National Renewable Energy Laboratory

Innovation for Our Energy Future

Towards High wt%, Room Temperature Reversible, Carbon-Based Hydrogen Adsorbents

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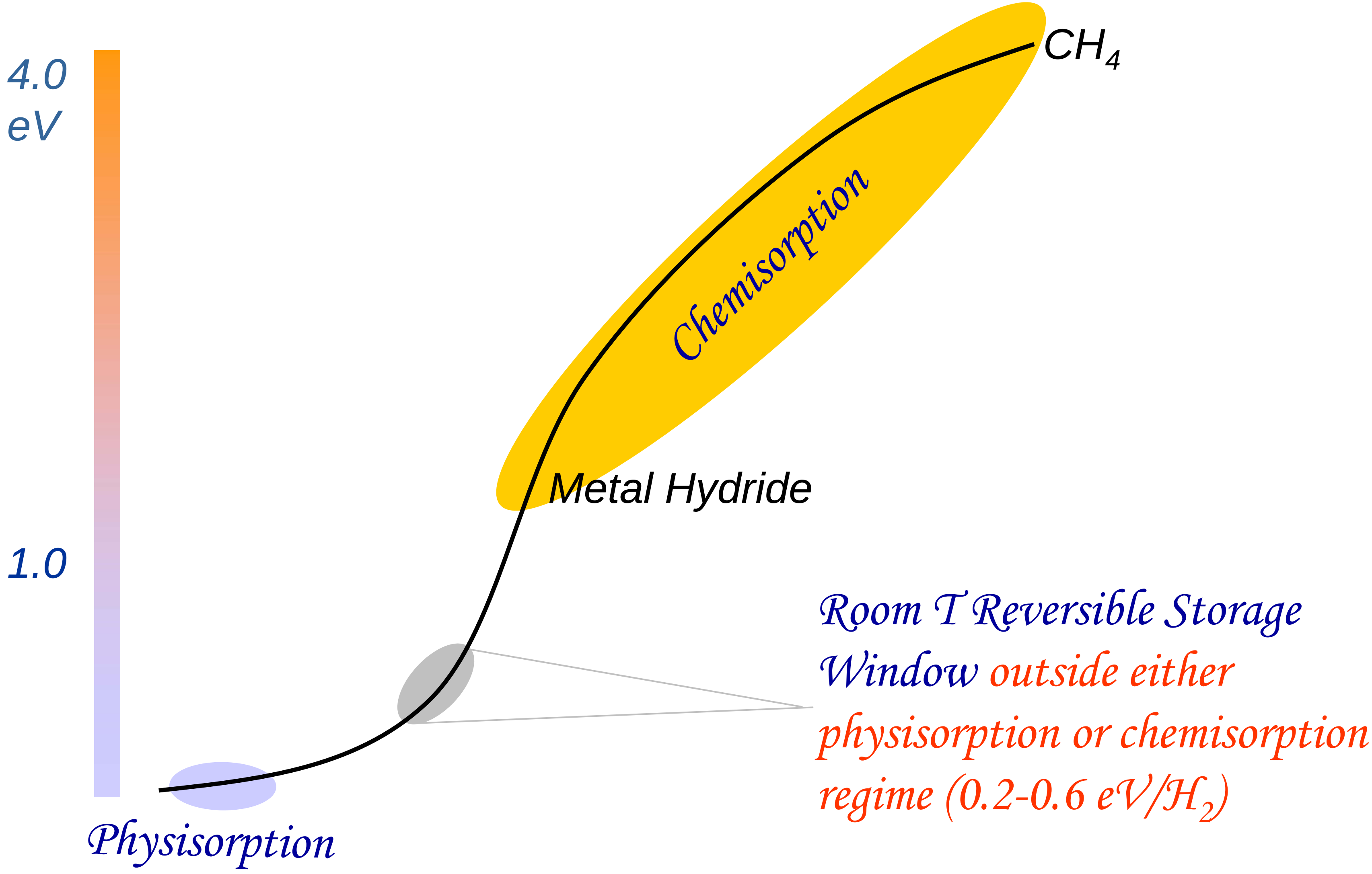
The Current Situation



Room T Reversible Storage Window outside either physisorption or chemisorption regime (0.2-0.6 eV/H$_2$)

- Need material that chemically binds H_2 non-dissociatively

Some Interesting Experimental Observations

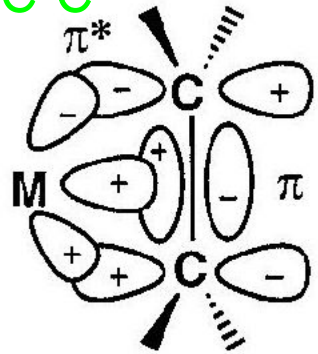
- Non-dissociative H adsorption on single wall (20 kJ/mol) [Dillon et al., Nature (1997)] and multiwall nanotubes (54 kJ/mol) (Dillon et al., Mat. Res. Soc. Proc.)

- Despite numerous recent efforts, however, high weight-percent hydrogen storage in pure carbon nanotubes and/or fullerenes is yet to be demonstrated

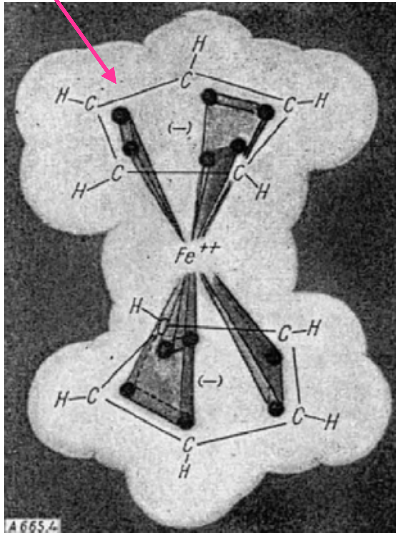
- The removal of the TM catalysts that were present in the original samples is correlated with a reduction in the amount of hydrogen being adsorbed (Dillon et al.)

Organometallic Molecules

Ligand 1: C-C

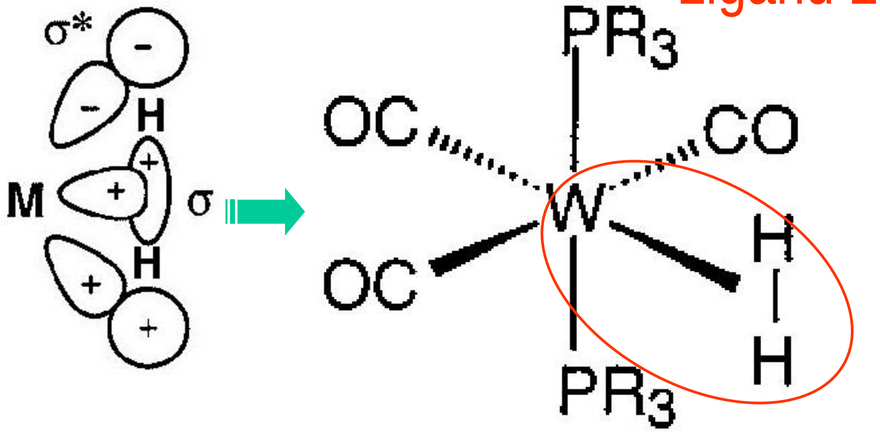


cyclopentadienyl (Cp) ring

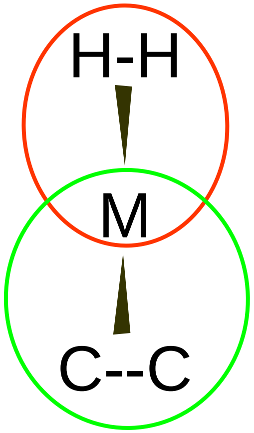


Fischer and Jira, J. Organometallic Chem. ***637***, *7 (2001).*

Ligand 2: H-H



Kubas, J. Organometallic Chem. ***635***, *37 (2001)*



H_2 loaded organometallic molecule ?

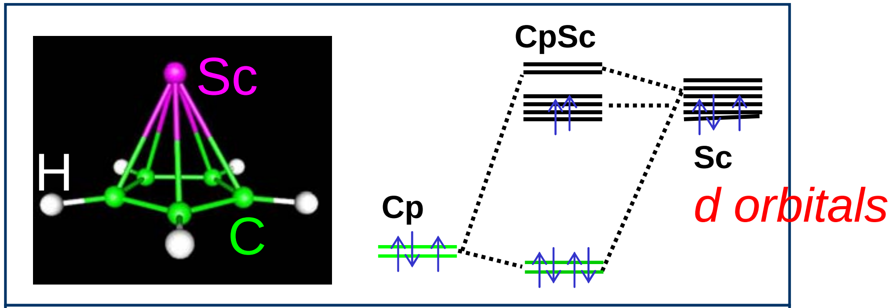
Scandium & Cp Ring: The Binding Mechanism

Configurations

Binding Energies

Sc + Cp

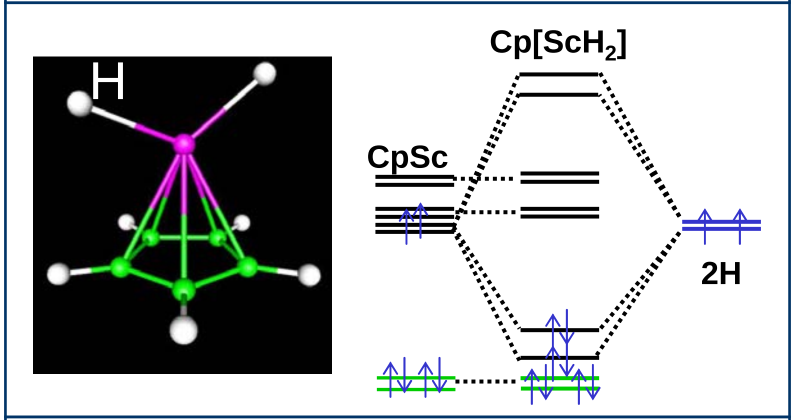
one electron transfer
-> Coulombic



3.76 eV/Sc

ScCp + H_2

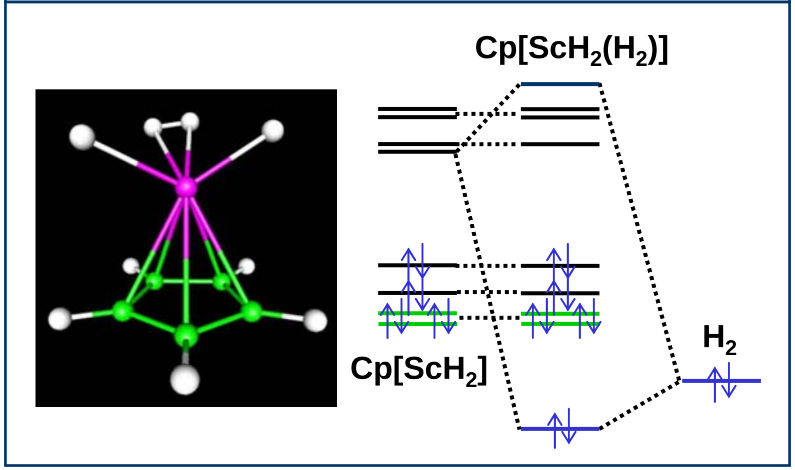
coupling between
two nearly
degenerate states



