Metal-organic framework materials for hydrogen storage in aerospace applications

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1. Hydrogen in aerospace applications

Timeline of hydrogen (H₂) within aerospace:

- 1783 – First hydrogen balloon flight
- 1900 – First airship flown purely on hydrogen (Zeppelin L21)
- 1954 – Hydrogen peroxide Sikorsky Helicopter
- 1966 – Hydrogen batteries in satellite (NTS-2)
- 1969 – Hydrogen cryocooler on Mariner 6
- 1988 – First hydrogen aircraft prototype (Tuoplev-Tu-155)
- 2011 – Large Aviation/DLR Antares H3 – hydrogen fuel cells (piloted and unmanned), 6000 km, >50 hrs

Conventional storage methods: Compression or liquefaction.

Problem: Low H₂ densities and high investment costs.
Possible Solution: Physisorption onto a porous material.

BUT: Each additional kg sent into space costs ~ $ thousands!

2. Materials

Desired properties of solid adsorbent:
- Light
- High surface area
- Large pore volume
- Robust
- Low cost
- Good cycle life

Metal-organic framework (MOF) chosen for study:

NH₂-MIL-101(Al)
[SBU*: 634.04 g mol⁻¹]

NH₂-MIL-101(Cr)
[SBU*: 712.37 g mol⁻¹]

(*Secondary Building Unit)

Synthesis of NH₂-MIL-101(Al) [2]

3. Characterization of the MOF

Comparison of analogues

NH₂-MIL-101(Al) : 2540 m² g⁻¹
NH₂-MIL-101(Al) : 1298 m² g⁻¹

Max. hydrogen uptake at 77 K:

- NH₂-MIL-101(Al) : 0.77 cm³ g⁻¹
- NH₂-MIL-101(Al) : 0.52 cm³ g⁻¹
- NH₂-MIL-101(Al) : 0.77 cm³ g⁻¹

Comparison of hydrogen excess isotherms for MIL-101 analogues at 77 K

3.1. Thermogravimetric analysis of NH₂-MIL-101(Al) (ramp rate - 5 °C min⁻¹)

- Indicates guest solvent removal between 80-200 °C.
- Reveals interesting thermal degradation steps.

4. Ongoing work

As seen in the figure below:
- Lighter analogue shows increased H₂ uptake.
- Removal of amine from NH₂-MIL-101(Cr) increases H₂ uptake.
- Potential for even higher uptake from removal of amine from NH₂-MIL-101(Al)?

5. Summary

- NH₂-MIL-101(Al) has greater BET surface area and H₂ uptake than the heavier Cr analogue.
- Removal of the NH₂ group from NH₂-MIL-101(Al) may result in very promising hydrogen uptake.
- Good initial results, but more materials need to be studied for potential commercial use.

References: