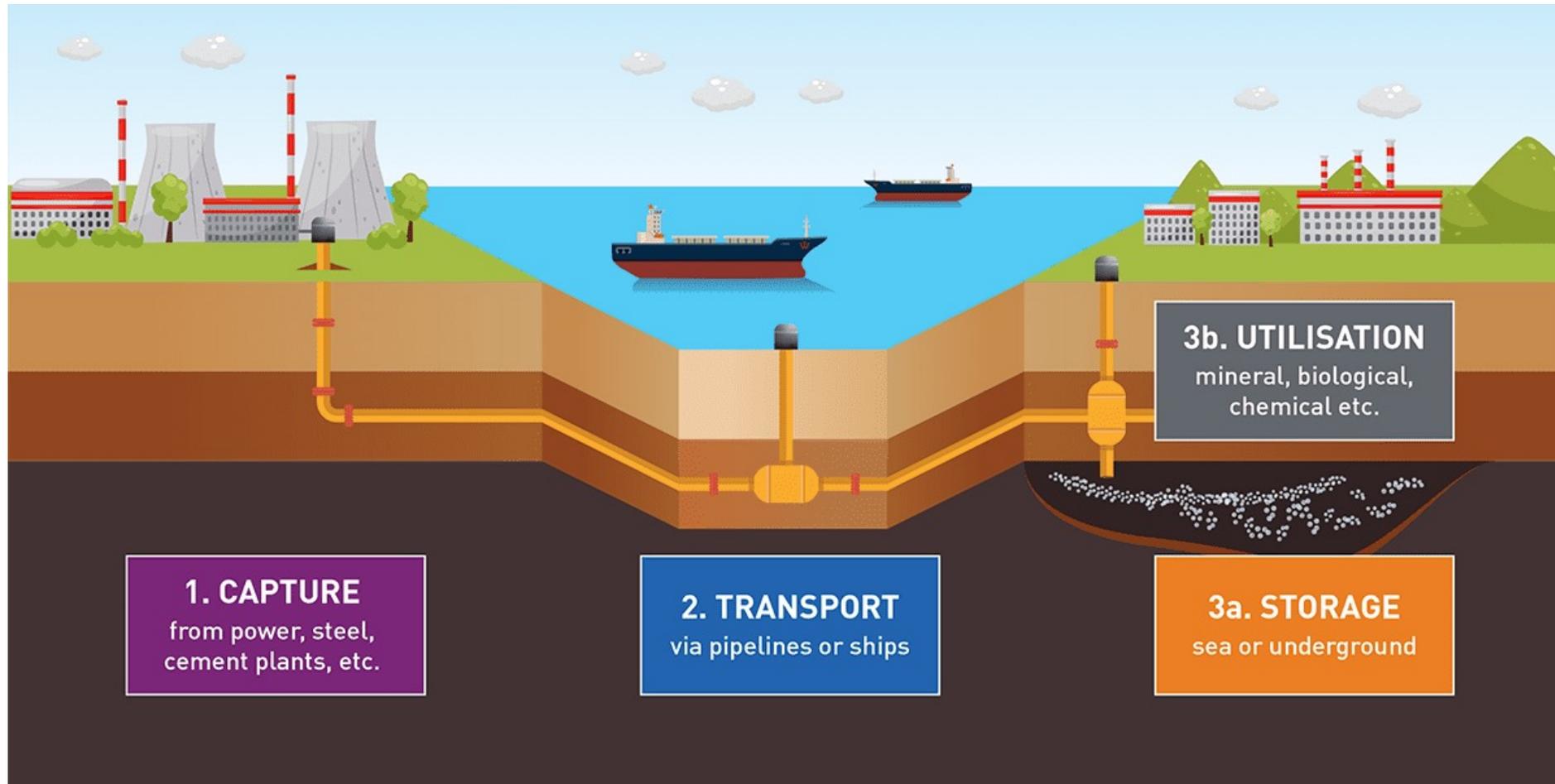
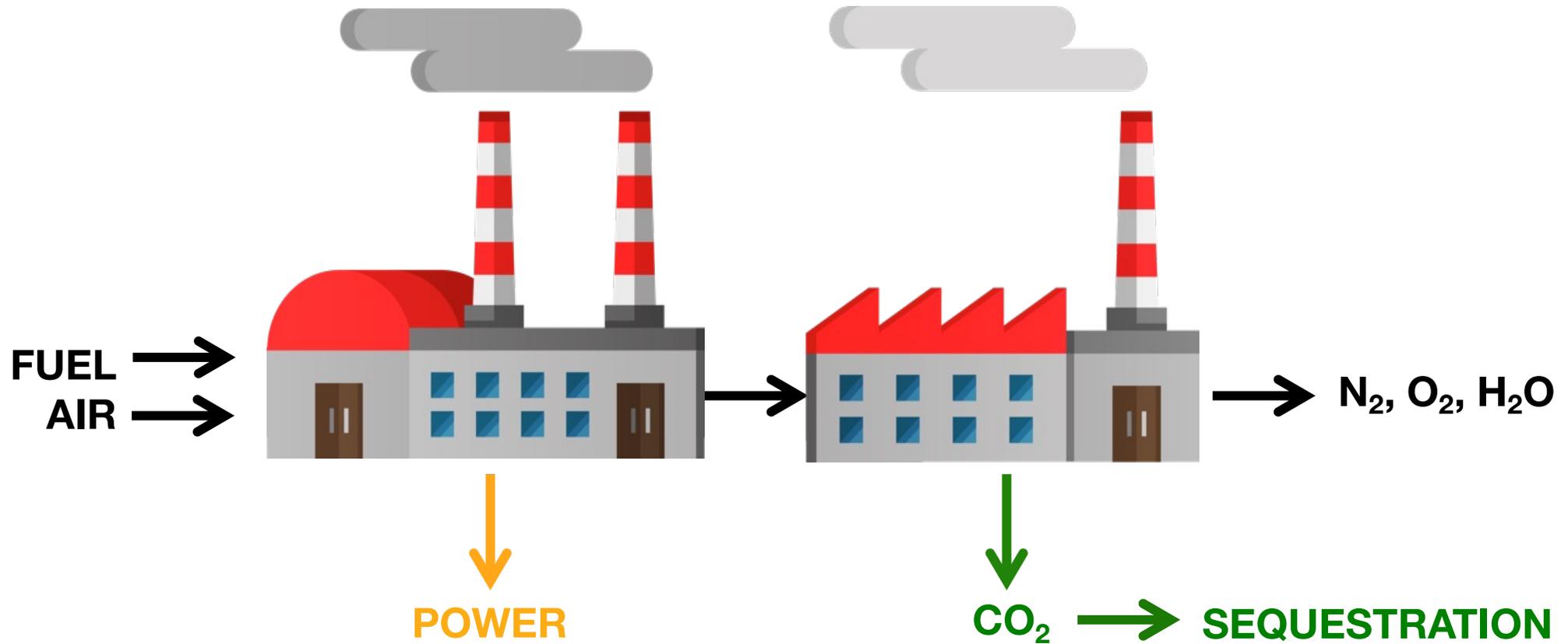


Image adapted from: <https://www.iogp.org/blog/news/developing-low-carbon-technologies/>

# Post-Combustion Capture from a Point-Source



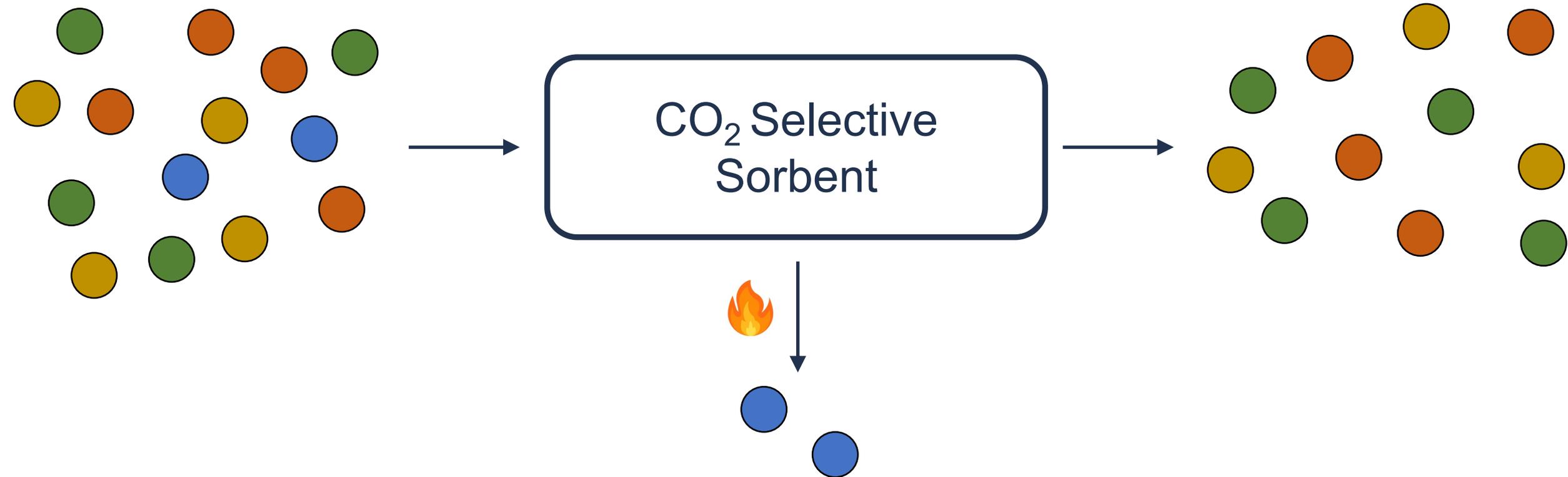
- 70% of cost of CCUS is associated with selective capture of CO<sub>2</sub>

# Capture: Selective Removal of CO<sub>2</sub> from Gas Mixtures



- **Grand Scientific Challenge:** Need to selectively remove a minority component from a complex mixture, **BUT** also release the gas on demand without massive energy penalties

