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Reversible Hydrogen Storage by Metastable Hydrides in Functionalized Porous Hosts

Mark D. Allendorf, Sandia National Laboratories

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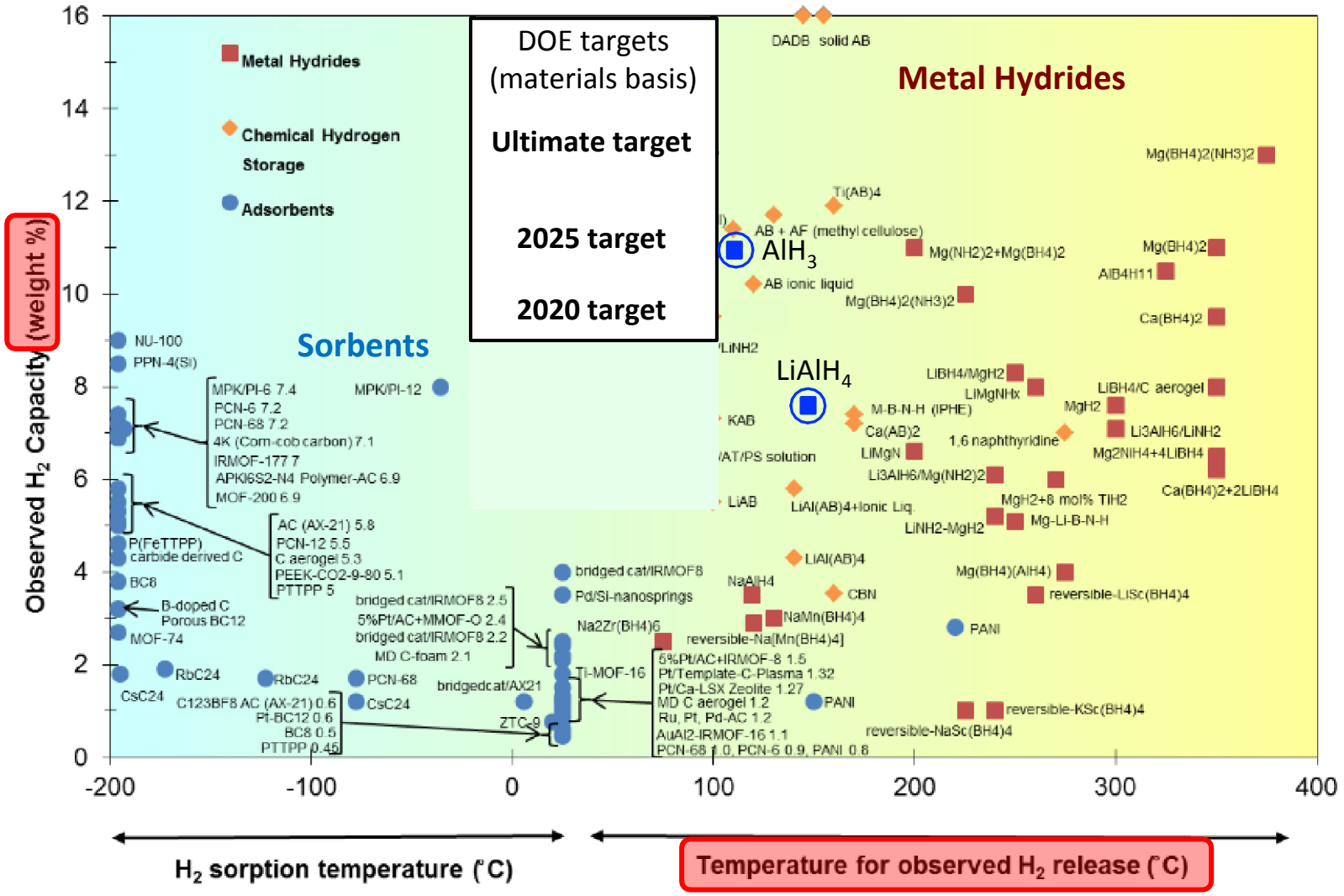
Metastable Metal Hydrides



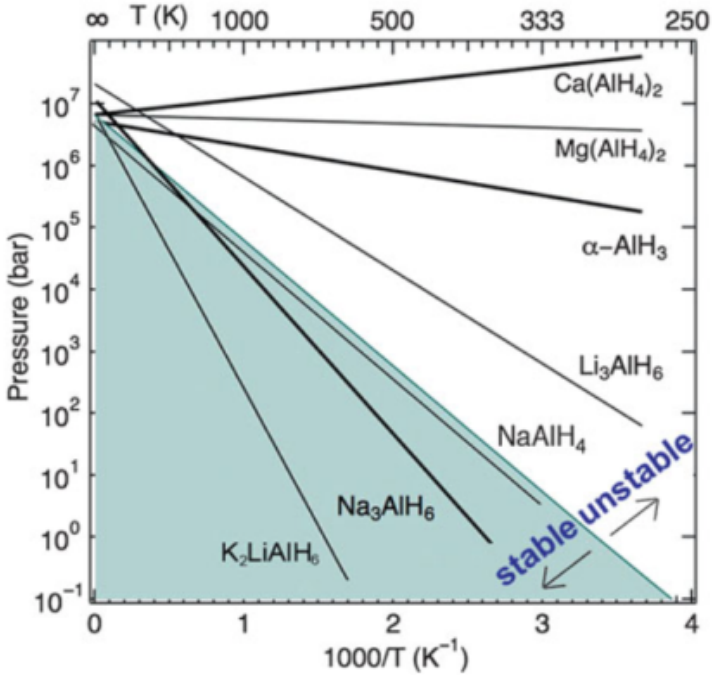
- **Thermodynamics**
- **Kinetics**

- **Metastable hydrides**

  Alane (AlH_3) properties:
  - Very high grav. capacity
  - Vol. capacity 2X L-H_2 (148 g H_2/L)

  Lithium alanate ($LiAlH_4$)
  - Fast desorption
  - Vol. capacity ~ L-H_2 (80 gH_2/L)

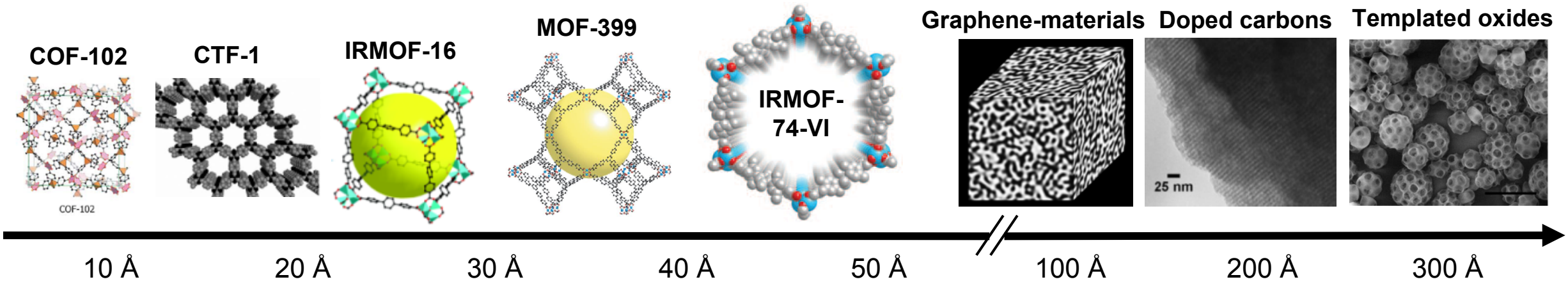
  Neither can be directly rehydrogenated



Graetz & Reilly
Scripta Mater. **56** (2007), 835

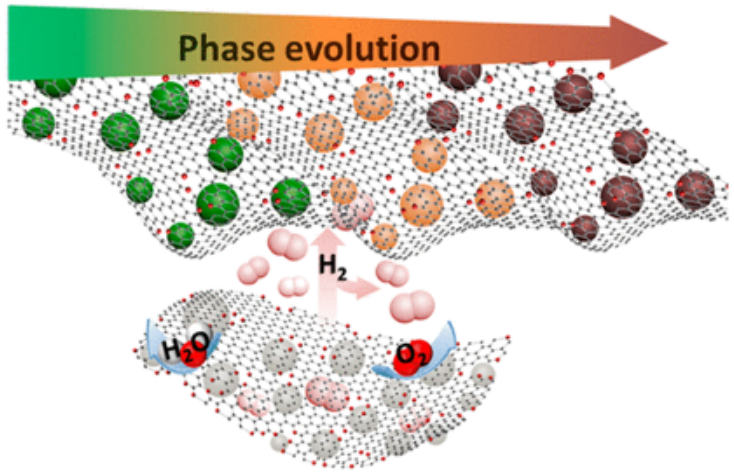
Size-dependent physical and chemical properties of metal hydrides

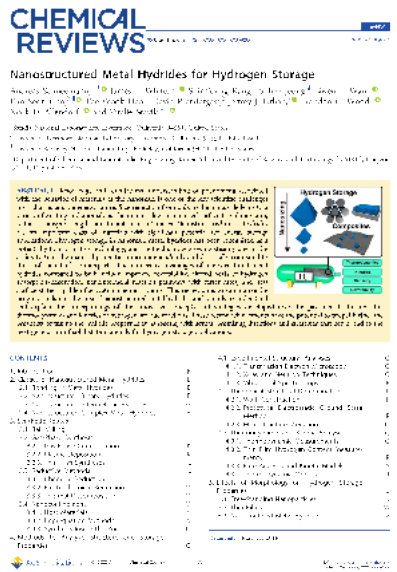
Nanoscaling of metal hydrides has the potential to weaken metal-hydrogen chemical bonds, accelerate the kinetics, alter reaction pathways, and enable reversibility

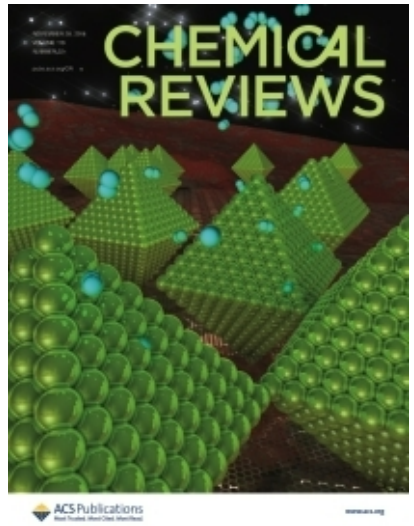


We want to determine which factors contribute to:

- ⇒ ***Improved thermodynamics***
- ⇒ ***Increased reaction rates***
- ⇒ ***Reversible H_2 uptake and release***
- ⇒ ***High selectivity for hydrogen gas***
- ⇒ ***Low concentration of intermediates and byproducts***



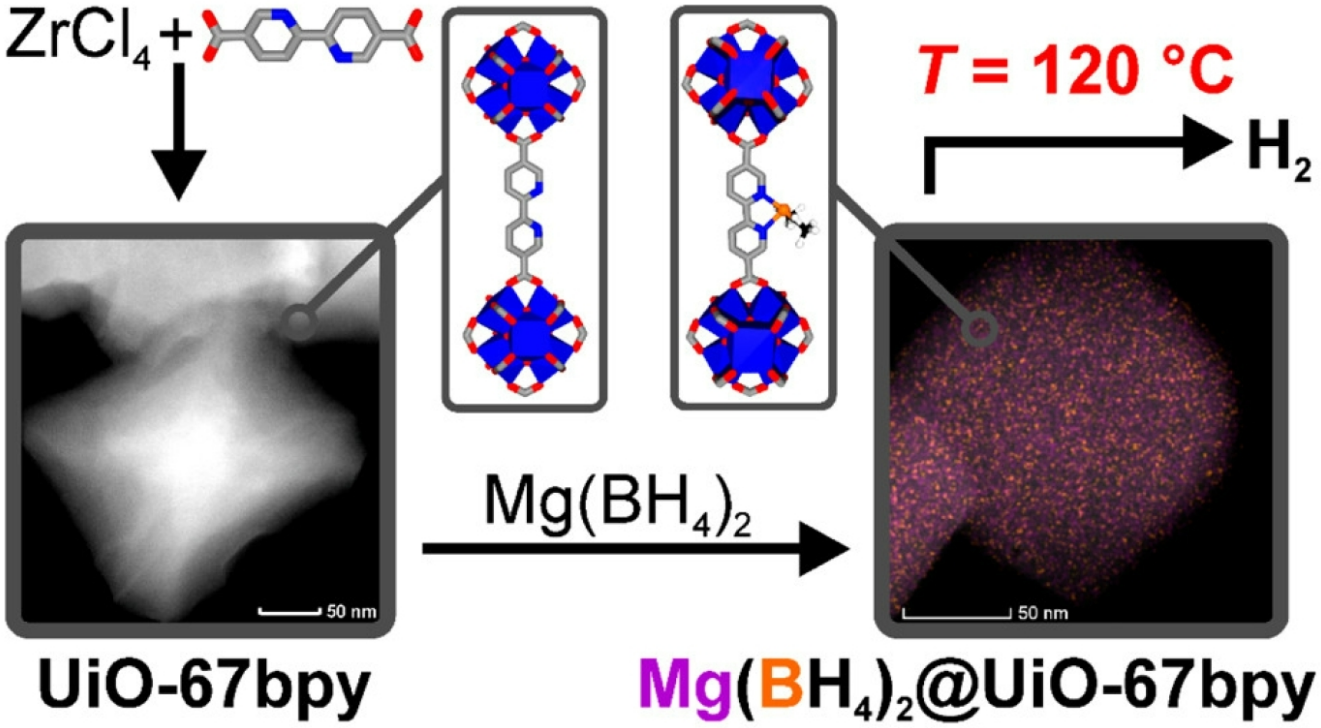


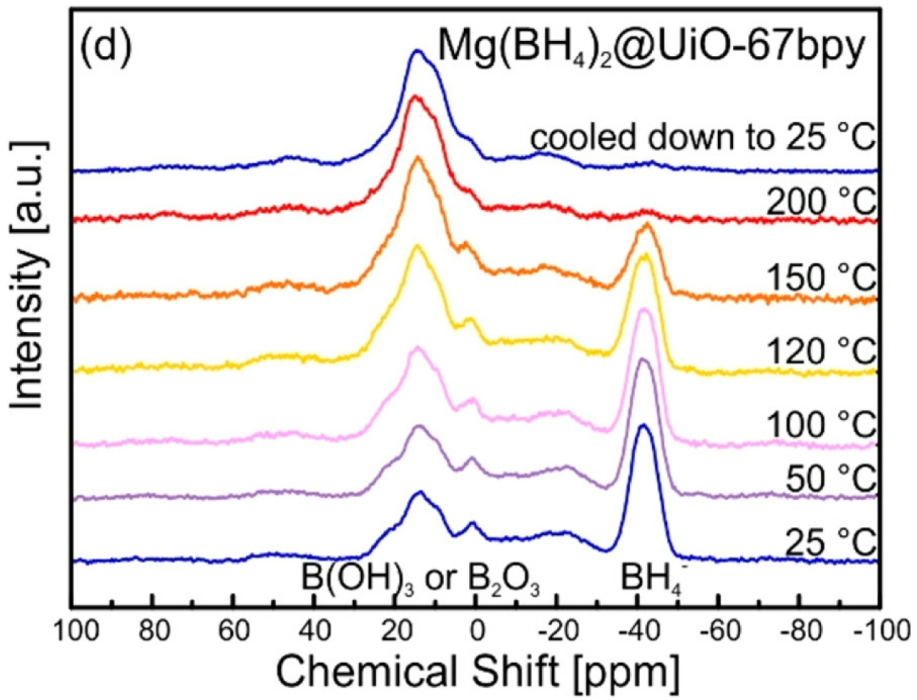


📖 Andreas Schneemann *et al. Chemical Reviews,* **2018**, *118,* 10775.

Molecular $Mg(BH_4)_2$ nanoconfined in a Metal-Organic Framework

H_2 release 150 °C lower than bulk, complete desorption by 200 °C





H_2 desorption from $Mg(BH_4)_2$@UiO-67bpy is irreversible, likely due to hydride attack on the Zr-carboxylate linkages and subsequent MOF collapse