1.3 eV/H_2

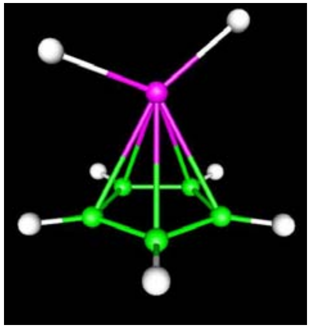
$ScCpH_2 + H_2$

coupling between
two states
energetically distant

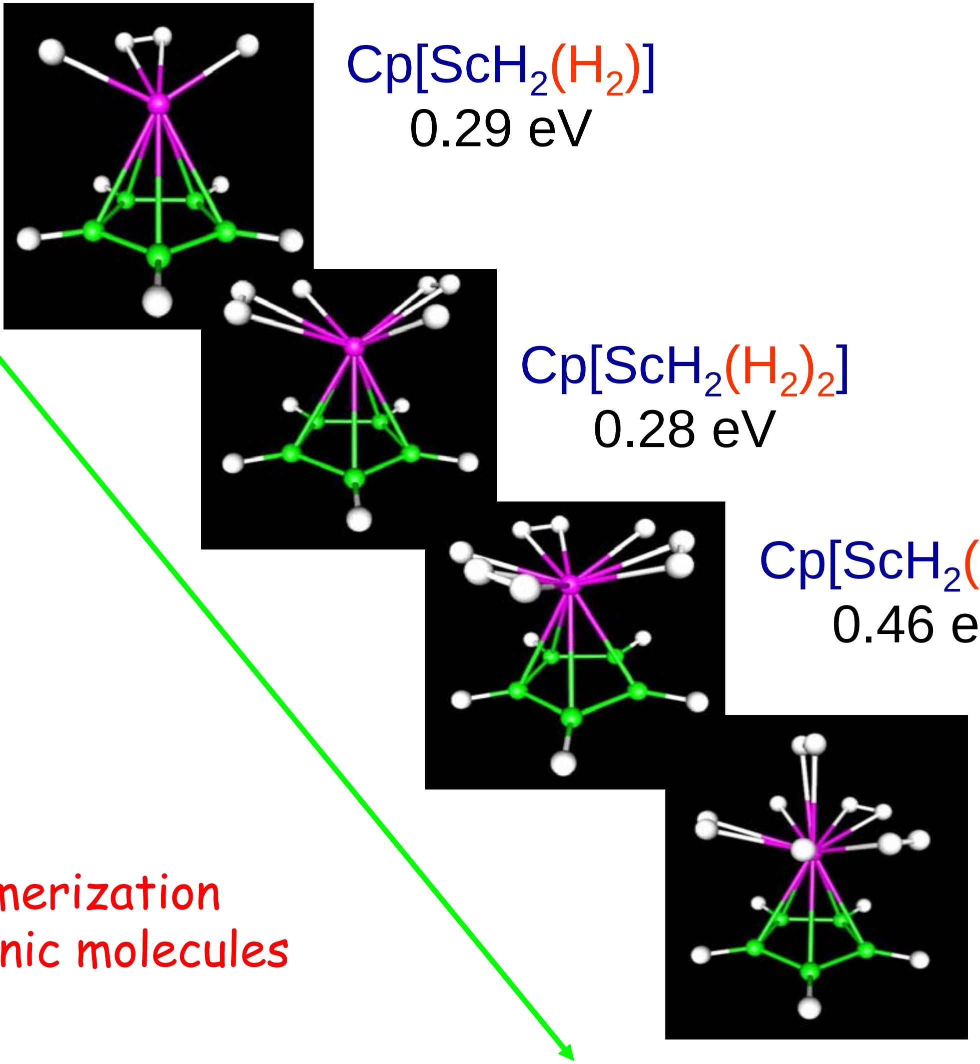


0.29 eV/H_2

Consecutive H_2 Loading to Maximum 6.7 wt%



$Cp[ScH_2]$

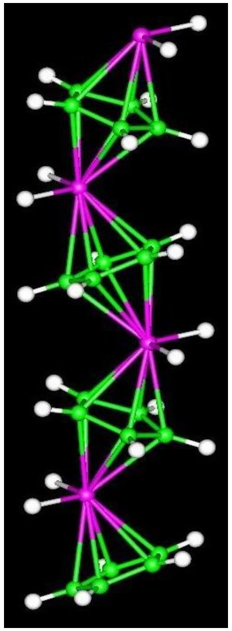


$Cp[ScH_2(H_2)]$
0.29 eV

$Cp[ScH_2(H_2)_2]$
0.28 eV

$Cp[ScH_2(H_2)_3]$
0.46 eV

$Cp[ScH_2(H_2)_4]$
0.23 eV

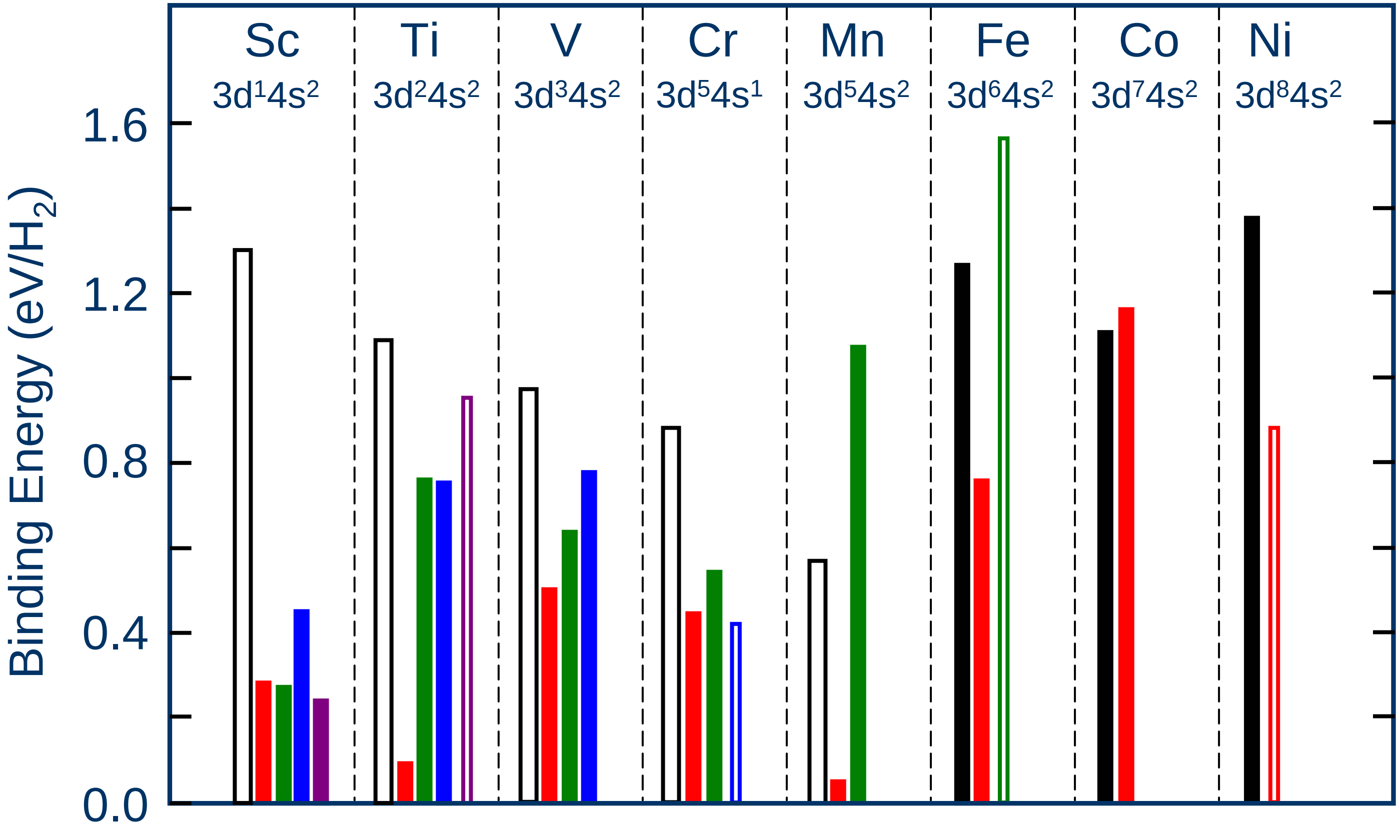


$Cp[ScH_2]_{chain}$

Polymerization
of ionic molecules

Consecutive binding of H_2

Consecutive H_2 Binding in All Cp/3d Transition Metals



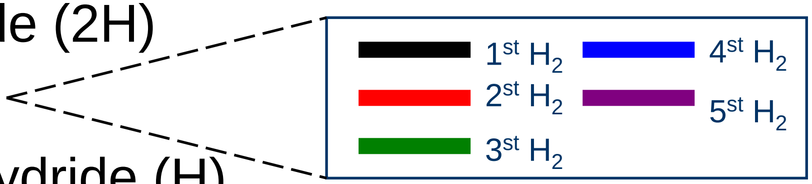
H-H Bond Lengths (A)