# Capture: Selective Removal of CO<sub>2</sub> from Gas Mixtures



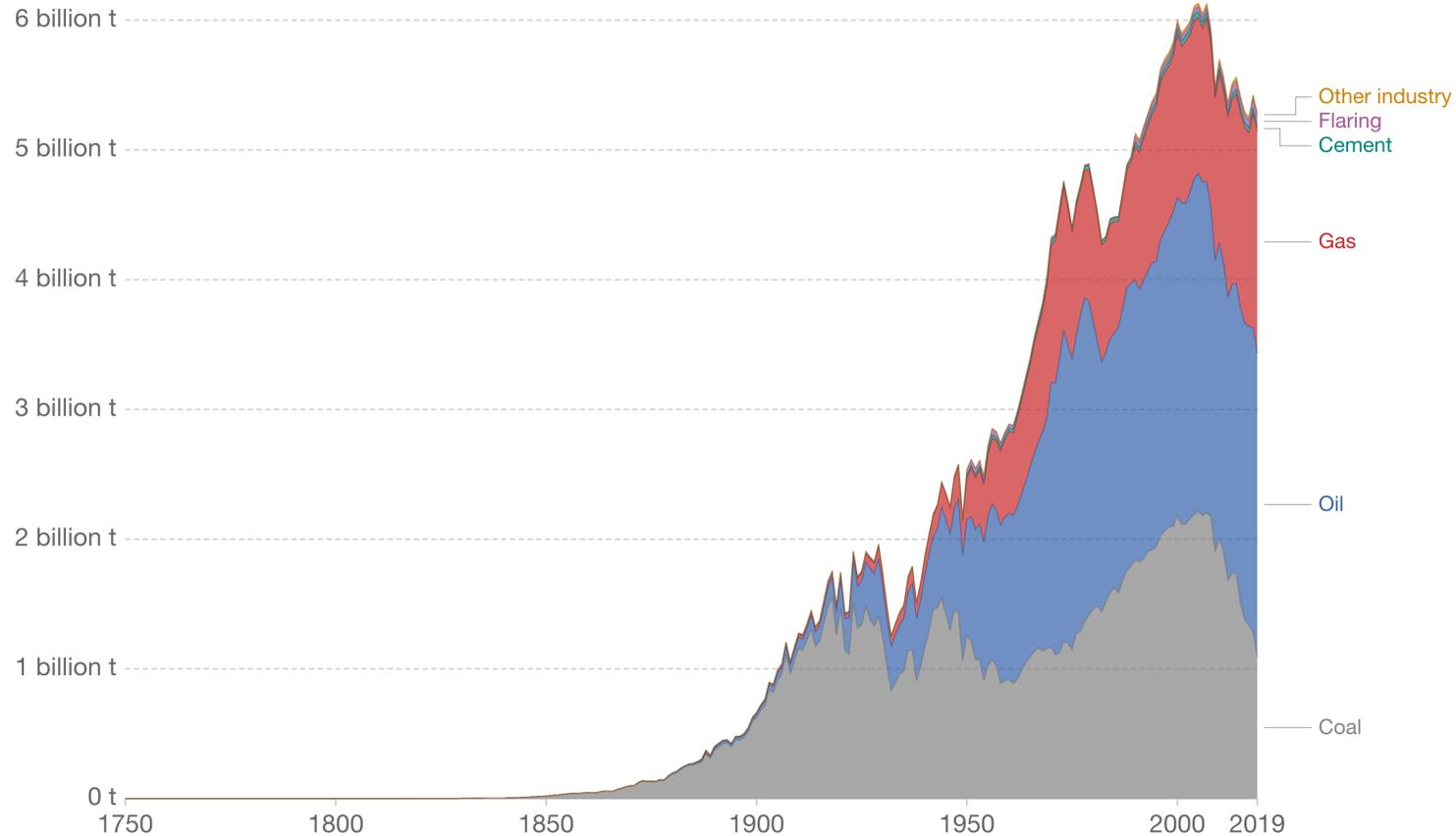
- **Grand Scientific Challenge:** Need to selectively remove a minority component from a complex mixture, **BUT** also release the gas on demand without massive energy penalties

# Diverse Sources of Anthropogenic CO<sub>2</sub> Emissions

## CO<sub>2</sub> emissions by fuel type, United States

Annual carbon dioxide (CO<sub>2</sub>) emissions from different fuel types, measured in tonnes per year.

Our World  
in Data



Source: Global Carbon Project

[OurWorldInData.org/co2-and-other-greenhouse-gas-emissions/](https://OurWorldInData.org/co2-and-other-greenhouse-gas-emissions/) • CC BY

# Diverse Targets for CO<sub>2</sub> Capture

## *Iron, Steel and Cement Production*



~20% CO<sub>2</sub>  
Target: ≤ 20 mbar

## *Post-Combustion Natural Gas and Coal Flue*



**NG:** 3-5% CO<sub>2</sub>  
Target: ≤ 3-5 mbar  
**Coal:** 12-14% CO<sub>2</sub>  
Target: ≤ 12-14 mbar

## *Direct Air Capture*

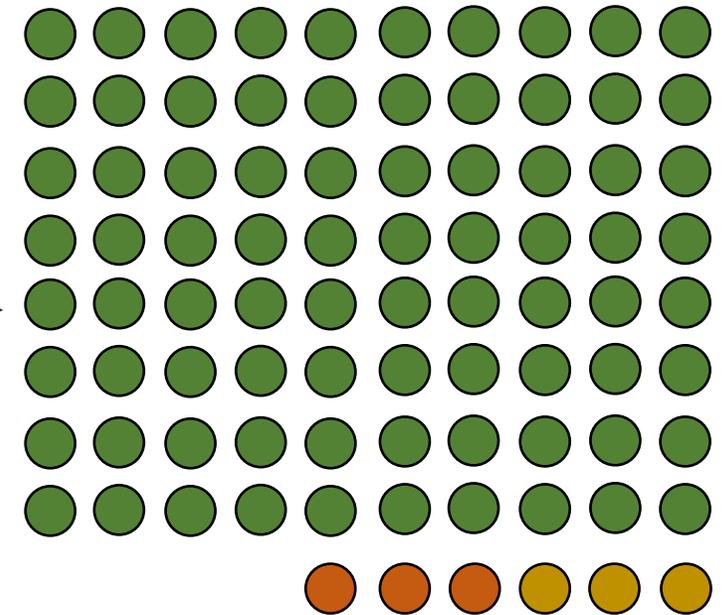
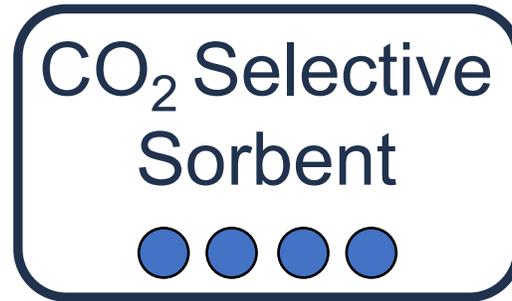
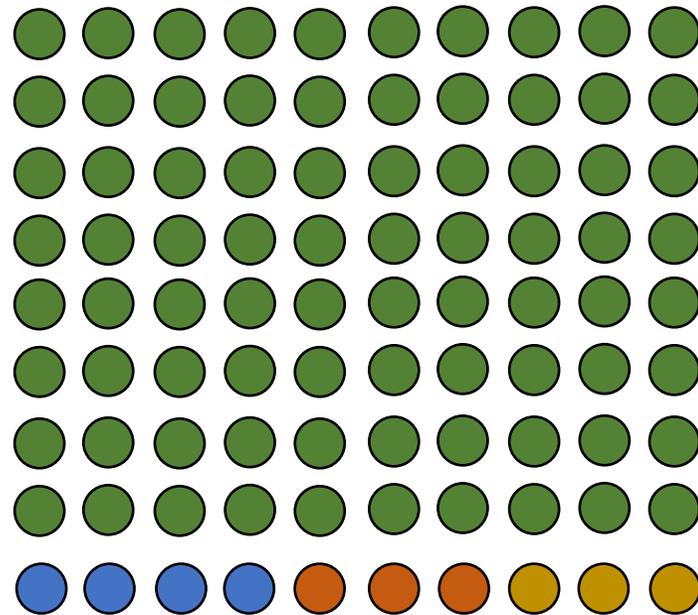
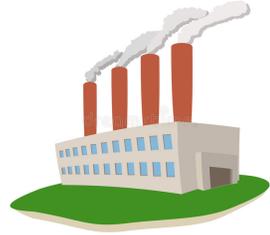


~0.040% CO<sub>2</sub>  
Target: ≤ 0.04 mbar

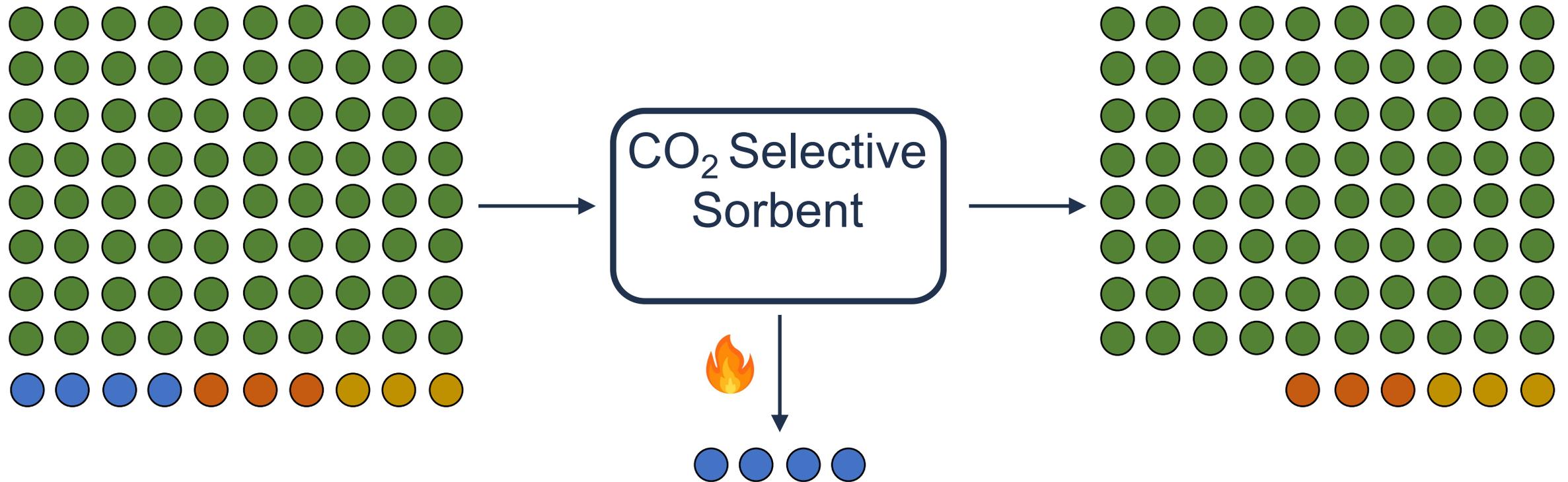
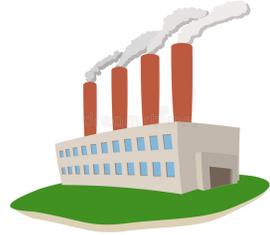
- Want ≥ 90% reduction in [CO<sub>2</sub>] from a given source