A. Schneemann et al. *ACS Nano* 2020, 14, 8, 10294-10304

Lithium alanate ($LiAlH_4$) nanoconfinement in porous carbon

Bulk $LIAlH_4$

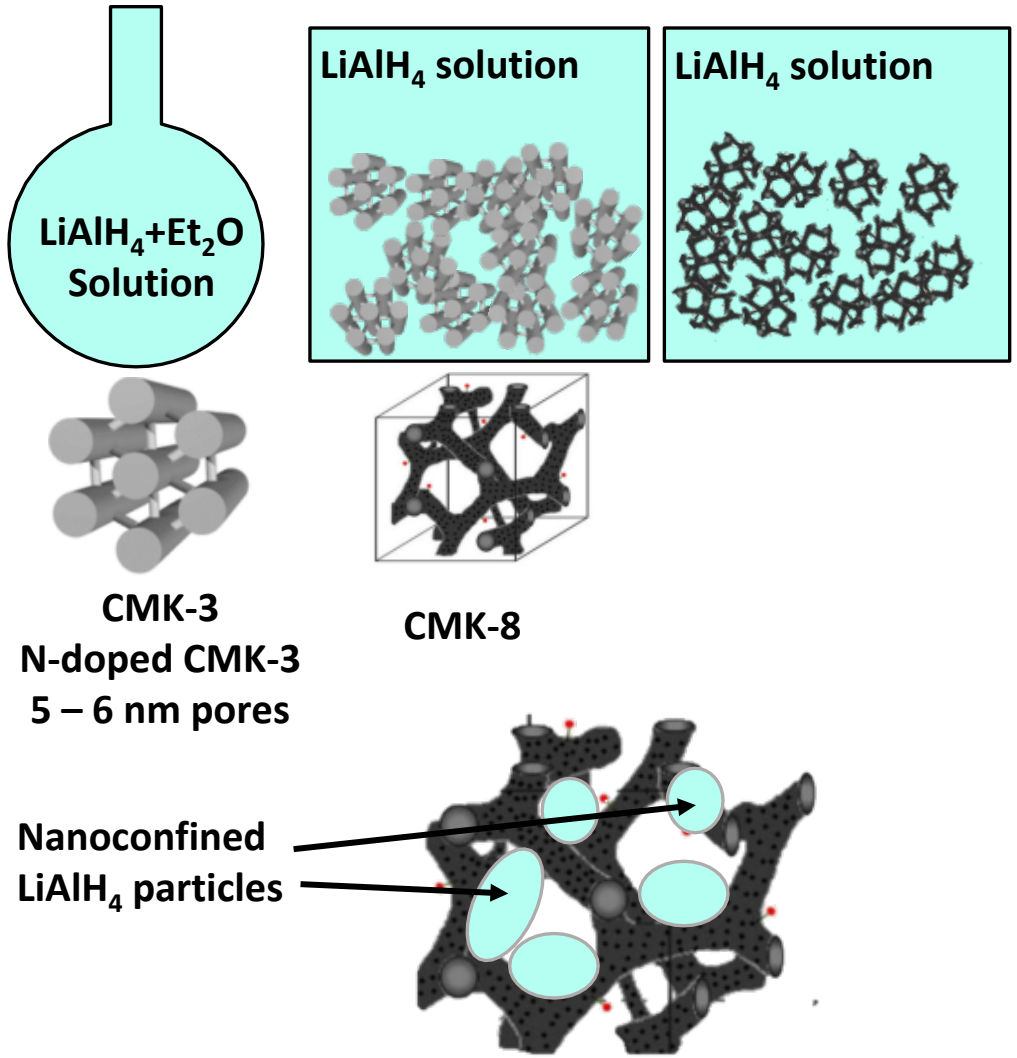
$LiAlH_{4(s)} \rightarrow LiAlH_{4(l)}$ 150 – 175 °C (endo) melting

$LiAlH_{4(l)} \rightarrow 1/3Li_3AlH_{6(s)} + 2/3Al_{(s)} + H_{2(g)}$ 150 – 200 °C (exo) 5.3 mass% H_2

$Li_3AlH_{6(s)} \rightarrow 3LiH_{(s)} + Al_{(s)} + 3/2H_{2(g)}$ 200 – 270 °C (endo) 2.6 mass%H_2

$LiH_{(s)} + Al_{(s)} \rightarrow LiAl_{(s)} + 1/2H_{2(g)}$ 400 – 440 °C (endo) 2.6 mass%H_2

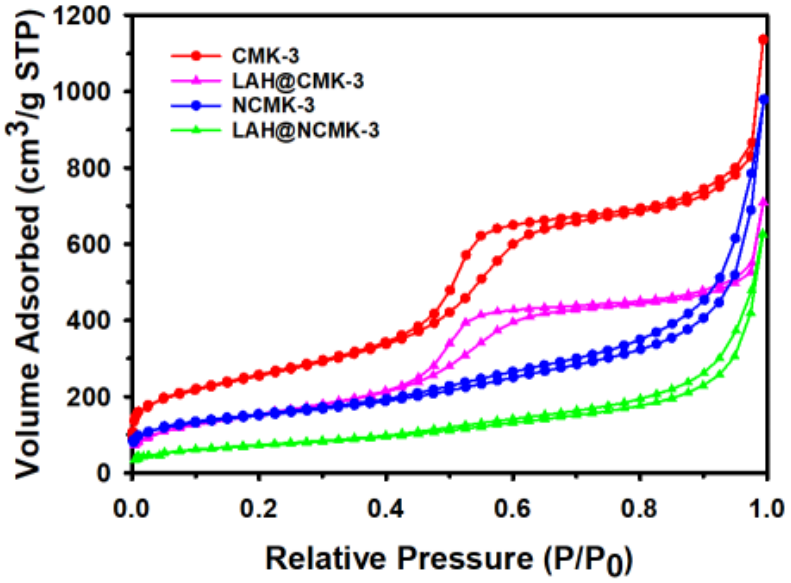
- **10.6 wt%** capacity (**7.9 wt%** for the first two decompositions), fast desorption kinetics
- First decomposition is **exothermic** due to high Li_3AlH_6 lattice energy
- $\Delta H<0$, $\Delta S>0$ → thermodynamically **irreversible**
- $LiAlH_4$ solvation (diglyme, THF, and Me_2O), Ti catalyst have been employed
- **Direct reversibility of bulk thought to be impossible**



Nanoconfinement accelerates H_2 release from nanoscale $LiAlH_4$

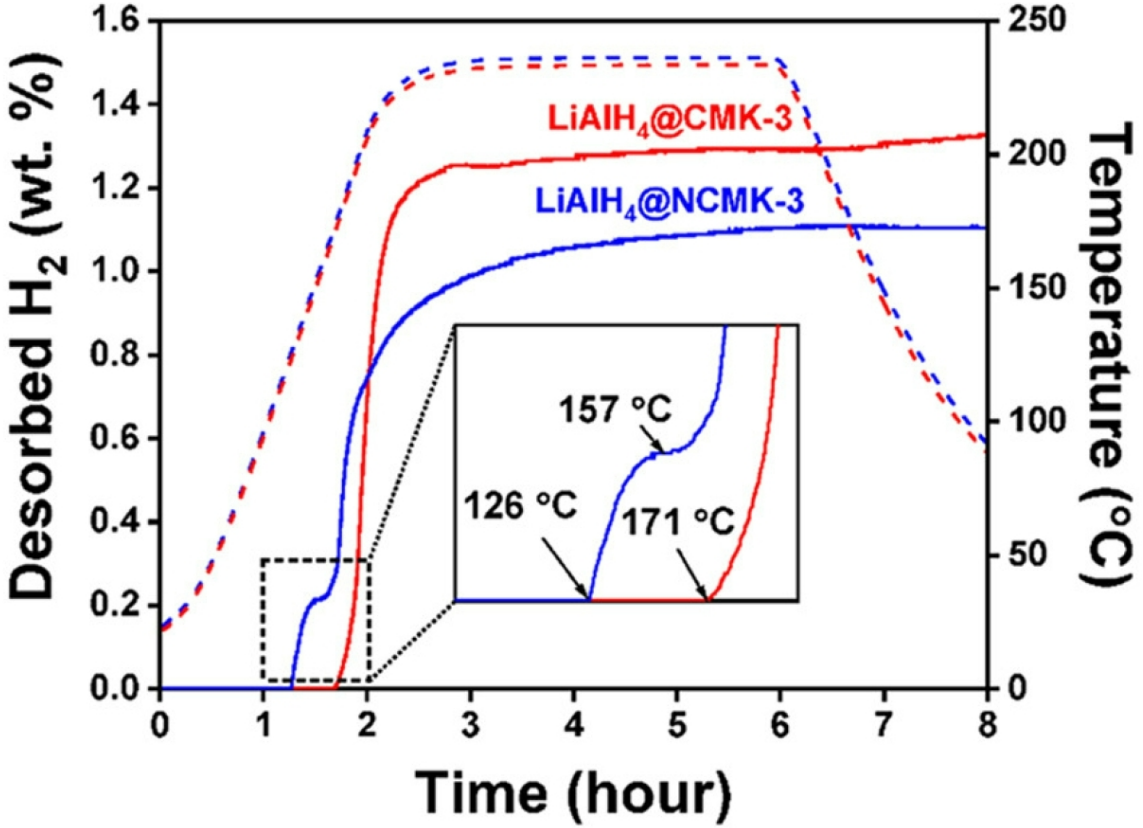
Reversibility is only achieved using nitrogen-doped CMK-3 with no evidence of Li_3AlH_6 formation

N_2 adsorption/desorption isotherms



Sample	BET surface area ($m^2\ g^{-1}$)	Total volume ($cm^3\ g^{-1}$)
CMK-3	911	1.76
LAH@CMK-3	560	1.10
NCMK-3	534	1.51
LAH@NCMK-3	261	0.97