Sc	4x0.80
Ti	4x0.85
V	3x0.9
Cr	3x0.96
Mn	3x0.94
Fe	2x0.95
Co	2x1.10
Ni	1x0.94

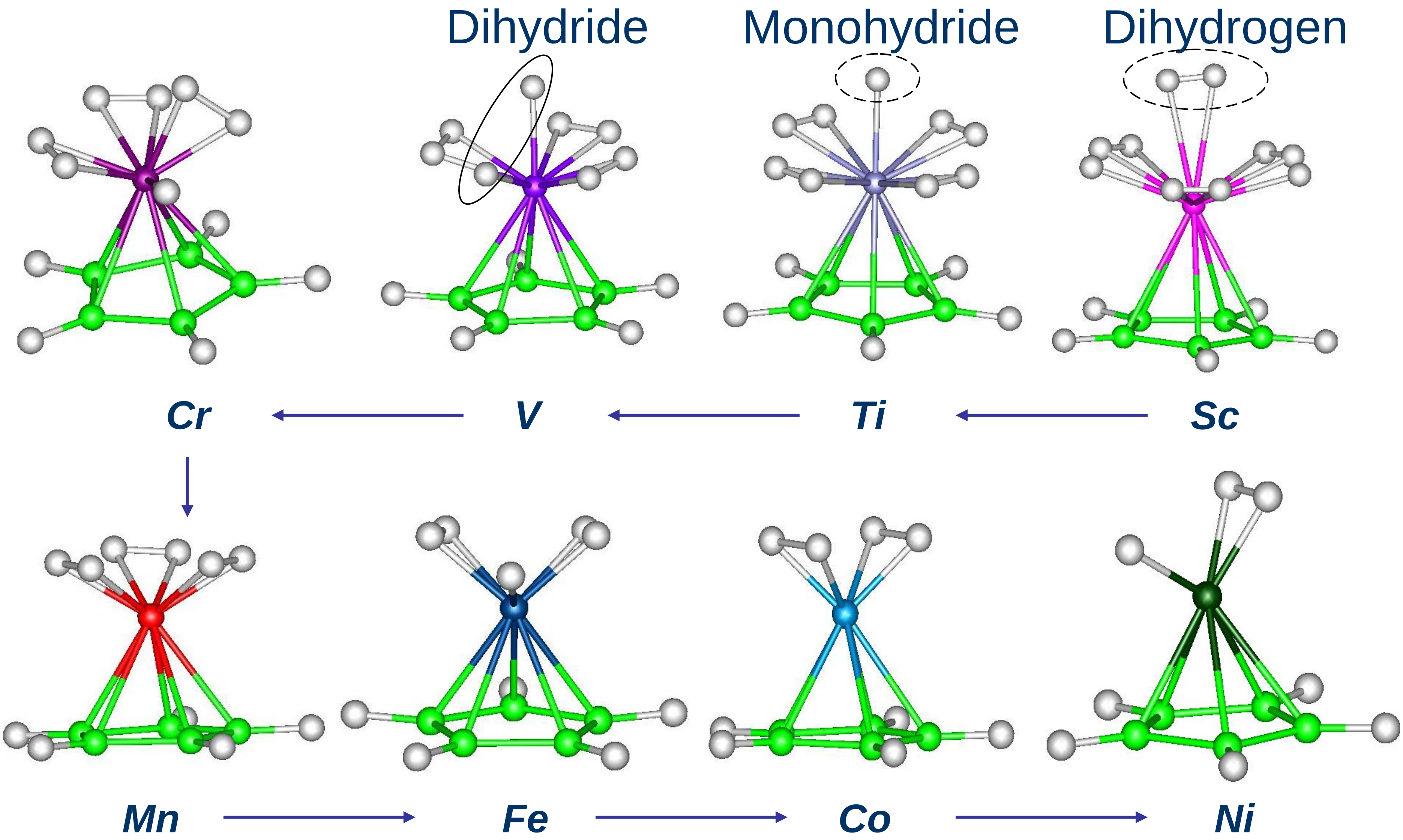
Full width open bar for dihydride (2H)

Solid bars for dihydrogen (H_2)

Half width open bar for monohydride (H)



Maximum H_2 Loading in Cp/3d Transition Metals



Dihydride

Monohydride

Dihydrogen

Cr ← ***V*** ← ***Ti*** ← ***Sc***

Mn → ***Fe*** → ***Co*** → ***Ni***

The 18-Electrons Rule Concerning CpM-*n*H

$$n_v + N_H + 5 = 18$$

n_v: number of valence electrons of the TM

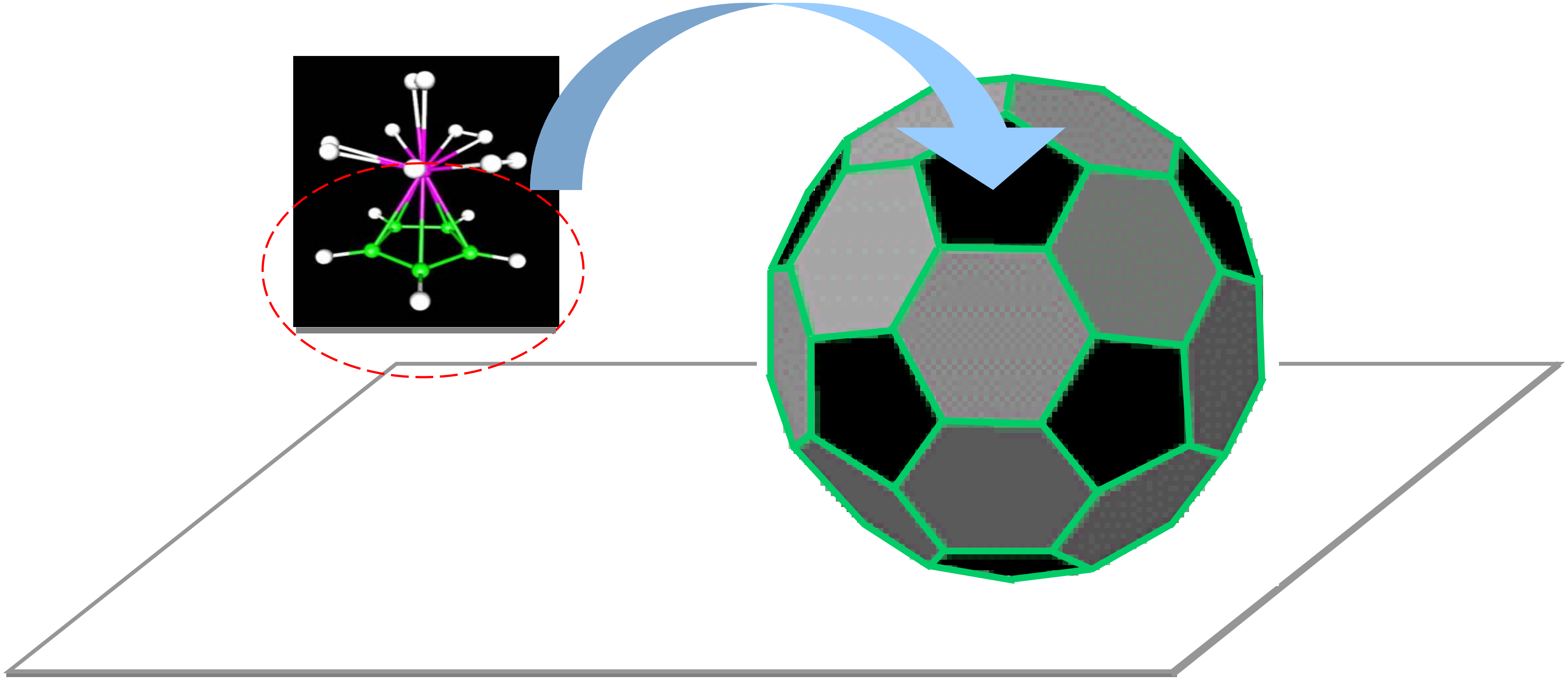
N_H : number of the H atoms the TM can bind