Herron, S.; Zoelle, A.; Summers, M. "Cost of Capturing CO<sub>2</sub> From Industrial Sources", NETL, 2014

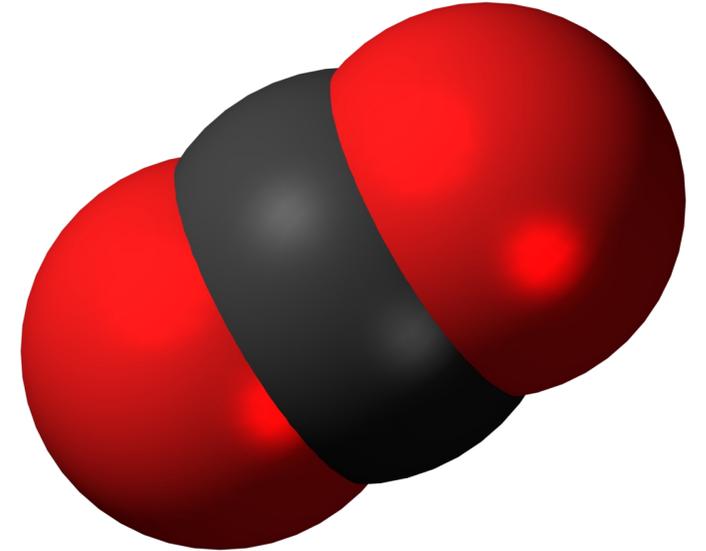
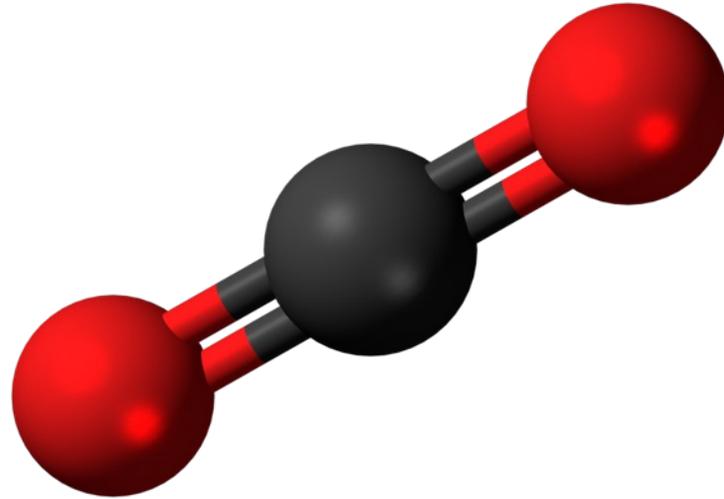
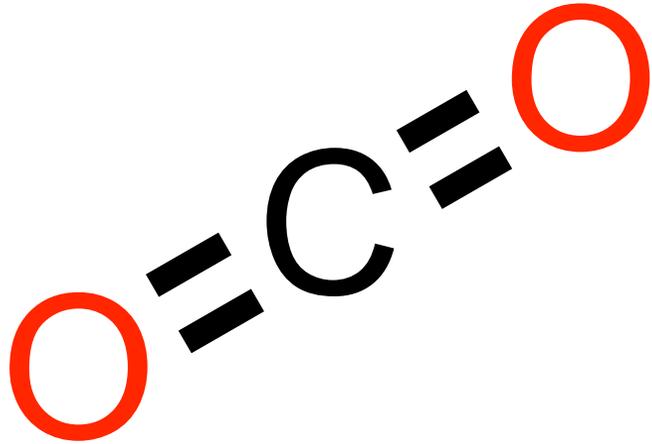
# A Representative Picture of Selectivity Required



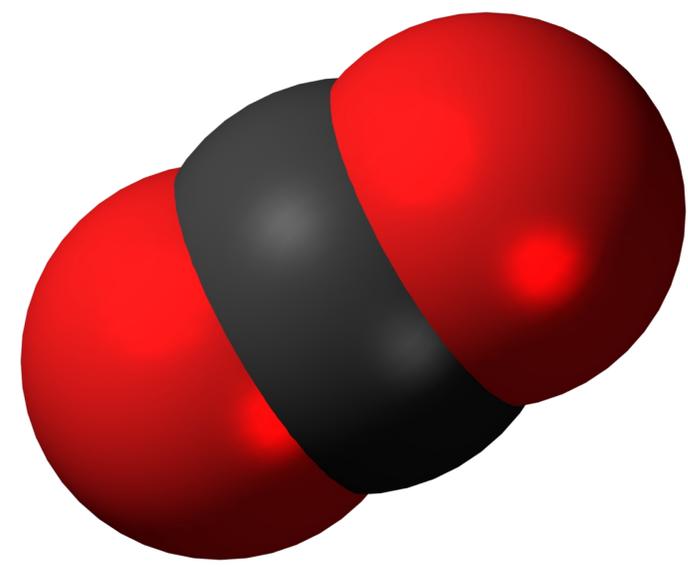
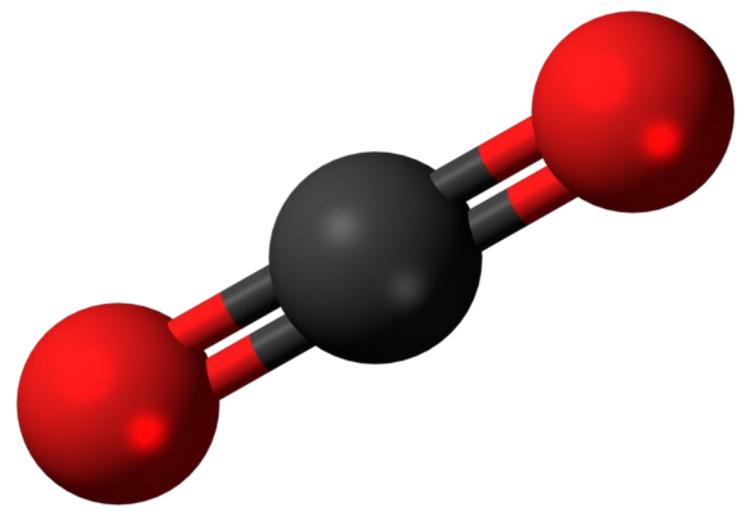
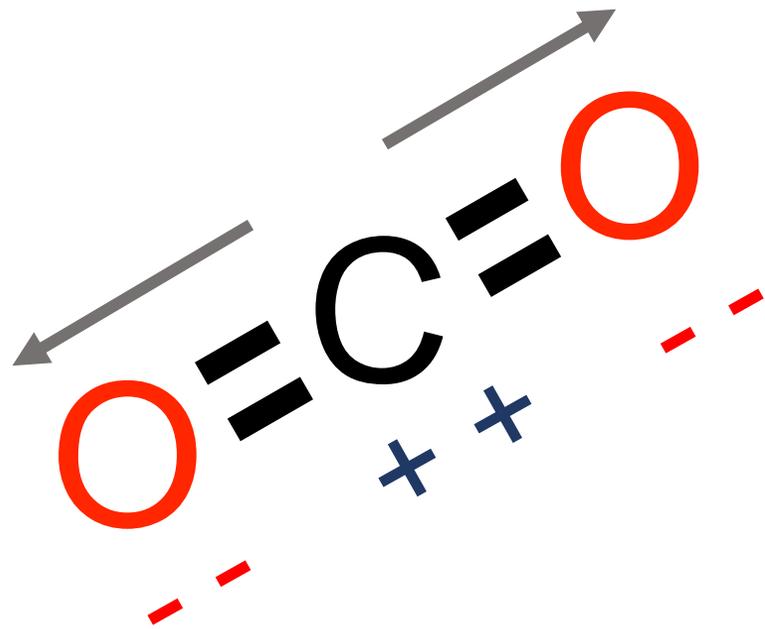
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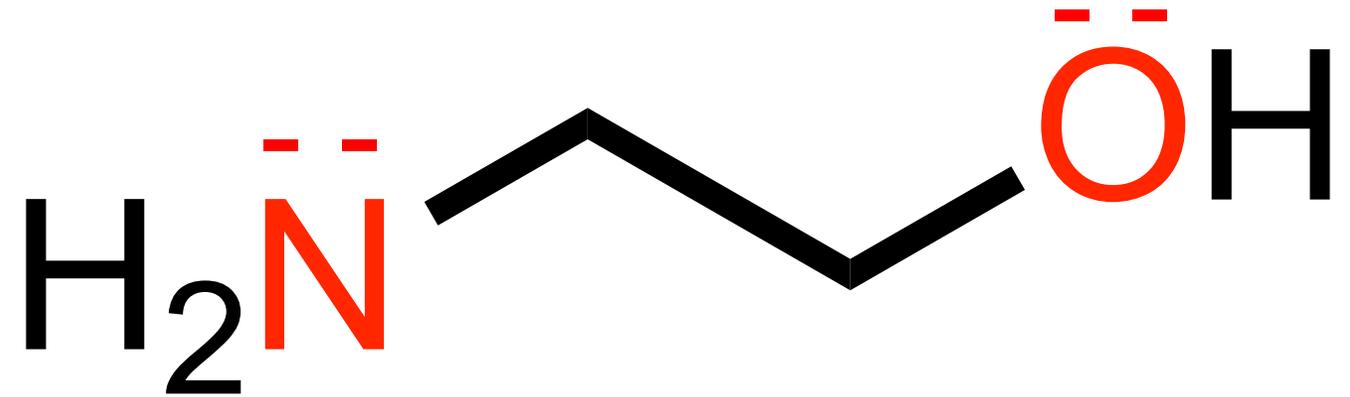
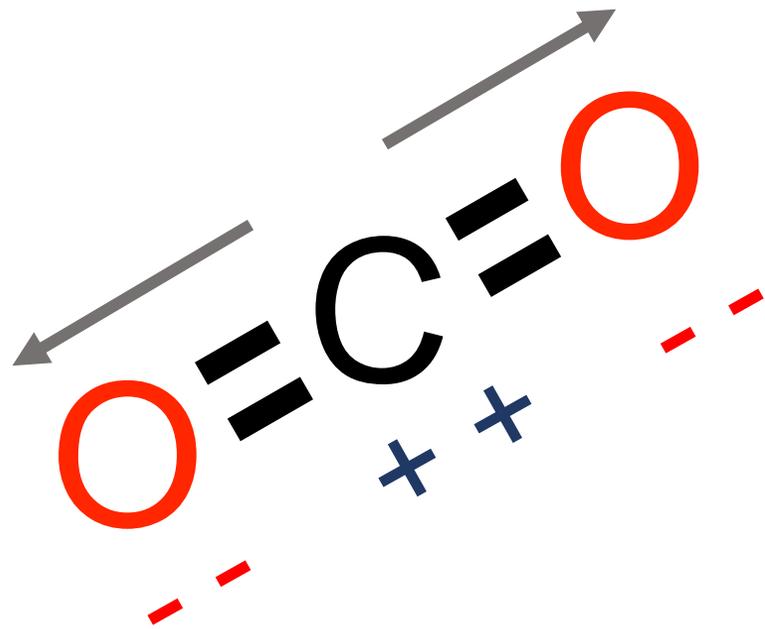
# We Are Lucky That CO<sub>2</sub> is a Reactive Molecule



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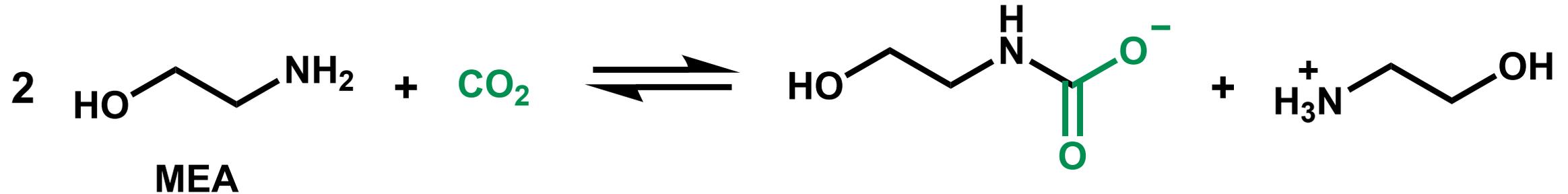


# We Are Lucky That CO<sub>2</sub> is a Reactive Molecule



# Aqueous Amine-Based Scrubbing of CO<sub>2</sub>

In use since the **1930s**



- High selectivity for CO<sub>2</sub>
- Operates in presence of water

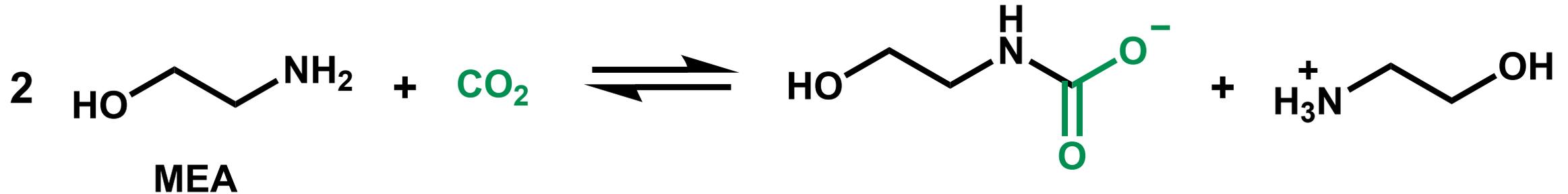
Rochelle, G. T. *Science* **2009**, 325, 1652

Sumida, Rogow, Mason, McDonald, Bloch, Herm, Bae, Long. *Chem. Rev.* **2012**, 112, 724

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In use since the **1930s**



- High selectivity for CO<sub>2</sub>
- Operates in presence of water

- Low working capacity (3–5%)
- Thermally degradable
- Corrosive
- High regeneration energy penalty (35%)
  - Huge heat capacity of water

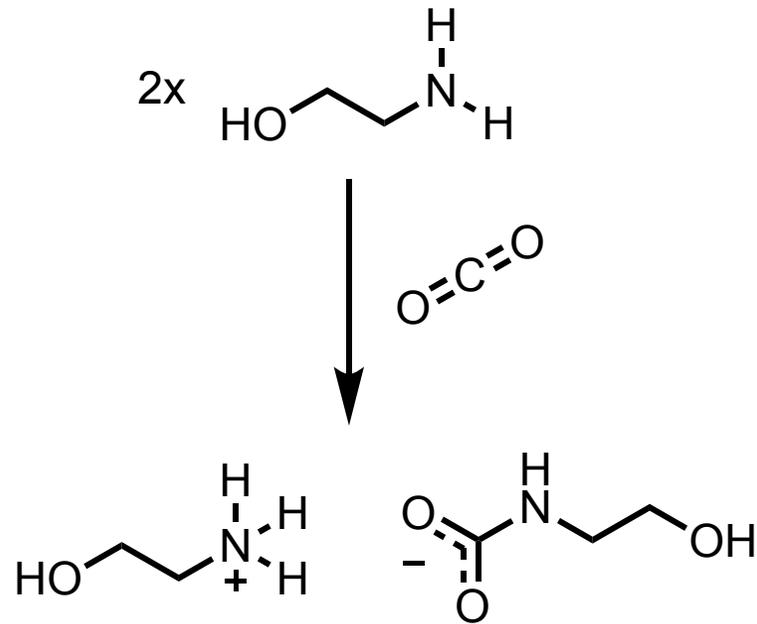
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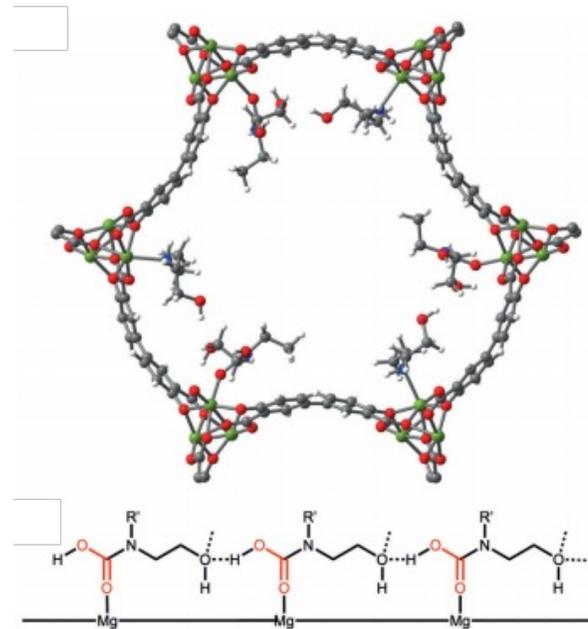
Wang, Lawal, Stephenson, Sidders, Ramshaw, C. *Chem. Eng. Res. Des.* **2011**, 89, 1609

# Moving to Solid Adsorbents for Chemical CO<sub>2</sub> Capture

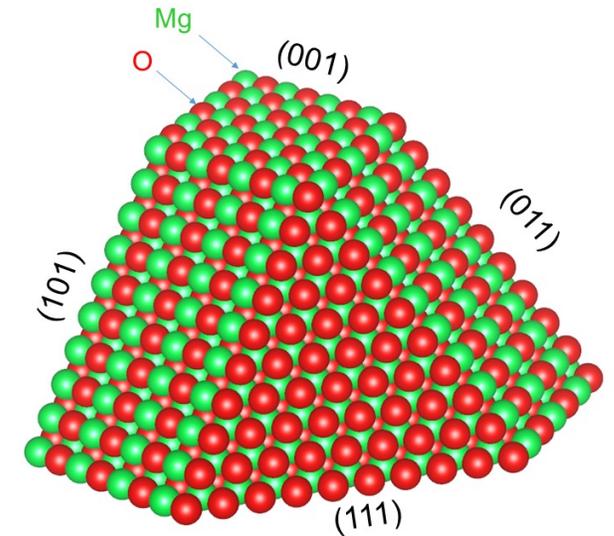
*Aqueous Amines*



*Porous Frameworks*

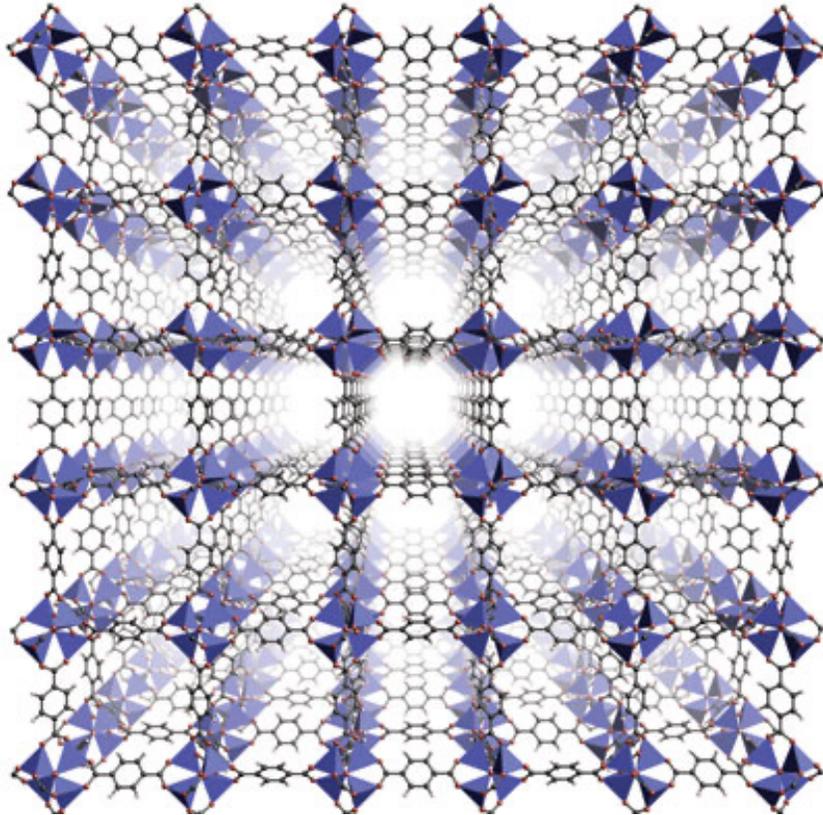


*Faceted Metal Oxides*



<https://carbonengineering.com/our-technology/>  
Mao, V.; Milner, P. J.; Lee, J.-H.; Forse, A. C.; Kim, E.; Siegelman, R. L.; McGuirk, C. M.; Porter-Zasada, L.; Neaton, J. B.; Reimer, J. A.; Long, J. R.  
*Angew. Chem. Int. Ed.* **2020**, 59, 19468– 19477