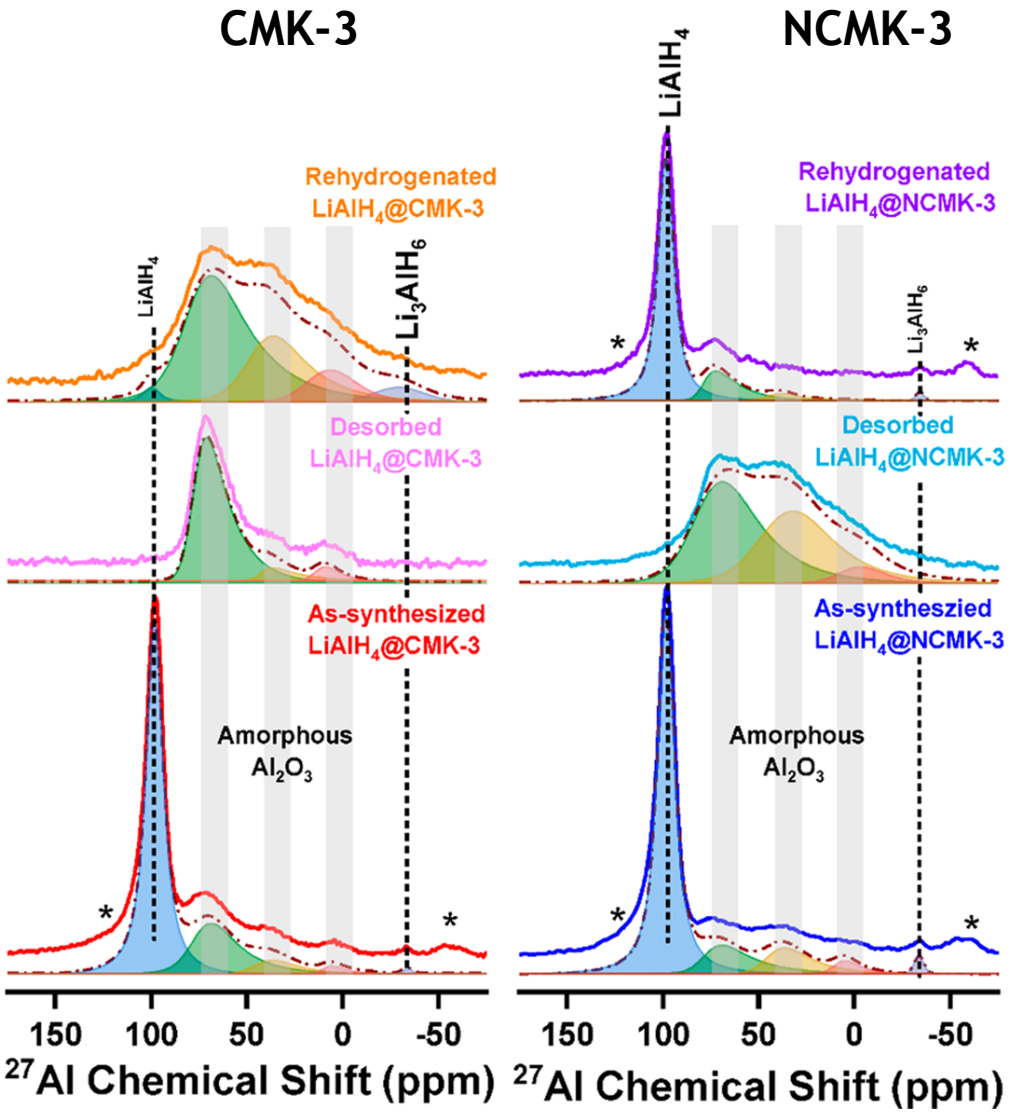
Sieverts data for H_2 desorption



Y. Cho et al. *ACS Nano* **15** (2021) 10163

Reversible H_2 release from $LiAlH_4$@NCMK-3 demonstrates hydride-host charge transfer is required for reversibility

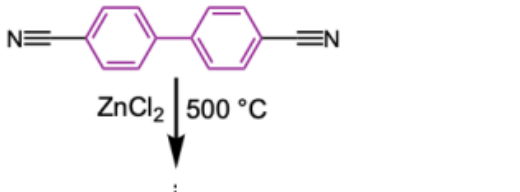
Only $LiAlH_4$ hosted by nitrogen-doped NCMK-3 exhibits reversibility (1000 bar H_2, 50 °C)

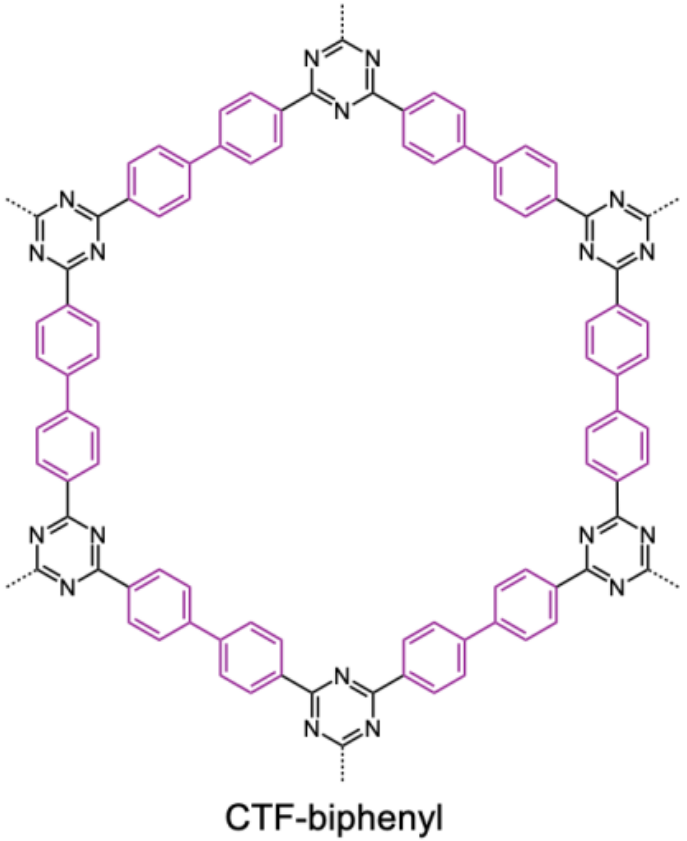


Y. Cho et al. *ACS Nano* **15** (2021) 10163

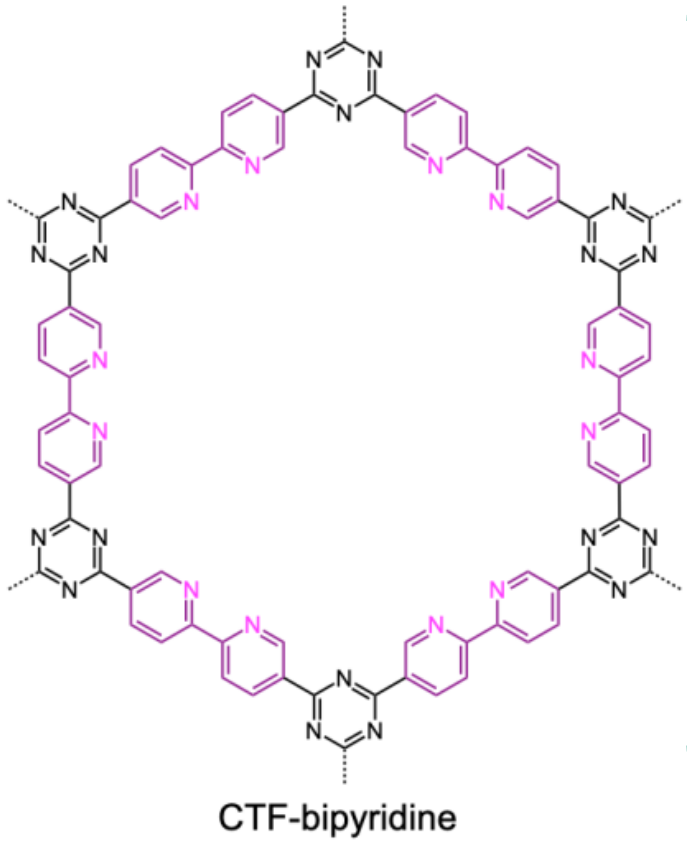
Nanoconfinement of alane (AlH_3) in Covalent Triazine Frameworks (CTF)

CTF-biphenyl





CTF-bipyridine



Bulk AlH_3 properties:

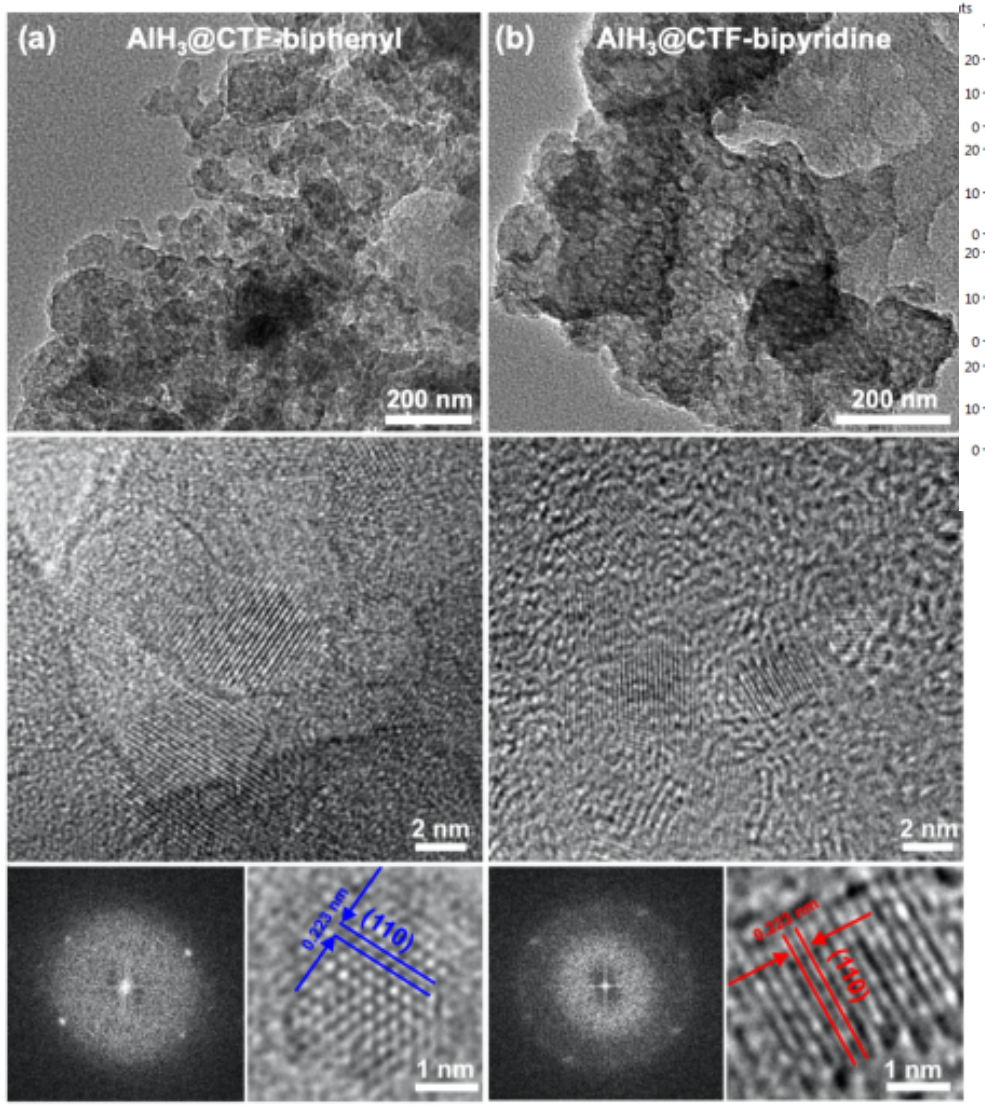
- ~10.4 wt% grav. capacity
- Vol. capacity 2X L-H_2 (148 g H_2/L)
- Fast desorption
- Rehydrogenation thought to be thermodynamically impossible

+ AlH_3 toluene/ Me_2EtN → **AlH_3@CTF**

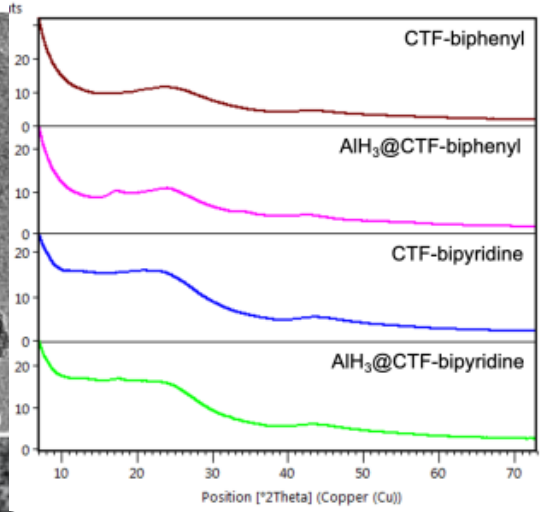
V. Stavila et al. *Angew. Chem. Int. Ed.* doi.org/10.1002/anie.202107507

Spectroscopy indicates AlH_3 is uniformly distributed throughout CTF pores

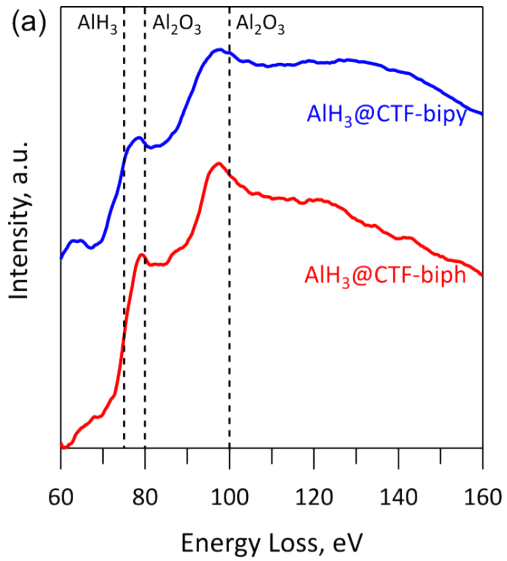
TEM and electron diffraction
(Primarily amorphous with some larger crystalline particles)



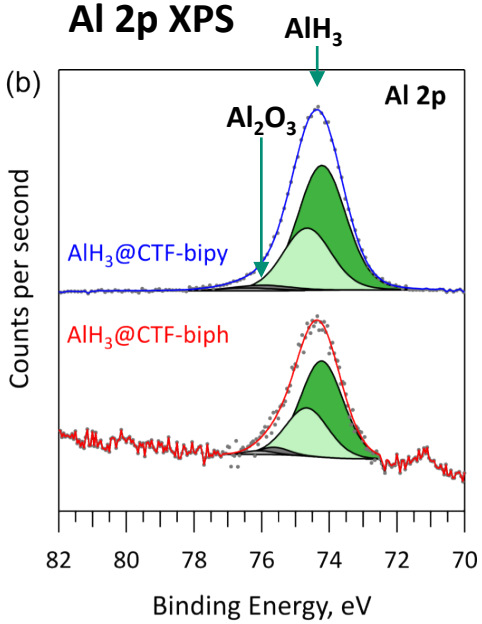
PXRD



EELS

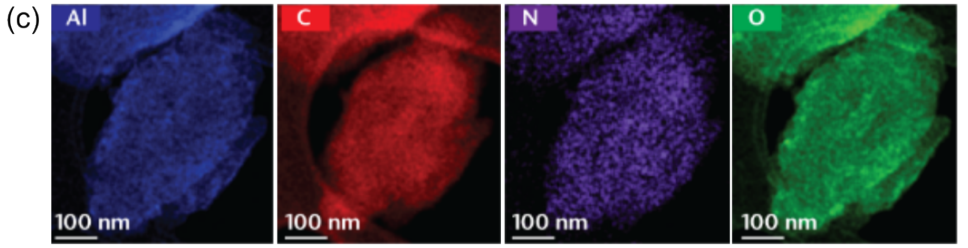


Al 2p XPS

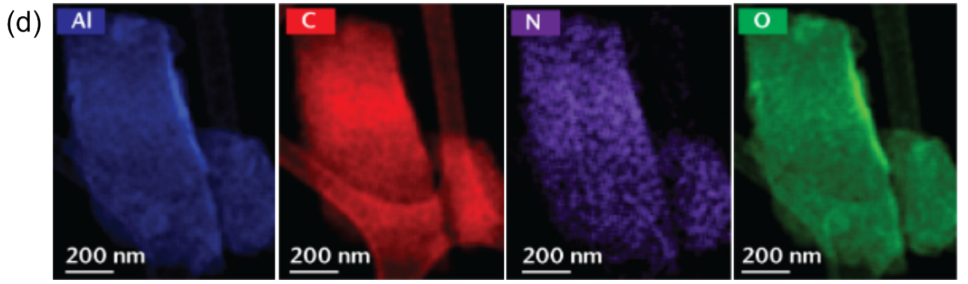


EDS maps:

AlH_3@CTF-biph



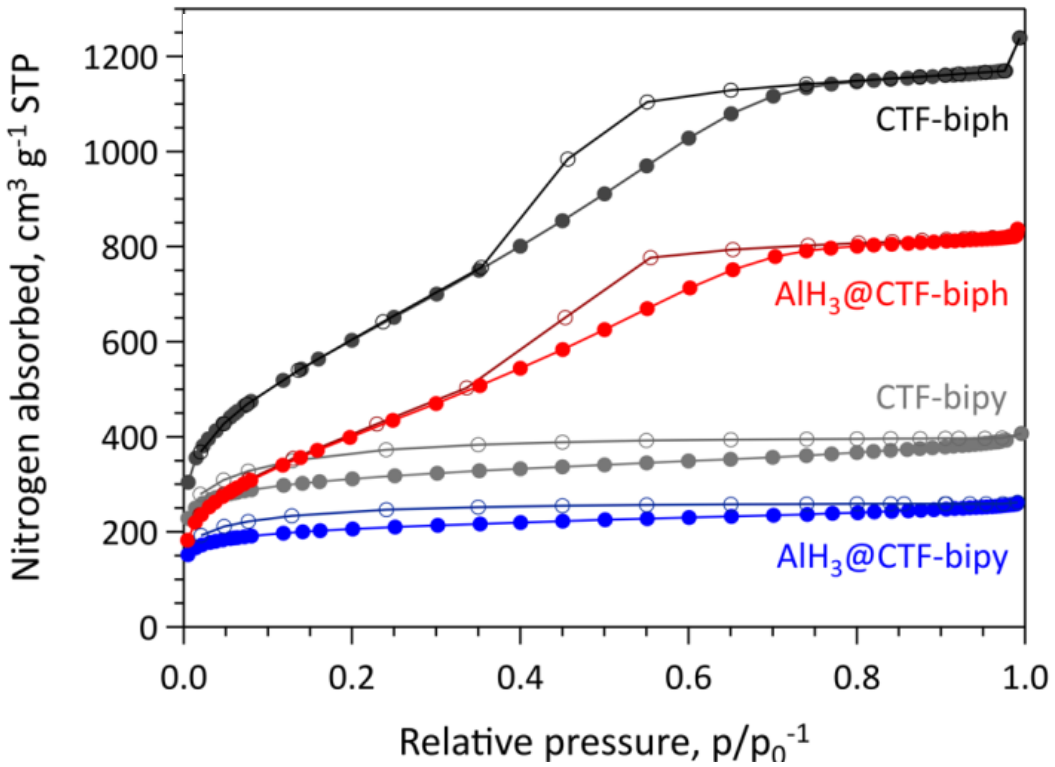
AlH_3@CTF-bipy



V. Stavila et al. *Angew. Chem. Int. Ed.* doi.org/10.1002/anie.202107507

Only AlH_3@CTF-bipyridine displays reversibility

N_2 adsorption isotherms (77 K)



Bulk rehydrogenation:

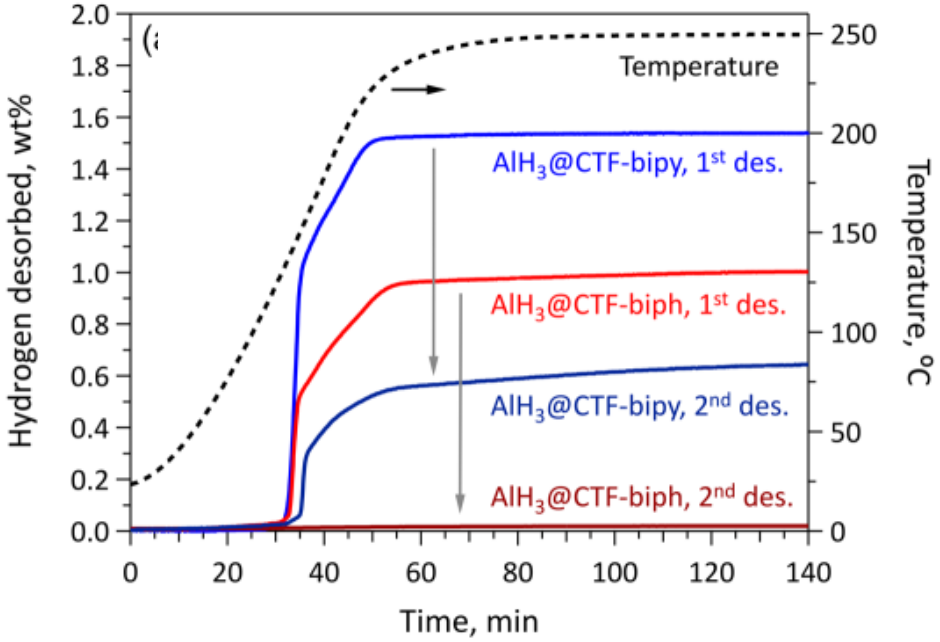
- **330 °C/49000 bar (4.9 GPa) (Saitoh et al. 2008)**
- **Ab initio: $\Delta G < 0$ above 7000 bar at 27 °C (Graetz et al. 2006)**

→ Nanoscaling reduces rehydrogenation pressure by > 10X

Sieverts data for H_2 desorption

	AlH_3@CTF-bipy	AlH_3@CTF-biph
Cycle 1	1.52 wt%	1.00 wt%
Cycle 2	0.65 wt%	0 wt%
Cycle 3	0.58 wt%	--
Cycle 4	0.57 wt%	--