5: number of the π electrons in a Cp ring

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
n_v	**3**	**4**	5	6	7	8	9	10
N_H	**10**	**9**	8	7	6	5	4	3
E_b(eV)	**3.76**	**3.87**	3.47	2.30	2.69	2.97	3.27	3.02

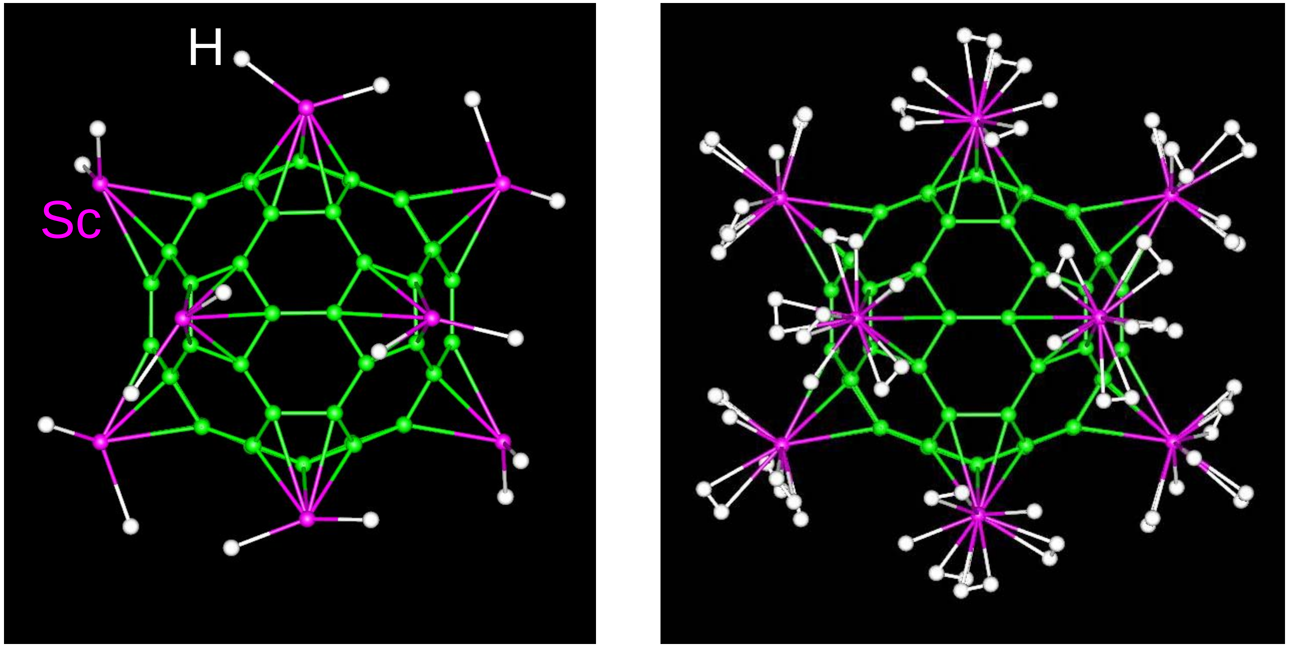
- Sc has the second largest E_b

From Cp Ring to Larger Carbon Molecules



- Transfer the Cp-metal-H clusters onto a buckyball to eliminate the dipole induced polymerization

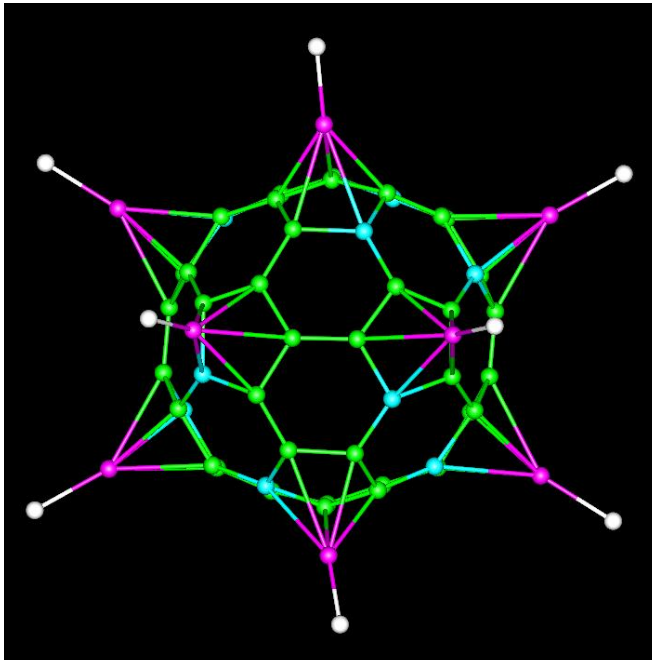
12-ScH_2 Loaded C_{60}: 7.0 wt% Storage Capacity

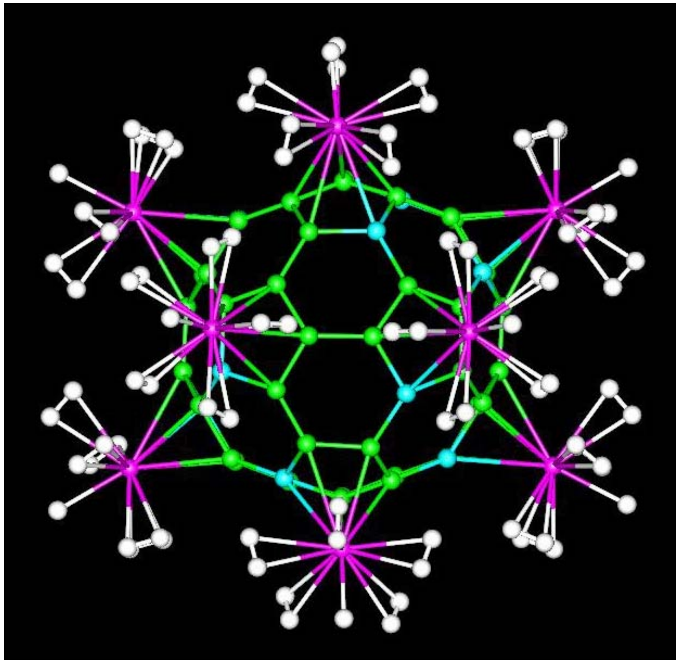


$$C_{60}[ScH_2]_{12} \xrightleftharpoons{48H_2} C_{60}[ScH_2(H_2)_4]_{12}$$

- Very similar binding energies to those of a Cp ring for the hydrides and the H_2 molecules