# Metal–Organic Frameworks: Nanoscale Synthetic Sponges



MOF-5

BET surface areas up to 7100 m<sup>2</sup>/g

Density as low as 0.13 g/cm<sup>3</sup>

Tunable pore sizes up to 10 nm

Channels connected in 1-, 2-, or 3-D

Internal surface can be functionalized

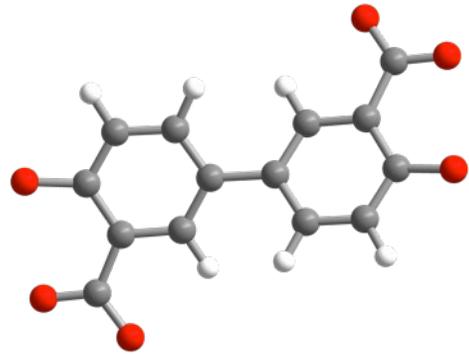
Yaghi et al. *Nature* **2003**, 423, 705

Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, 43, 2334

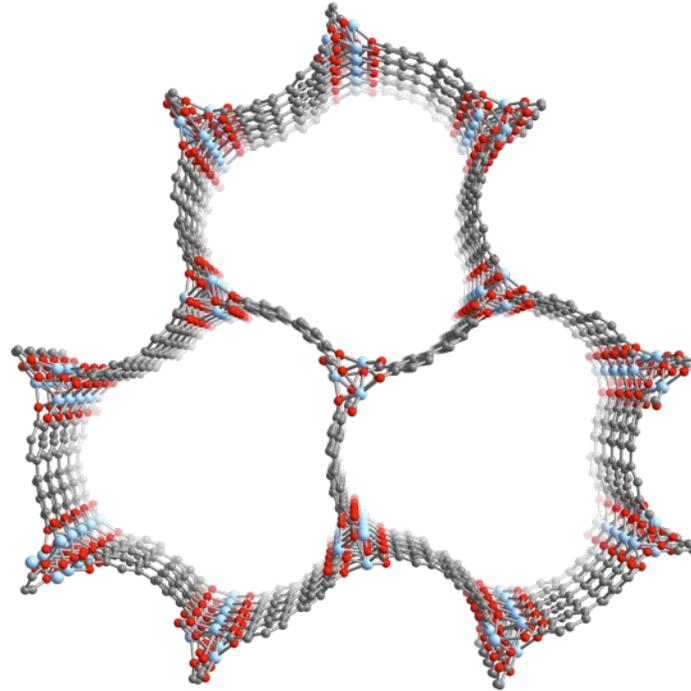
Férey *Chem. Soc. Rev.* **2008**, 37, 191

# MOFs are Customizable for CO<sub>2</sub> Capture

Organic Linker

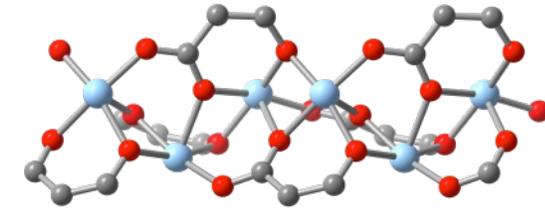


- High surface areas
- High tunability
- High working capacities



Zn<sub>2</sub>(dobpdc)

Inorganic Unit

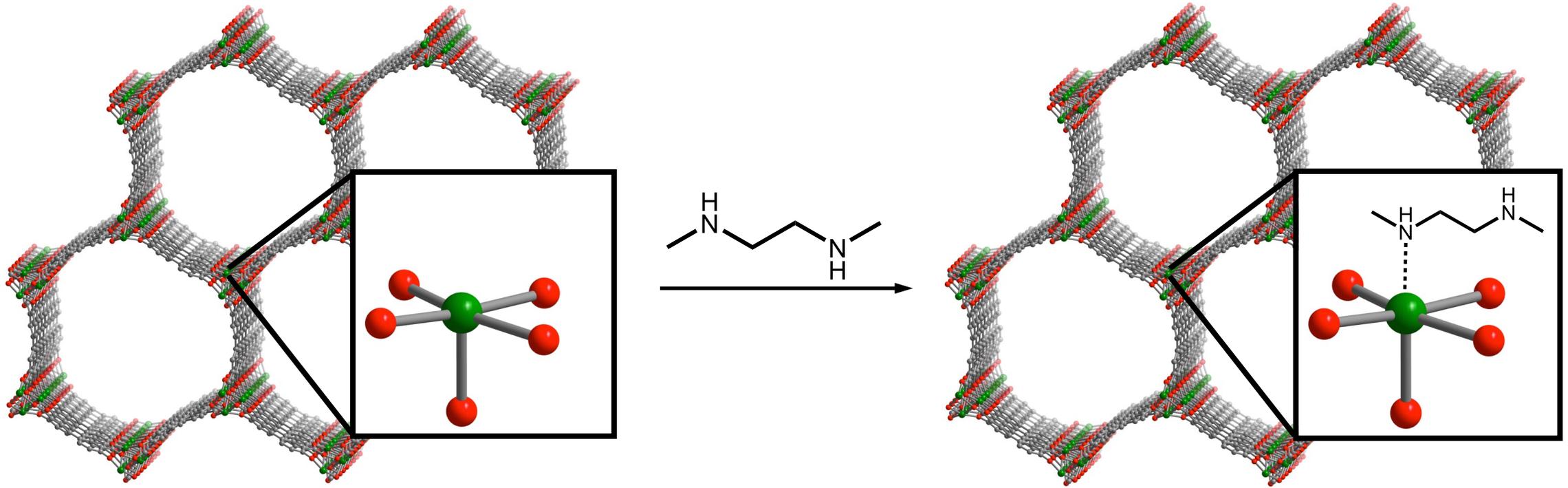


- Lower CO<sub>2</sub> selectivity
- **Generally do not work in the presence of water**

Sumida, Rogow, Mason, McDonald, Bloch, Herm, Bae, Long. *Chem. Rev.* **2012**, 112, 724

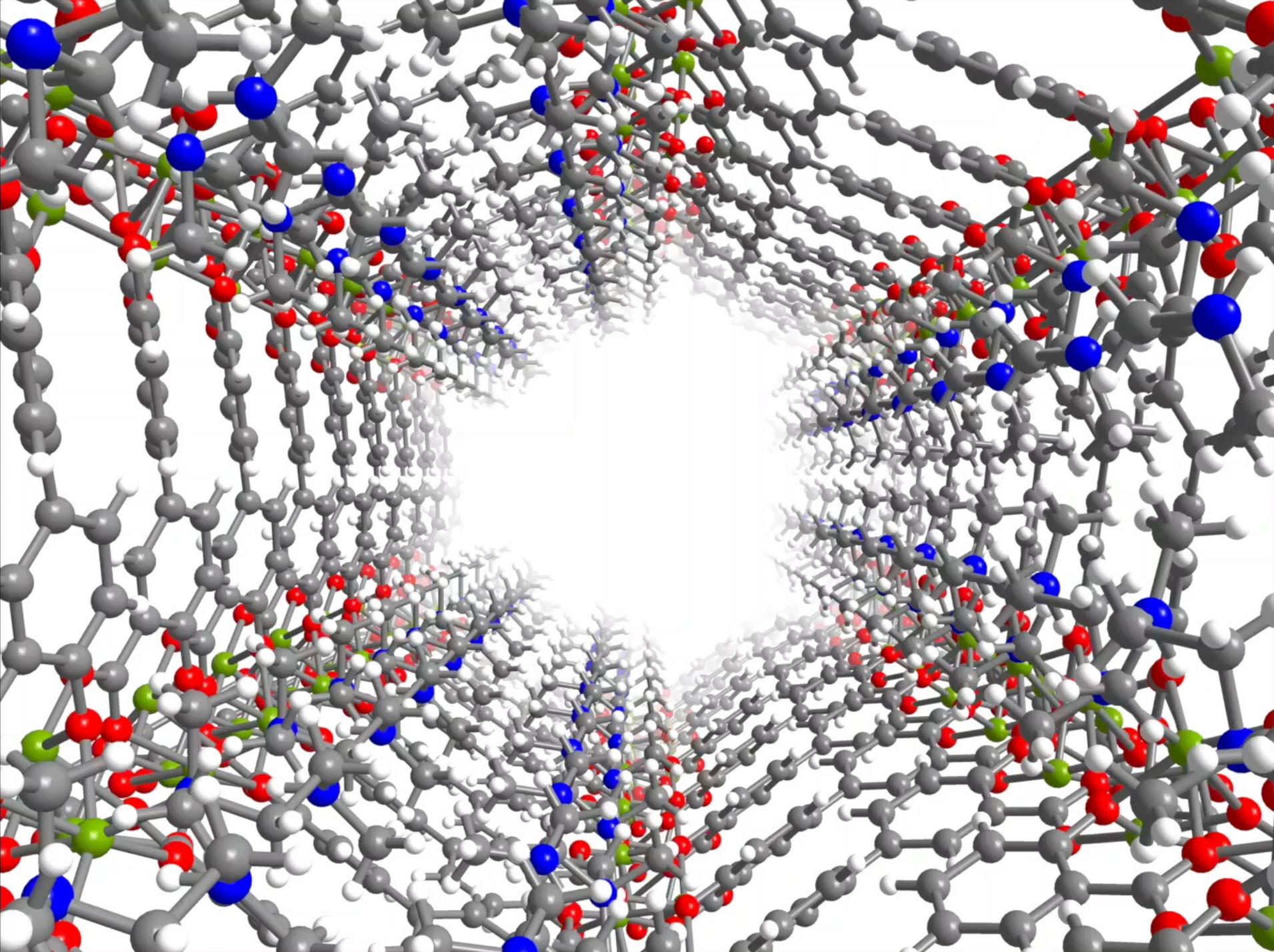
Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhowan, Long. *J. Am. Chem. Soc.* **2017**, 139, 10526