Rehydrogenation at 60 °C, 700 bar H_2



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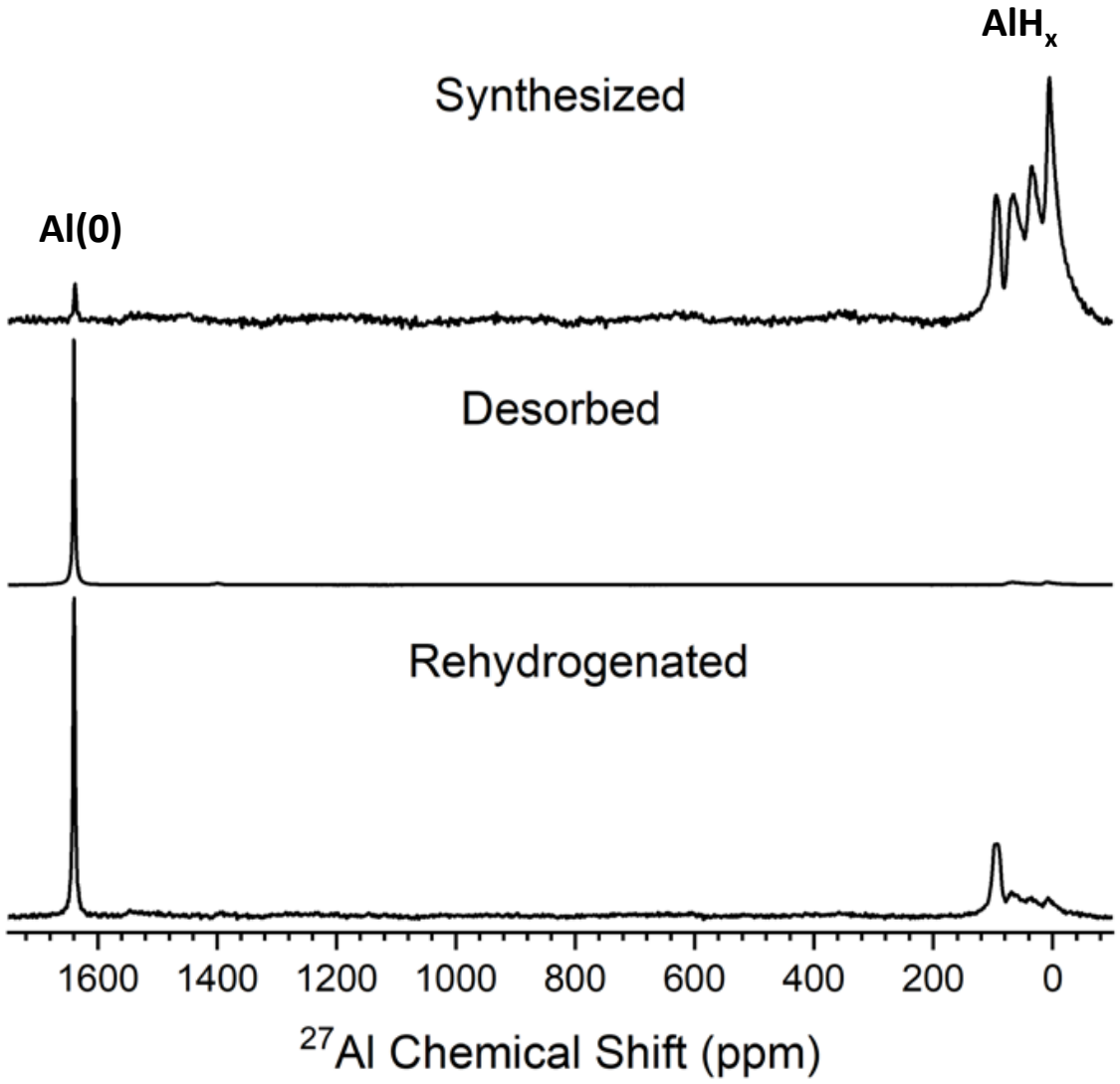
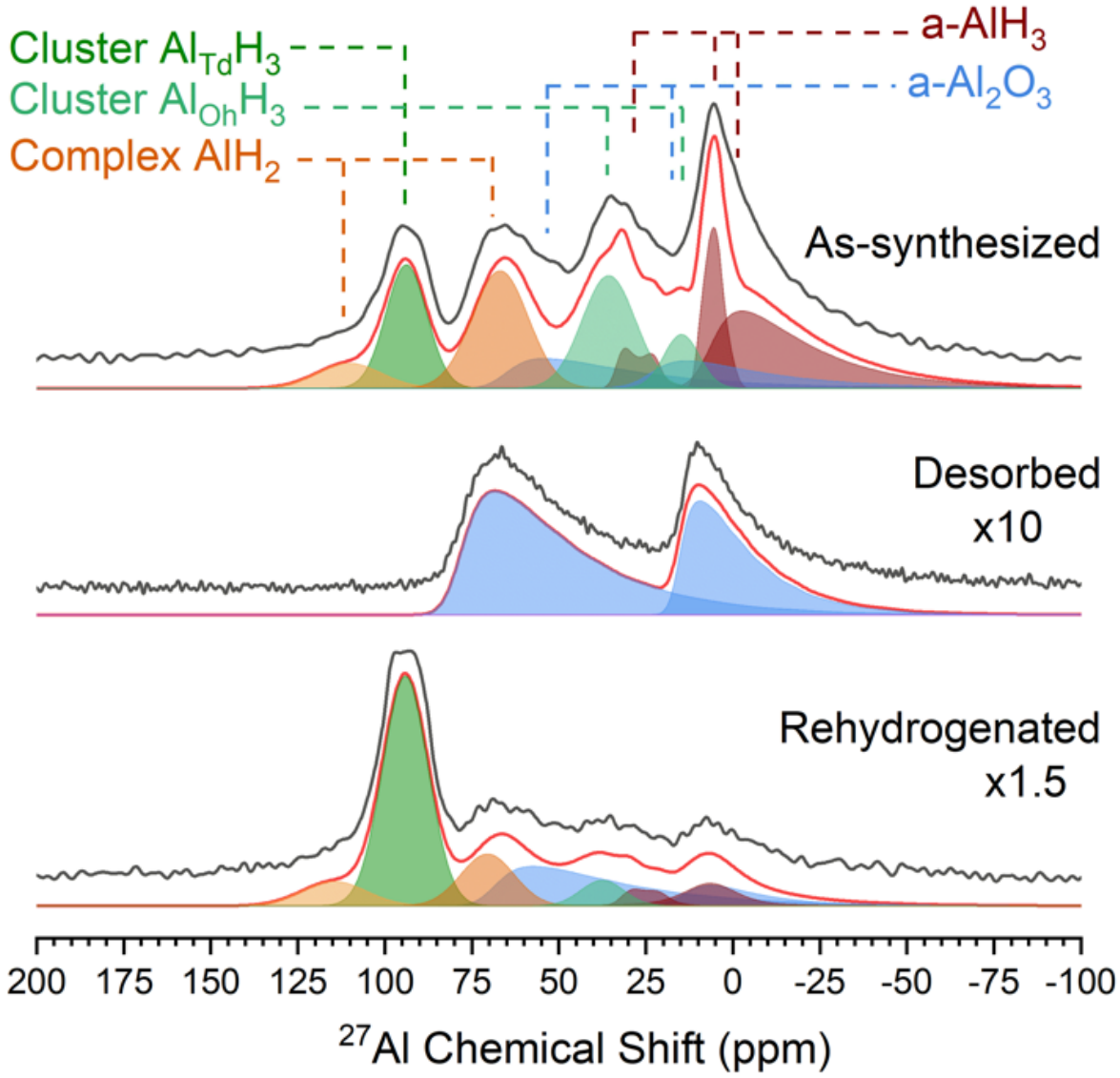
Magic Angle Spinning-NMR characterization of cycled AlH_3@CTF-bipy

Spectra show evidence of small AlH_x clusters and complexed Al





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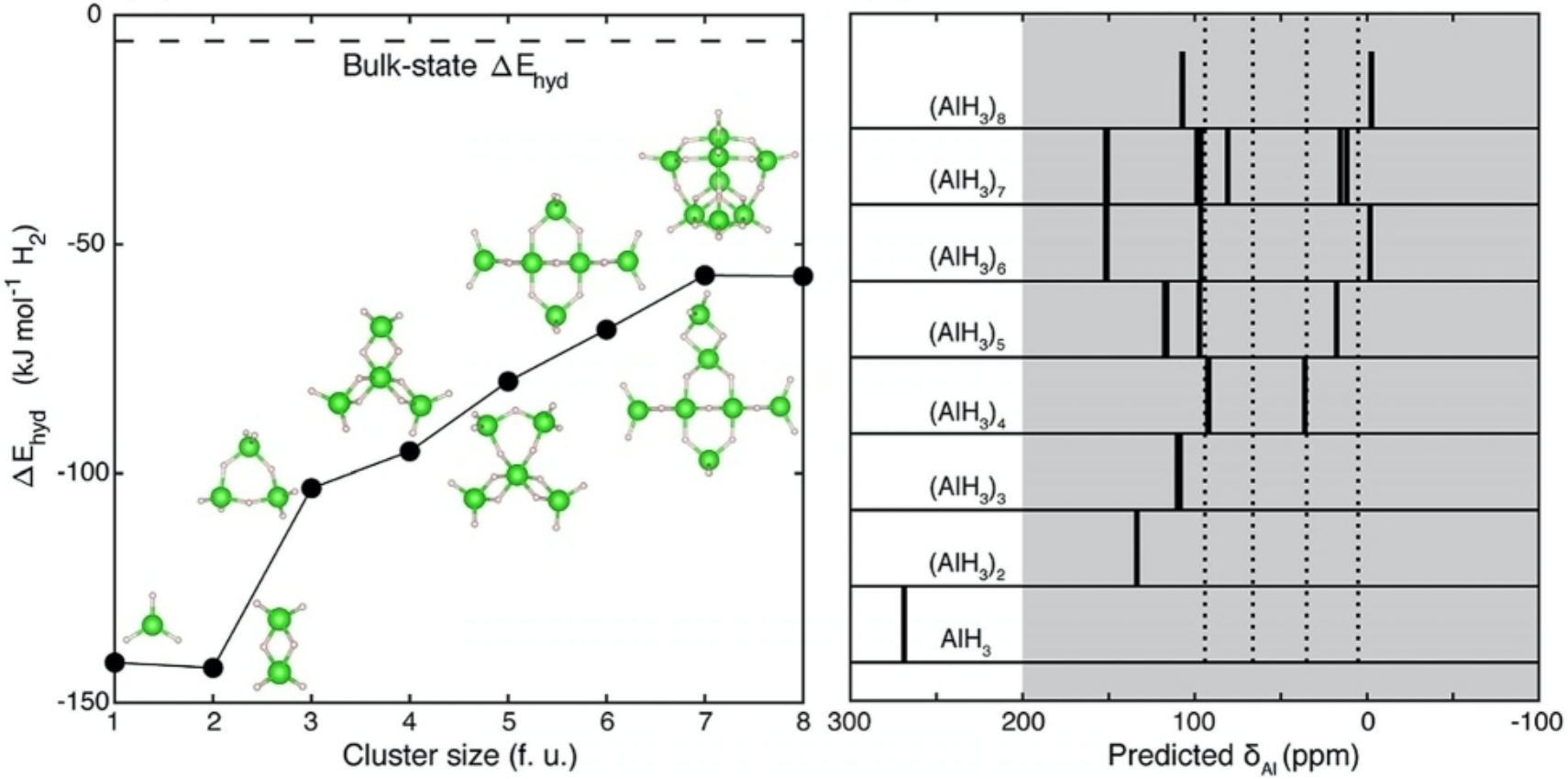
DFT cluster model allows ^{27}Al NMR peaks to be assigned



