Recent Progress in Hydrogen Storage in Nanoporous Materials
IEA-HIA Task 32
“Hydrogen-based Energy Storage”

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IEA HIA Task 32
“Hydrogen-based energy storage”
Storage by physisorption of hydrogen
Metal-organic frameworks (MOFs)
Volumetric storage density
Enhancing H₂ interaction with framework
Reproducibility of measurements
Conclusion and outlook
IEA HIA Task 32: “Hydrogen-based energy storage”

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Operating Agent: Michael Hirscher

18 countries, about 50 experts
Task 32 “Hydrogen-based energy storage”

Goals and objectives

I. Develop reversible or regenerative hydrogen storage materials fulfilling the technical targets for mobile and stationary applications

II. Develop the fundamental and engineering understanding of hydrogen storage materials and systems that have the capacity to fulfil Target I

III. Develop materials and systems for hydrogen-based energy storage including hydrogen storage for use in stationary, mobile and portable applications, electrochemical storage, and solar thermal heat storage


An international multi-laboratory investigation of carbon-based hydrogen sorbent materials


AN IMPLEMENTING AGREEMENT OF THE INTERNATIONAL ENERGY AGENCY
Task 32 working groups

- Porous materials (coordination polymer framework compounds, MOFs, ZIFs, COFs, and carbons)
- Magnesium-based hydrogen and energy storage materials
- Complex and liquid hydrides (borohydrides, alanates, amides/imides-systems, reactive hydride composites and rechargeable liquid hydrogen carriers)
- Electrochemical storage of energy (MH-batteries, ion-conduction)
- Heat storage – concentrated solar thermal using metal hydrides
- Hydrogen storage systems for mobile and stationary applications
Motivation and introduction

Compressed Hydrogen Storage System 5 wt%
Physisorption

Surface area
Outer surface area
Inner surface area (Nanosponge)
Metal-organic frameworks (MOFs)

Example: MOF-5
Structures and names

Absolute hydrogen uptake at 77 K
Development of hydrogen uptake @77K

At 77 K and 50 bar
Total uptake 12 -15 wt%

5 wt% system capacity can be easily reached, however only at 77 K!
Total volumetric vs. gravimetric density

Theoretical Limits of Hydrogen Storage in Metal–Organic Frameworks: Opportunities and Trade-Offs

Packing density of powder
Based on single crystal density
Interpenetrated frameworks

freely adapted from Ulrich Müller, BASF SE
Gravimetric and volumetric uptake 77 K

[Graph showing gravimetric and volumetric uptake data for different materials]

Correlation between volumetric and gravimetric capacity
Influence of pore size

Cryogenic conditions required!
Open metal sites (CPO-27)

Small fraction of available sites!

Enhanced hydrogen storage via “spillover”

Y. Li, R.T. Yang, JACS 128 (2006) 726 and 8136


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Spillover in un- and bridged MOFs - revisited

SEM-pictures of large MOF-5+AC/Pt5wt%+Sucrose crystals

SEM-pictures of large MOF-5+AC/Pt5wt% crystals

“If any spillover effect occurred it was below the detection limit.”

Mixing in vibration mill:
“the mortar is vibrating which leads to a soft motion of the grinding ball. This is a very controlled and reproducible technique which is as close as possible to the mortar and pestle method used by Li and Yang.”

**H adsorption in Pt catalyst/MOF-5 materials**


“No evidence of hydrogen spillover effect described previously on seemingly the same kind of samples was found for any of studied materials.”

- **5 wt.% Pt/AC**
- **10 wt.% Pt/AC**

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**Graphs:**
- Plot showing hydrogen uptake vs. pressure for different samples.
- Legend: MOF-5, Pt on AC, mixed, bridged.

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**Notes:**
- Pt catalyst/MOF-5 materials
- Comparative study of hydrogen adsorption
- Experimental data presented
Reasons for irreproducibility

- Measurement of hydrogen storage capacity of porous materials is difficult
- Sample and gas purity leading to unexpected reactions
- Limited quantity of material available
- Pressure to publish

Conclusion and outlook

- IEA-HIA Task 32 “Hydrogen-based energy storage”
- Hydrogen storage by physisorption on nanoporous materials
  - Metal-organic frameworks (MOFs)
  - Fast kinetics and reversibility
  - Large specific surface area limit 4500 - 5000 m²/g
  - High storage capacity at 77 K, excess ~ 8 wt%, total 12 – 15 wt%
  - Volumetric capacity strongly correlated to gravimetric capacity
- Enhancement of adsorption at RT by noble metal particles
  - “spillover process” → Irreproducibility!
- Measurements of hydrogen storage capacity
  - Porous materials → Lack of reproducibility!

Hydrogen-based Energy Storage
Applied Physics A - Topical Collection
Thank the organizers!

Thank you for your attention!

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