12-ScH Loaded $C_{48}B_{12}$: 8.8 wt% Capacity

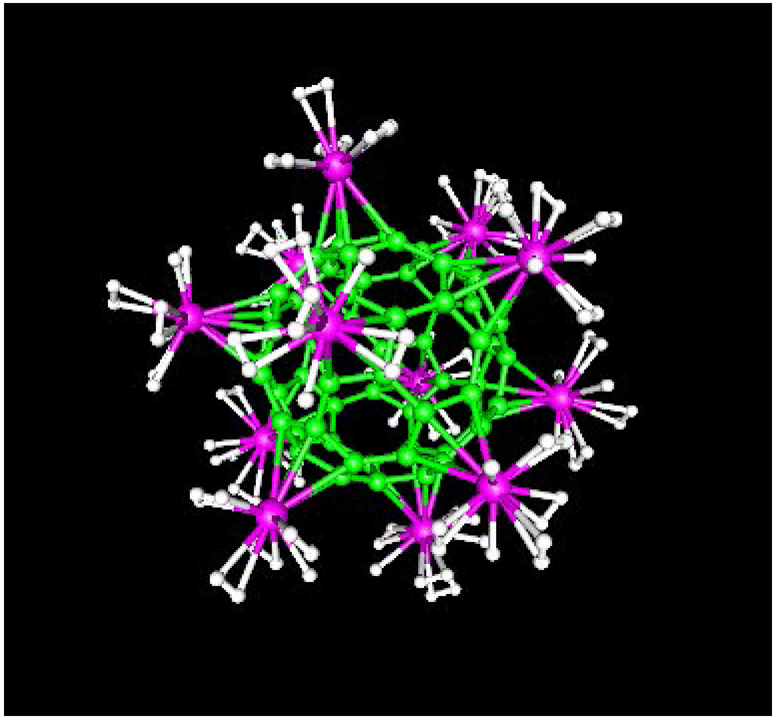




$$C_{48}B_{12}[ScH]_{12} \overset{60H_2}{\rightleftharpoons} C_{48}B_{12}[ScH(H_2)_5]_{12}$$

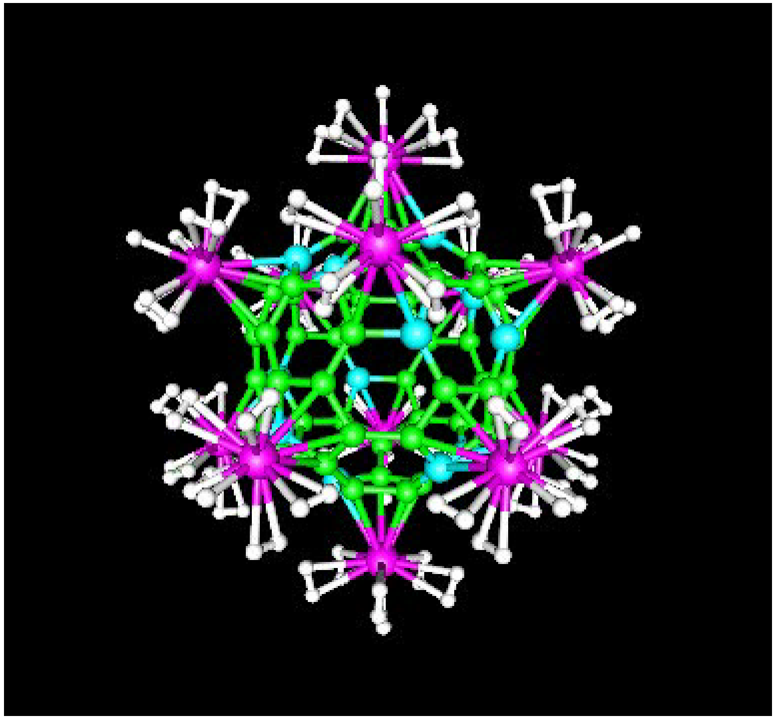
- One more electron is transferred from each Sc to the corresponding pentagon, which enhances both the Sc-C_{60} binding and the hydrogen storage capacity