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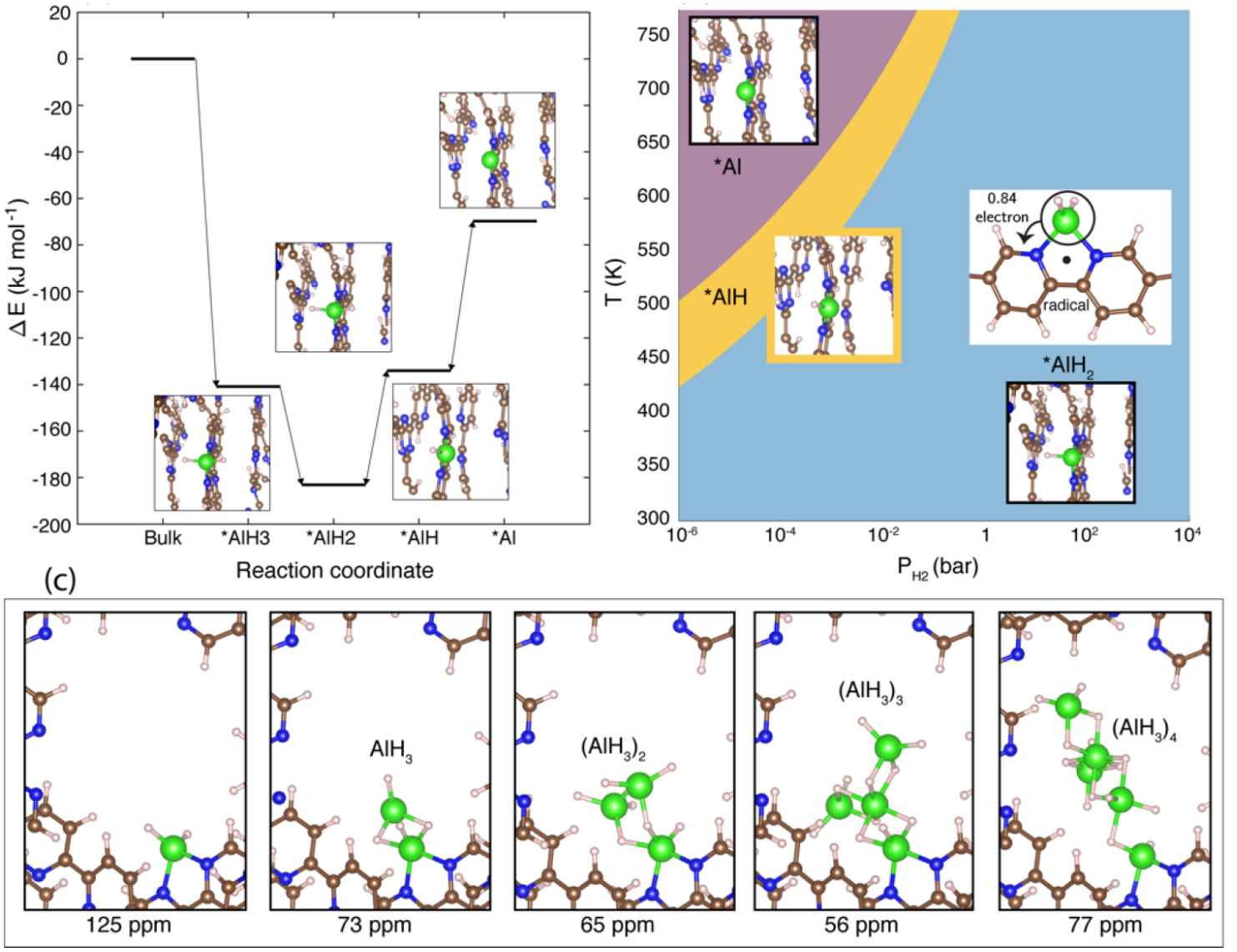
Periodic DFT model reveals a mechanism for AlH_3 reaction with CTF-bipy

Periodic DFT model

- AlH_3 dissociates on CTF-bipy to form (AlH_2+H)
- This is more stable than coordinated AlH_3



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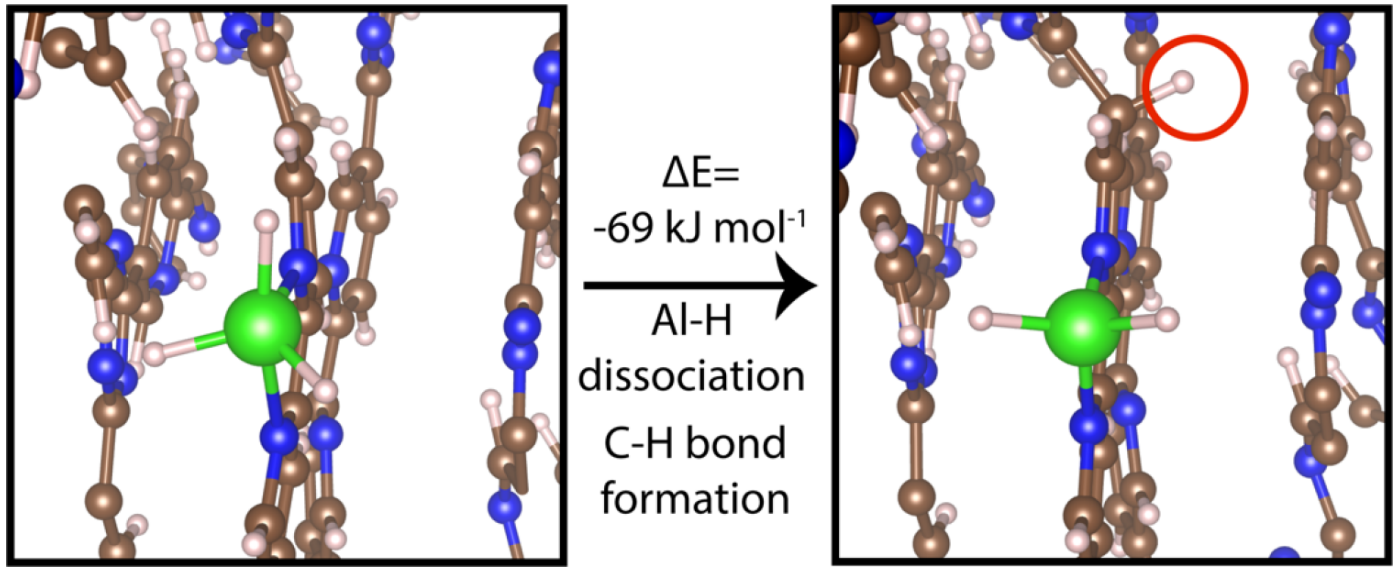
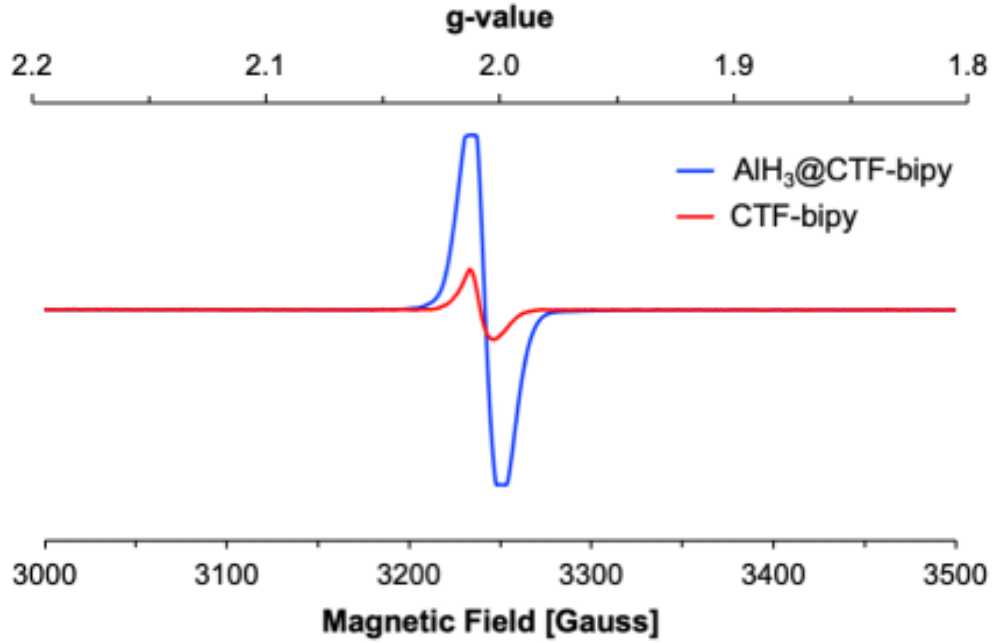
DFT calculations predict bipy-AlH_2 complex is a radical, confirmed by EPR spectroscopy

0.84e transferred from AlH_2 to CTF-bipy





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Enabling twice the energy density for onboard H_2 storage

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Backup slides

Characterization of CTF-biphenyl and CTF-bipyridine