# Amine-Chemistry Can be Incorporated into MOF Adsorbents

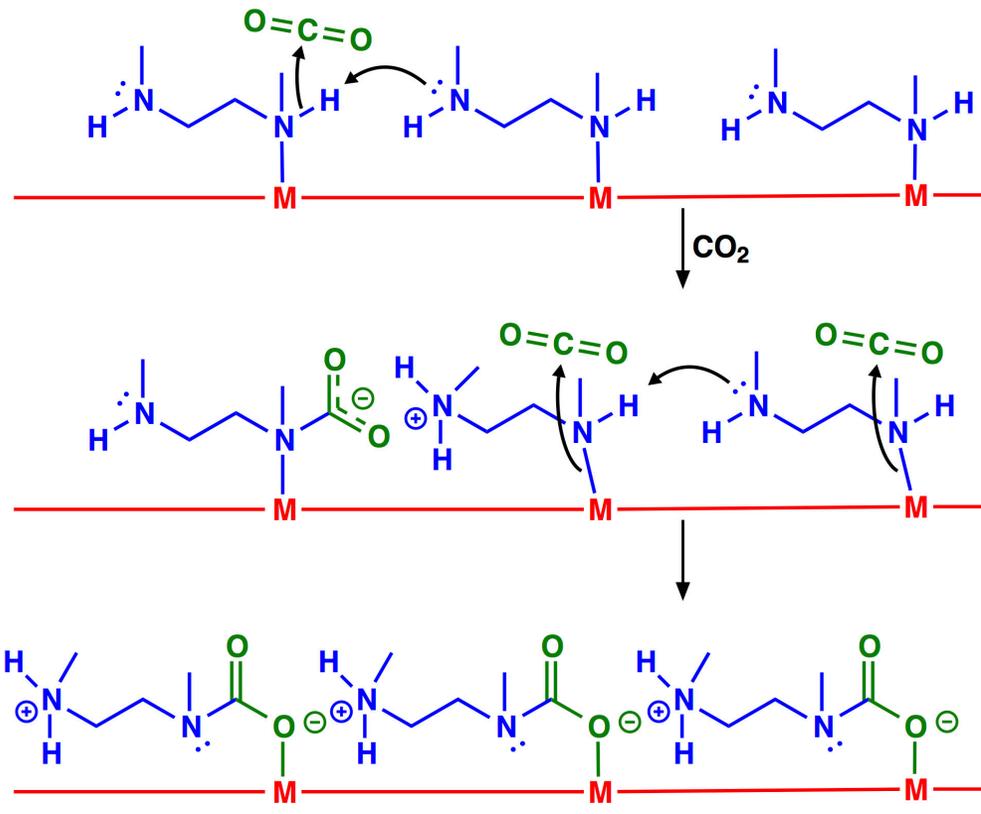
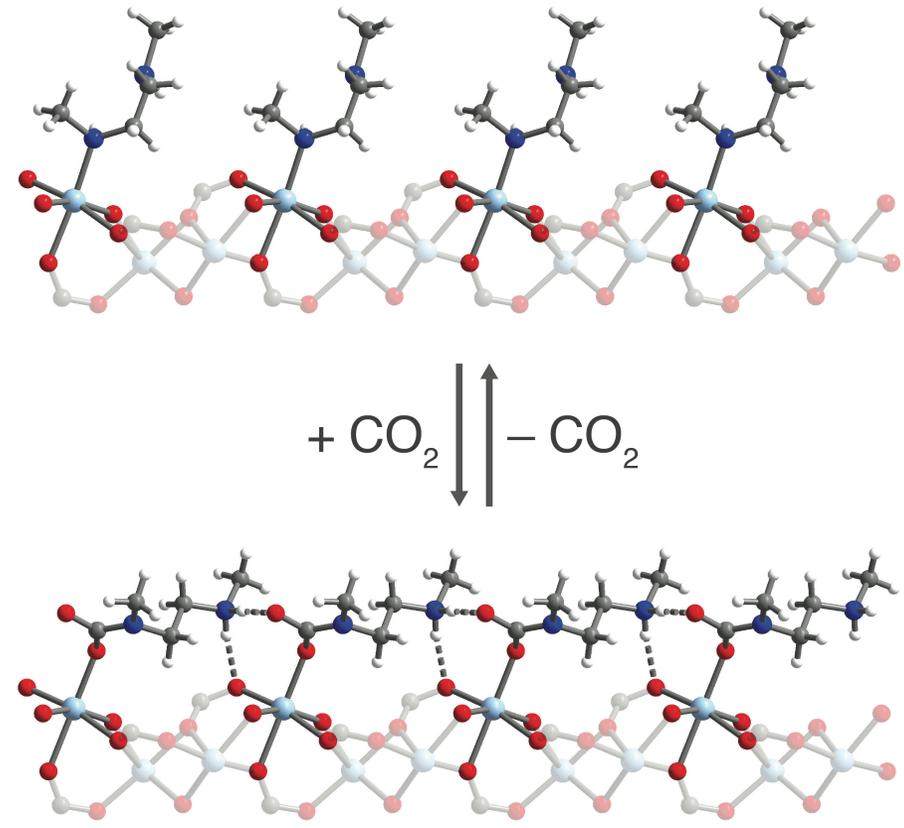


- This gives the combined benefit of solid adsorbent with low heat capacity and the chemical adsorption of amines

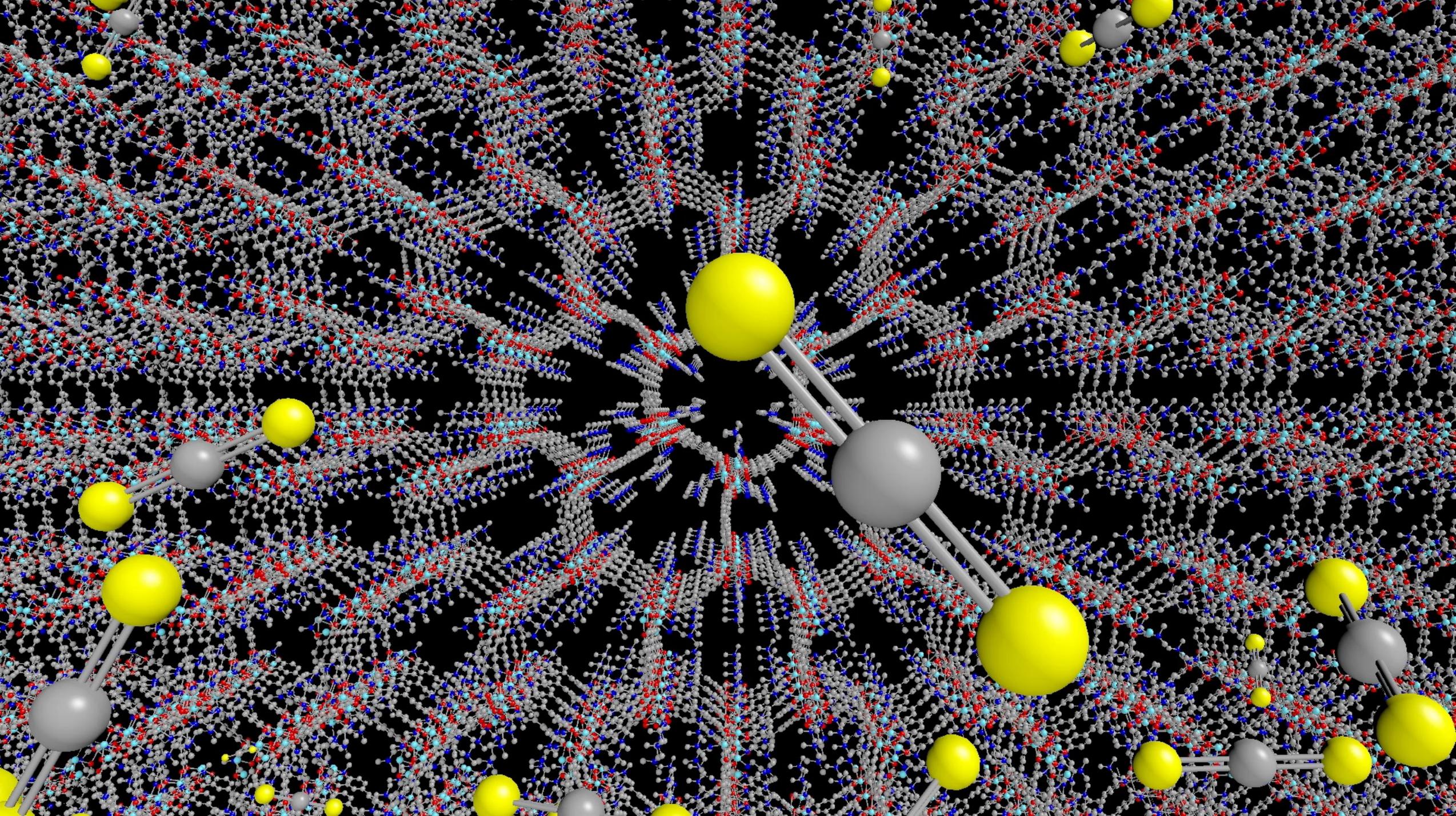
McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303



