

## Organic–Inorganic Hybrid Sorbents (Amine-containing sorbents)

### Concept:

Oldest and most widely used CO<sub>2</sub> capture method (amines in aqueous/solid form).

Supported amine sorbents react chemically with CO<sub>2</sub>, forming strong bonds → effective even at very low CO<sub>2</sub> levels (e.g., ambient air).

Higher heat of sorption and selectivity compared to physical sorbents.

### Reaction Mechanism:

Under dry (anhydrous) conditions: 1 CO<sub>2</sub> + 2 amine groups → ammonium carbamate (CO<sub>2</sub>/N ratio = 0.5).

With moisture present: formation of ammonium carbonate/bicarbonate.

Amine efficiency = moles CO<sub>2</sub> captured per mole of nitrogen.

### Performance Factors:

In microporous sorbents → pore size strongly affects uptake.

In mesoporous supports → CO<sub>2</sub> uptake mainly depends on amine loading, less on surface area.

Amine-functionalized mesostructured materials (e.g., SBA-15 silica, polymers) show high CO<sub>2</sub> capacity at low concentrations (<1%).

### Examples of Hybrid Materials:

PEI-SBA-15, DMA-SBA-15, HAS SBA-15 compared with PL hybrids.

PL hybrids showed higher adsorption efficiency at both 10% CO<sub>2</sub> (flue gas) and 400 ppm CO<sub>2</sub> (air).

Stable under multiple temperature swing cycles (adsorption at ~25 °C, desorption at ~110 °C).

### Other Supports:

Activated carbon, ion-exchange resins, and polymers functionalized with amines.

Carbon black functionalized with quaternary ammonium hydroxide groups for humidity-swing CO<sub>2</sub> capture.

### Advantages:

High selectivity and uptake at very low CO<sub>2</sub> partial pressures.

Stable under multicycle adsorption–desorption.

Well-suited for DAC applications.

### Drawbacks:

Possible amine emissions and waste disposal issues.

Support material adds extra mass → increases cost and regeneration energy.

Long-term degradation of amines can reduce

efficiency.....Utilizing MOFs and their Tunability for CO<sub>2</sub> Capture

### MOFs (Metal–Organic Frameworks):

Crystalline materials made of metal nodes + organic linkers, with extremely high surface area (1 g ≈ 1.5 football fields).

Can adsorb large amounts of CO<sub>2</sub> if designed properly.

### Advantages:

Lower regeneration temperature (<100 °C) compared to chemisorbents.

Reduces energy cost (no need to divert high-temp steam).

Highly tunable pores and chemistry → adaptable for CO<sub>2</sub>, biogas, natural gas, or direct air capture.

Examples:

HKUST-1, Mg-MOF-74: strong affinity and high uptake of CO<sub>2</sub> at low pressure.

Mg/DOBDC: exceptional performance, competitive with amine sorbents.

Zeolite 13X: inorganic physisorbent used in industry.

TEPA-SBA-15: amine-modified mesoporous silica (chemisorbent).

Challenges:

Moisture reduces CO<sub>2</sub> capture in pristine MOFs.

Regeneration can be difficult.

Improvement – Amines Tethered to MOFs:

Functionalizing MOFs (e.g., Mg-MOF-74) with ethylenediamine introduces free amine groups in pores.

Increases CO<sub>2</sub> uptake at ultralow concentrations (400 ppm).

Provides better stability and regenerability in cyclic use.

■ In short:

MOFs are highly tunable physisorbents with huge surface areas, lower regeneration energy, and strong CO<sub>2</sub> affinity (especially Mg-based). Modified with amines, they show excellent performance for DAC even at ambient CO<sub>2</sub> levels.....Methanol from CO<sub>2</sub>

Importance of Methanol

Versatile: raw material for plastics, textiles, paints, adhesives, solvents.

Fuel/fuel additive; lower carbon compared to petrol/diesel.

Current global methanol use emits ~165 Mt CO<sub>2</sub>/year (~0.3% of total).

Sustainable methanol = bridge fuel for net-zero economy.

Methanol Economy (India focus)

Produced from: coal, agri-waste, natural gas, CO<sub>2</sub>.

NITI Aayog programme: cut oil imports, reduce GHG, convert waste to methanol.

Uses: transport (road, rail, marine), DG sets, boilers, cooking fuel.

Benefits:

15% blending in gasoline → 15% lower imports + 20% less emissions.

Creates ~5 million jobs.

Saves ₹6000 crore annually (via DME in LPG).

Initiatives:

Asia's 1st methanol cooking fuel (Assam, 2018).

Railway & shipping trials on methanol fuel.

R&D; on coal-to-methanol plants by BHEL, Thermax, IIT Delhi.

Methanol Synthesis from CO<sub>2</sub> + H<sub>2</sub>

Reaction: CO<sub>2</sub> + 3H<sub>2</sub> → CH<sub>3</sub>OH + H<sub>2</sub>O.

Catalysts: mainly Cu/ZnO or Cu/ZrO<sub>2</sub>.

Reactor designs:

Quench (gas injection) – high catalyst volume.

Tube-Cooled Converter (TCC) – best efficiency, lower cost.

Steam-Raising Converter (SRC) – isothermal.

Cu/ZrO<sub>2</sub> catalyst: stable, both acidic & basic → high selectivity, resists CO formation.

Industrial Example – George Olah Plant (Iceland, 2011)

World's 1st CO<sub>2</sub>-to-methanol commercial plant.

Uses CO<sub>2</sub> from geothermal power plant + H<sub>2</sub> from electrolysis.

Capacity scaled from 1300 → 4000 t/y (recycling ~5500 t CO<sub>2</sub>).

Zero toxic by-products, small land footprint.

Reduces CO<sub>2</sub> by ~90% compared to petrol/diesel.

Inspired larger plants → e.g., China's Anyang facility (110,000 t/y methanol; captures 160,000 t CO<sub>2</sub>/year).

Electrochemical Reduction of CO<sub>2</sub> to Methanol

Challenge: CO<sub>2</sub> reduction competes with H<sub>2</sub> evolution.

Needs: catalysts that suppress H<sub>2</sub> and favor CH<sub>3</sub>OH formation.

Pathways: via CO intermediate or formate (HCOO<sup>-</sup>).

Catalysts: transition metals (Cu most effective).

Cu-based electrodes:

Industrial catalysts = Cu–Zn–Al oxides.

Oxidized Cu surfaces (Cu<sup>+</sup> species) show best activity/selectivity.

Nanostructured Cu thin films → highest CH<sub>3</sub>OH production.

■ In short:

Methanol from CO<sub>2</sub> is a clean fuel & chemical. India pushes "Methanol Economy" for energy security & lower emissions. Industrial synthesis uses Cu-based catalysts (Cu/ZnO, Cu/ZrO<sub>2</sub>), with reactor design crucial for efficiency. George Olah plant proved CO<sub>2</sub>-to-methanol feasible at scale. Future: electrochemical CO<sub>2</sub> reduction on Cu-based electrodes offers direct renewable pathway.