Three-Dimensional View of the Complexes



$C_{60}[ScH_2(H_2)_4]_{12}$

$C_{48}B_{12}[ScH(H_2)_5]_{12}$



Formation Energy of the Organometallic Buckyballs

Energy of carbon molecules

$$F = (E_{tot} - \varepsilon - n_H \mu_H) / n_M - \varepsilon_M$$

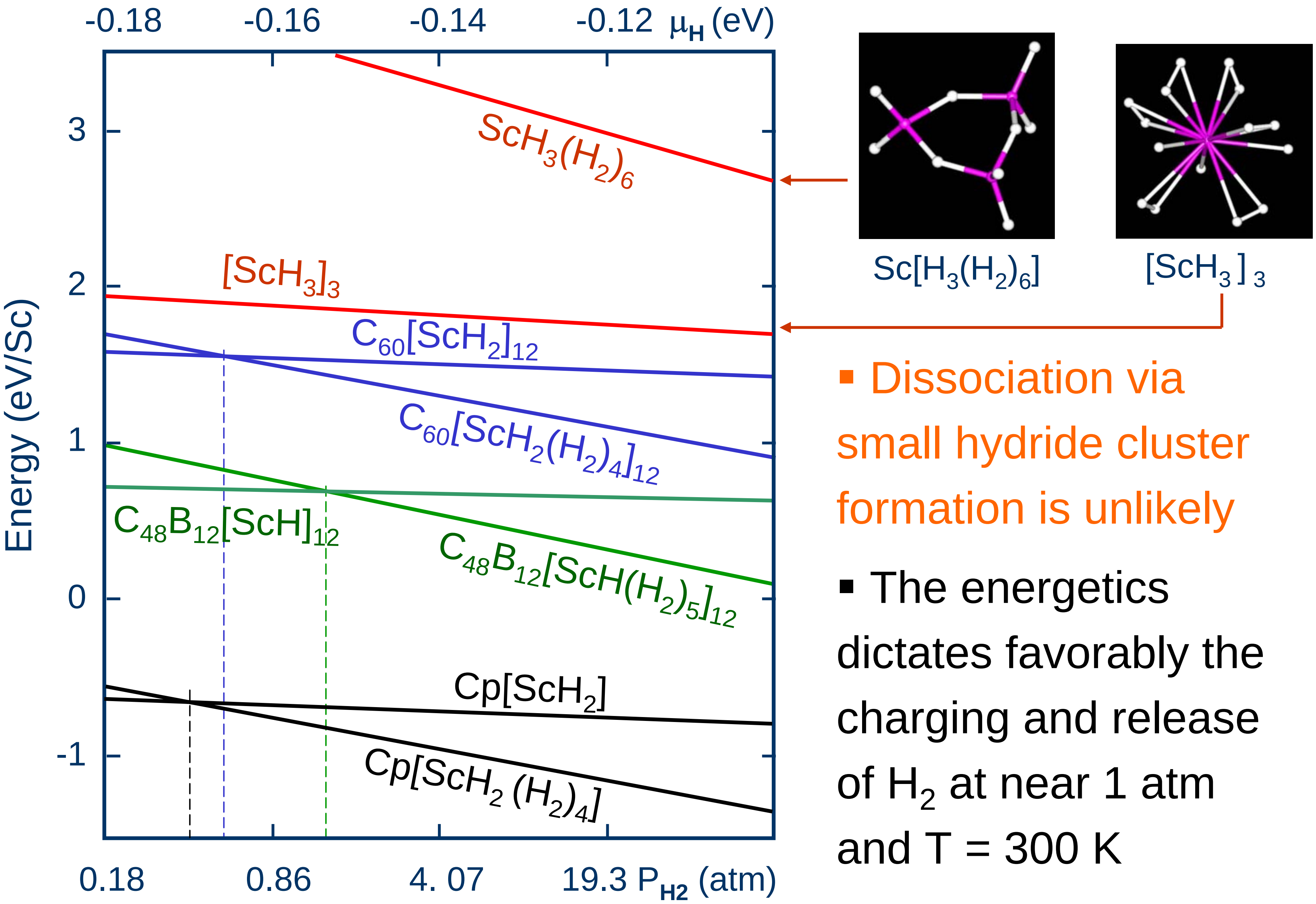
Total energy

Cohesive energy of metal crystal

$$\mu_H(T, p) = \mu_H(T, p^0) + \frac{1}{2} kT \ln(\frac{p}{p^0})$$

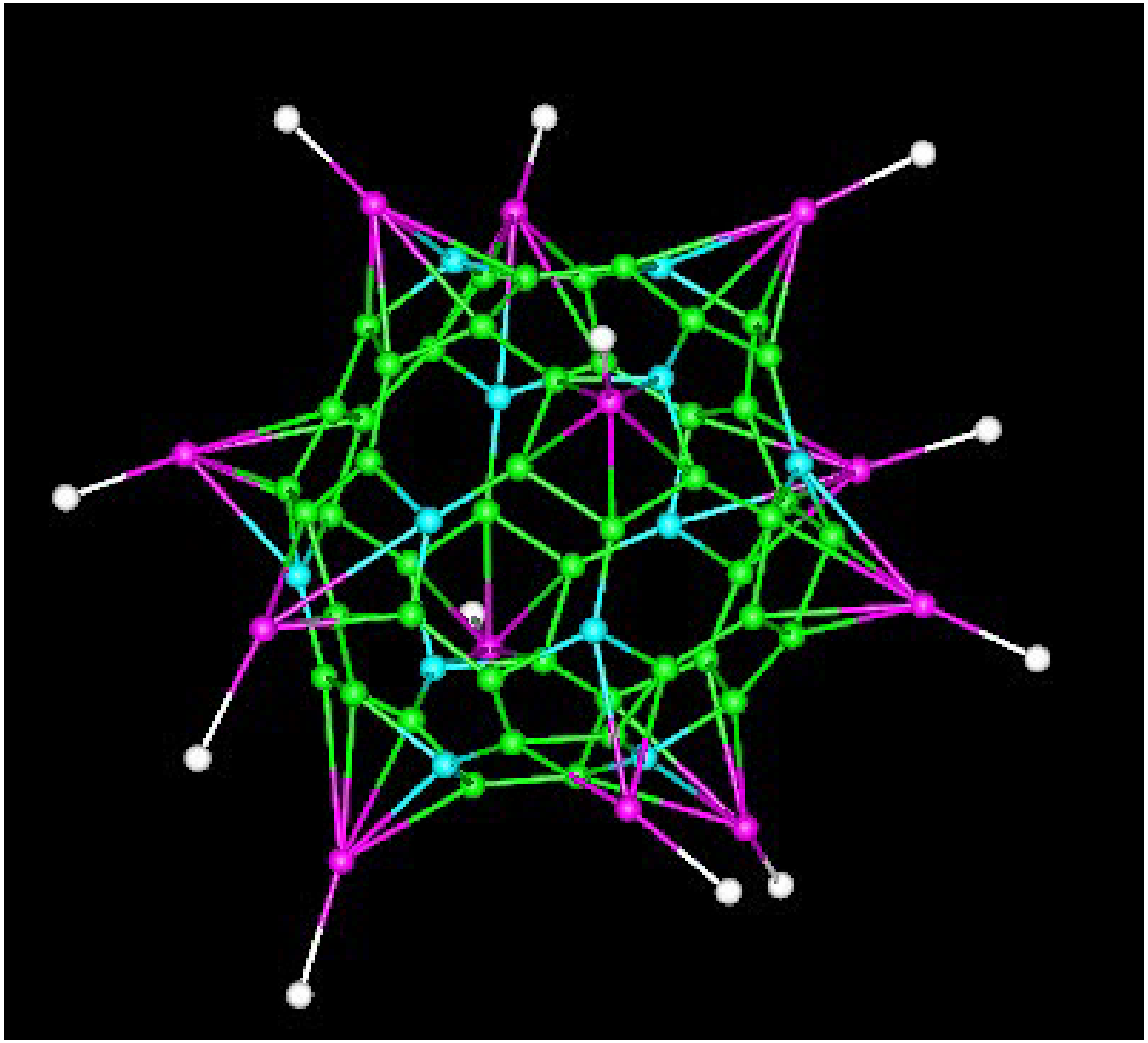
*Reuter and Scheffler, PRB **65**, 035406 (2001).*

Reversible Storage at Room Temperature



- Dissociation via small hydride cluster formation is unlikely
- The energetics dictates favorably the charging and release of H_2 at near 1 atm and T = 300 K

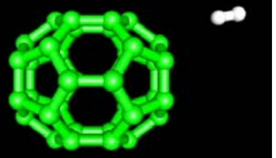
Molecular Dynamic Simulation of Host Stability



T = 1000K
t = 10000 x 0.4 fs after 4500 time step preheating

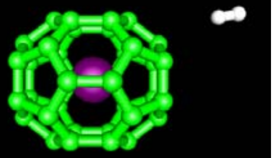
H Storage in Light Metal Doped Fullerenes