# Same Chemistry as Aqueous Amines, but on a Solid

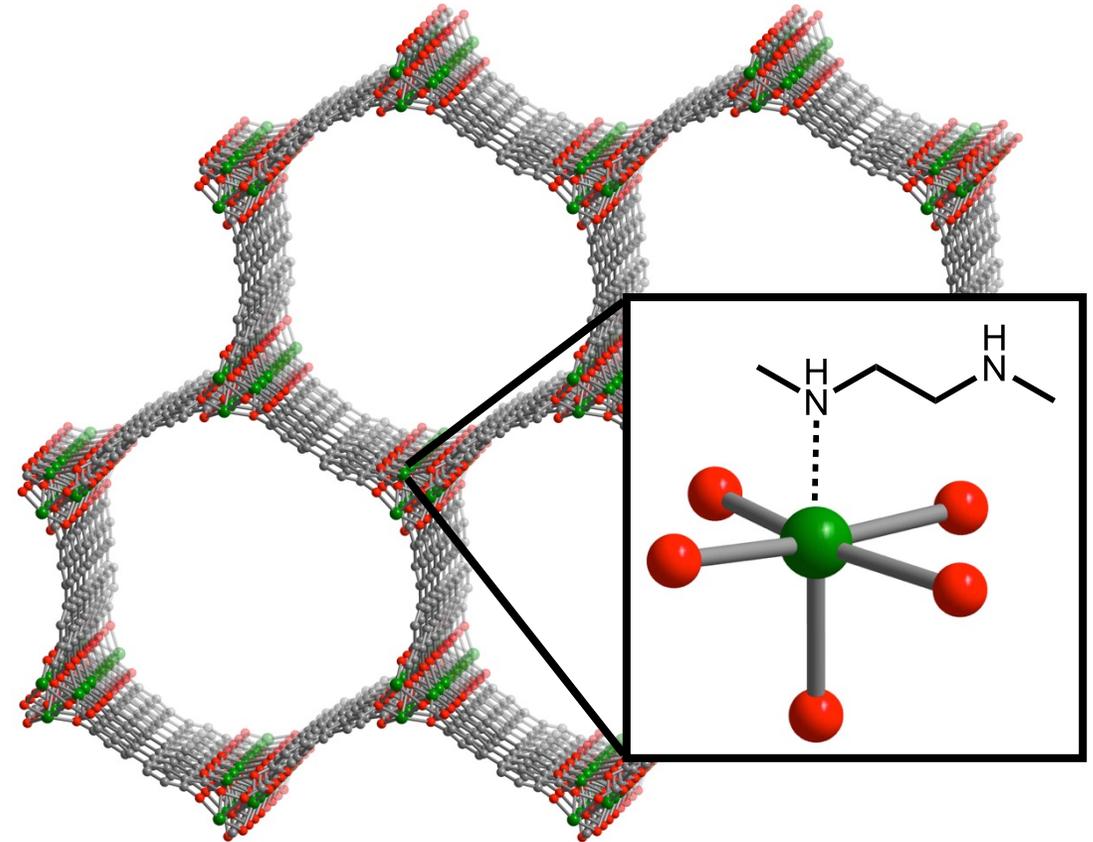


Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhowan, Long *J. Am. Chem. Soc.* **2017**, *139*, 10526  
 McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* **2015**, *519*, 303



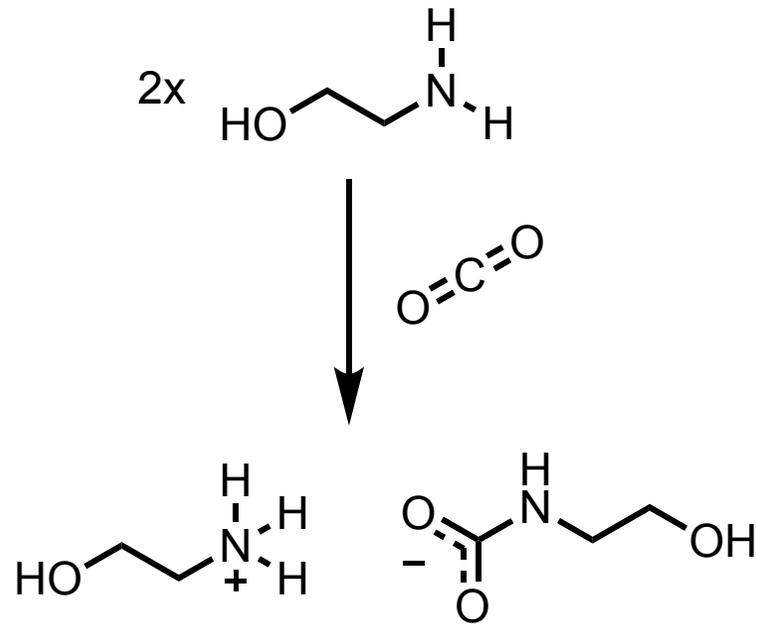
# Metal–Organic Frameworks for CO<sub>2</sub> Capture

- Low Regeneration Energy
- Tunability for Different Point Sources
- CO<sub>2</sub> Selectivity from Mixed Streams
- High capacities
- Questions around long-term use
- Production Cost
- But both are getting better everyday!!

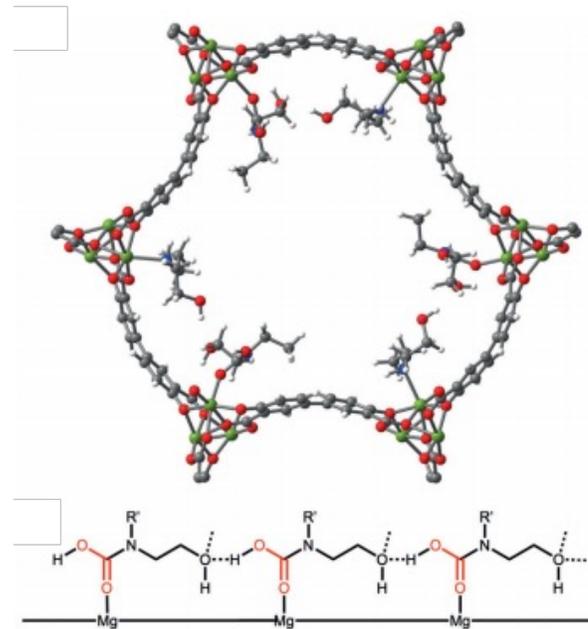


# Using Earth-Abundent Minerals for CO<sub>2</sub> Capture

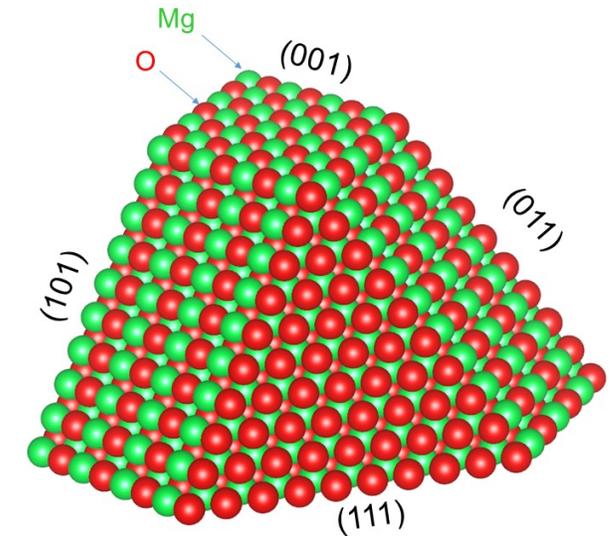
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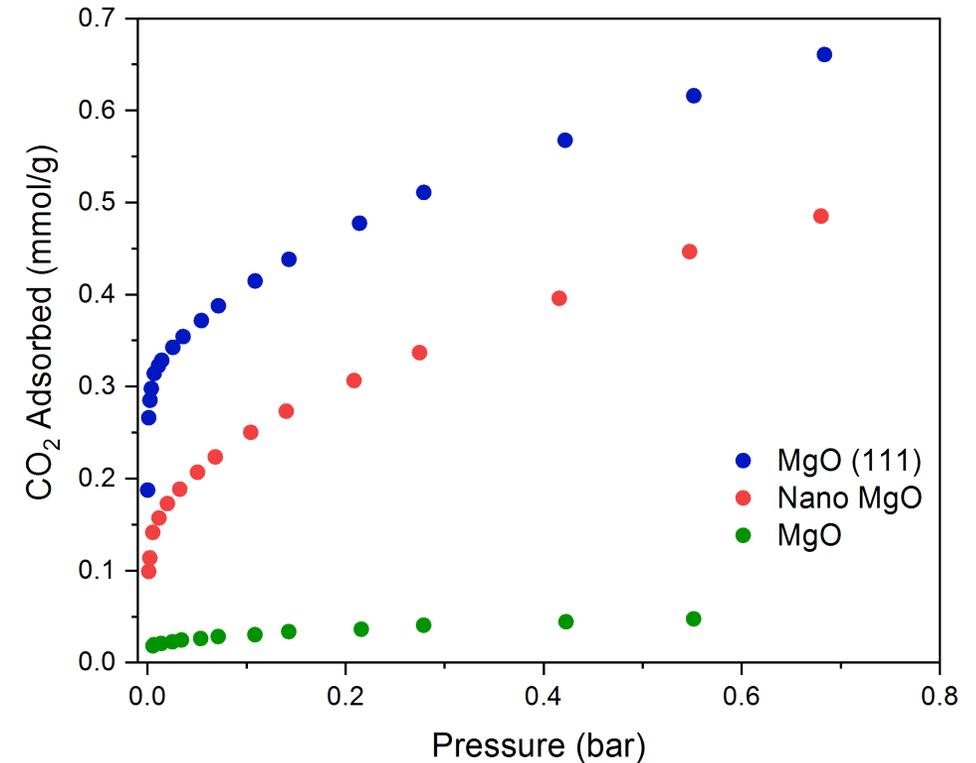
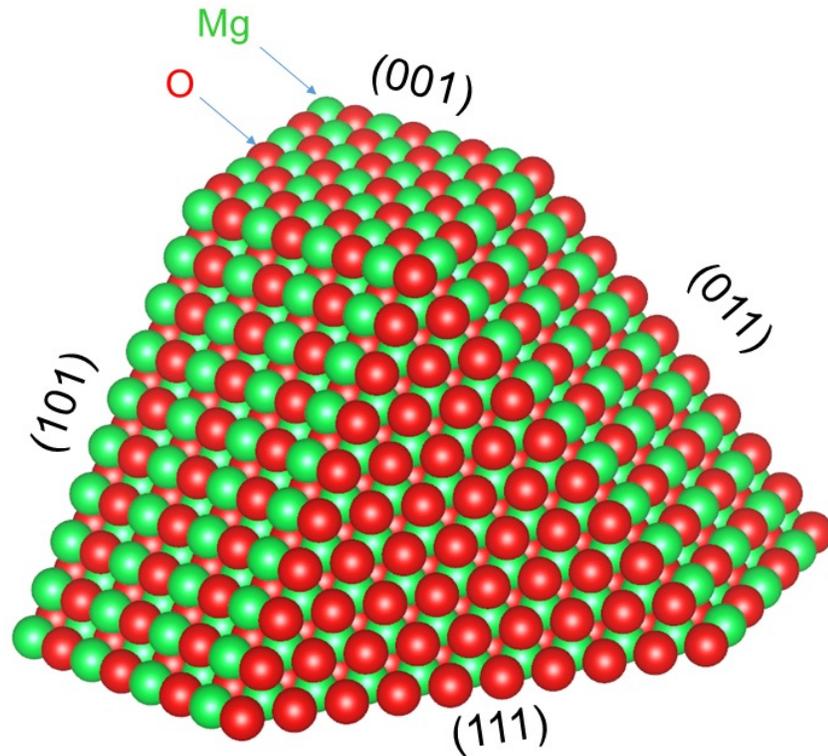


*Faceted Metal Oxides*



<https://carbonengineering.com/our-technology/>  
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*Angew. Chem. Int. Ed.* **2020**, 59, 19468– 19477

# We Can Turn Rocks into Potent CO<sub>2</sub> Capture Adsorbents



- Bulk MgO shows very poor CO<sub>2</sub> adsorption
- Faceted MgO shows very enhanced CO<sub>2</sub> adsorption, particularly at low partial pressures

Mutch, G. A.; Shulda, S.; McCue, A. J.; Menart, M. J.; Ciobanu, C. V.; Ngo, C.; Anderson, J. A.; Richards, R. M.; Vega-Maza, D. *J. Am. Chem. Soc.* **2018**, *140*, 4736–4742

# How Synthetic MgO Stacks Up for Point Source Capture

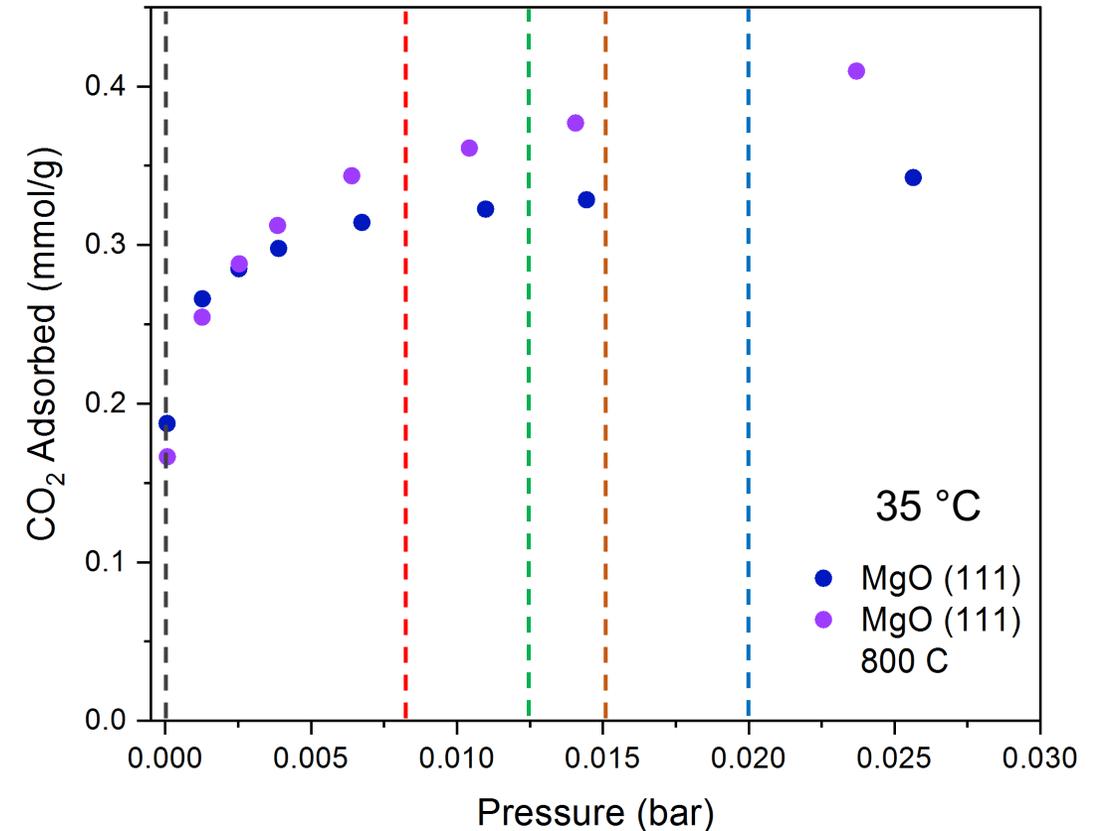
*Direct Air Capture*  
Target:  $\leq 0.04$  mbar

*Natural Gas Flue*  
Target:  $\leq 8-10$  mbar

*Coal Flue*  
Target:  $\leq 12-14$  mbar

*Tailpipe*  
Target:  $\leq 14-16$  mbar

*Cement/Iron/Steel*  
Target:  $\leq 20$  mbar

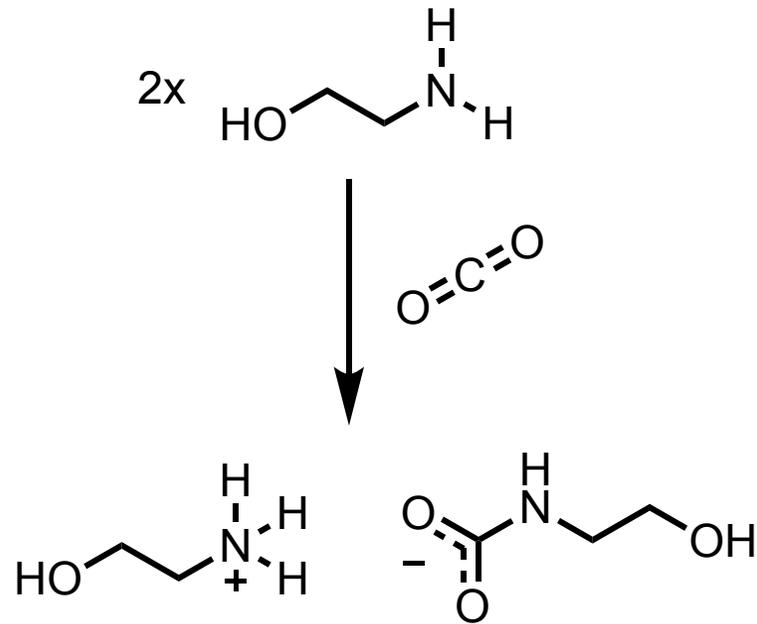


- Targets for **90 %** capture from respective post-combustion sources

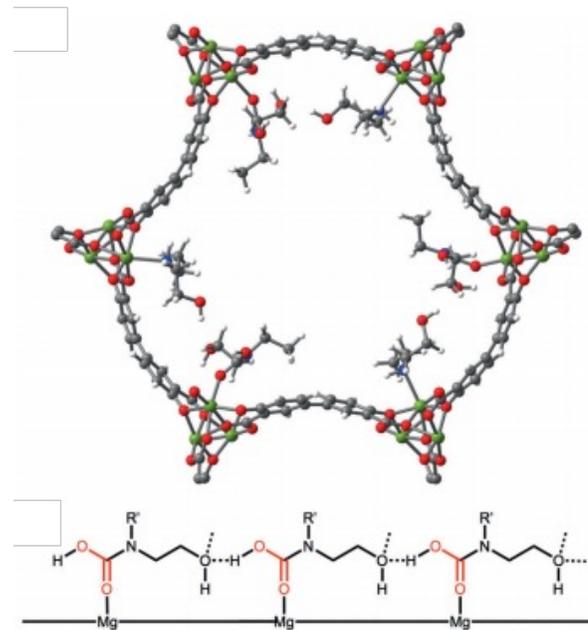
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Herron, S.; Zoelle, A.; Summers, M. "Cost of Capturing CO<sub>2</sub> From Industrial Sources", NETL, **2014**

# A Diverse Problem Requires Diverse Chemical Solutions

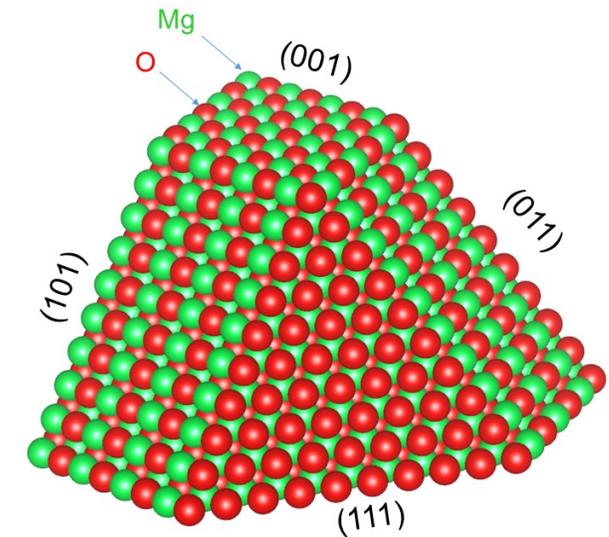
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