C_{36}



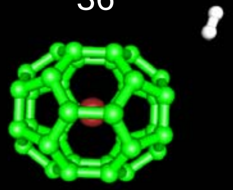
0.07

$C_{36}Li$



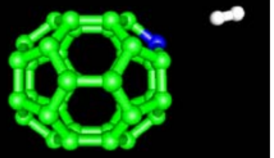
0.07

$C_{36}F$



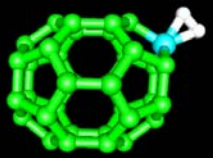
0.04

$C_{35}N$



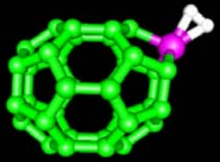
0.06

$C_{35}B$



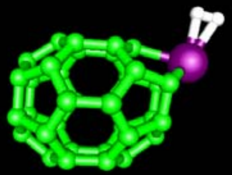
0.39

$C_{35}Be$



0.65

$C_{35}Li$

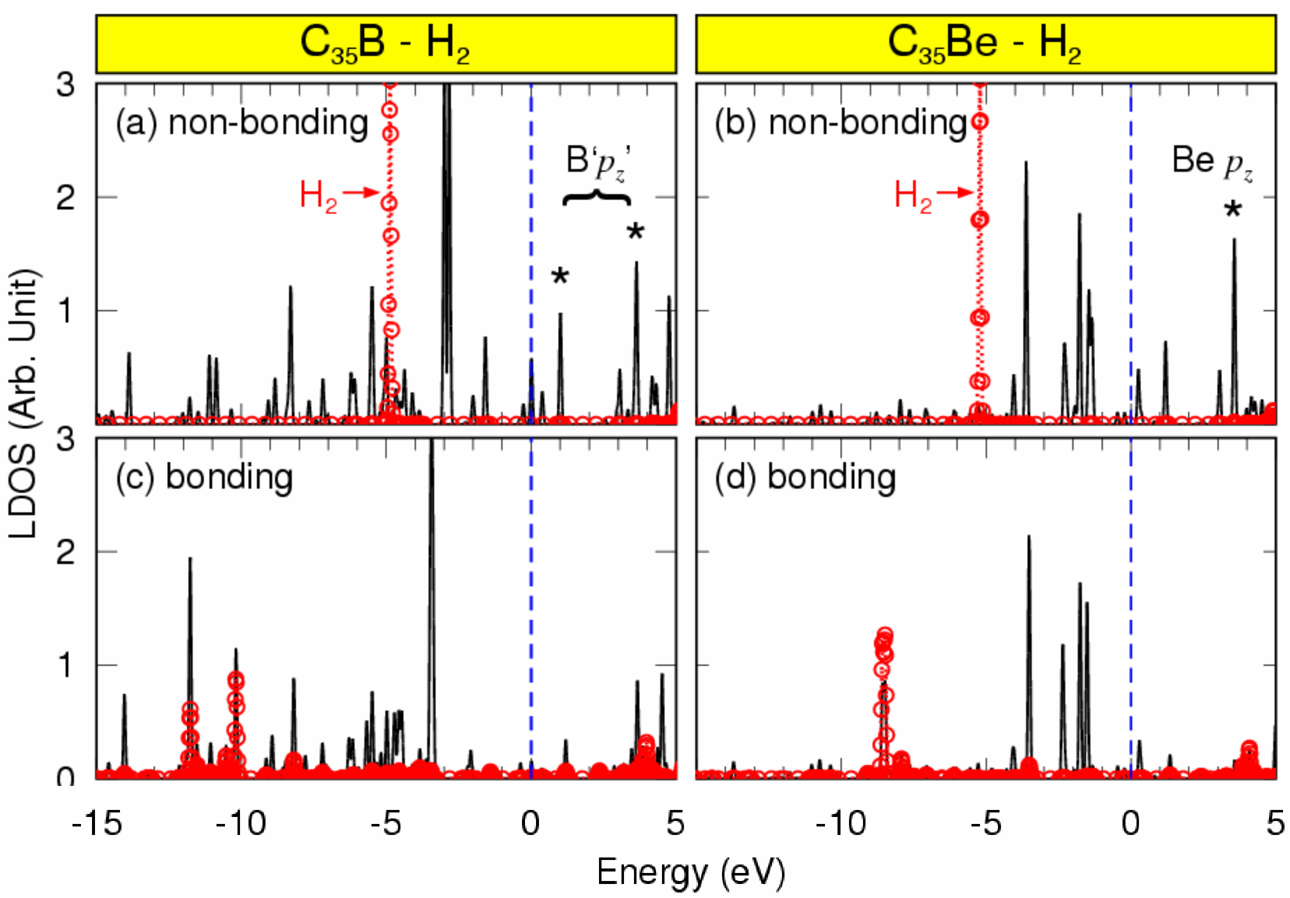


0.14

Unit: eV/H_2

- Exceptionally large binding energy for B and Be

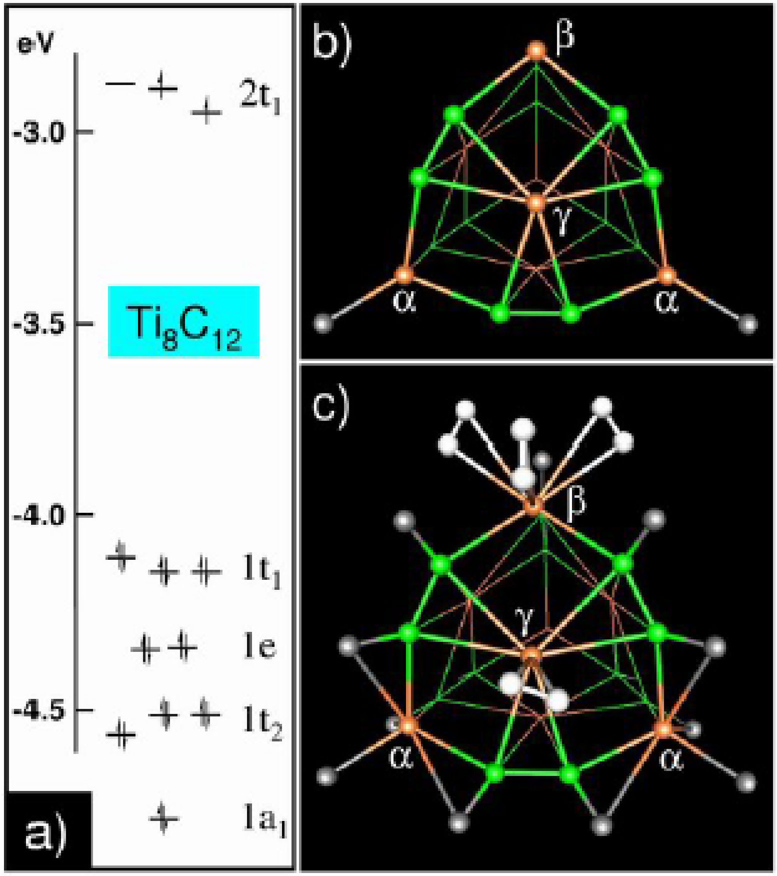
Dihydrogen Binding to Localized Empty *p* Orbital



- H_2 σ state and impurity p_z state are strongly affected as a result of dihydrogen binding
- A more localized Be p_z orbital (single peak) gives larger E_B

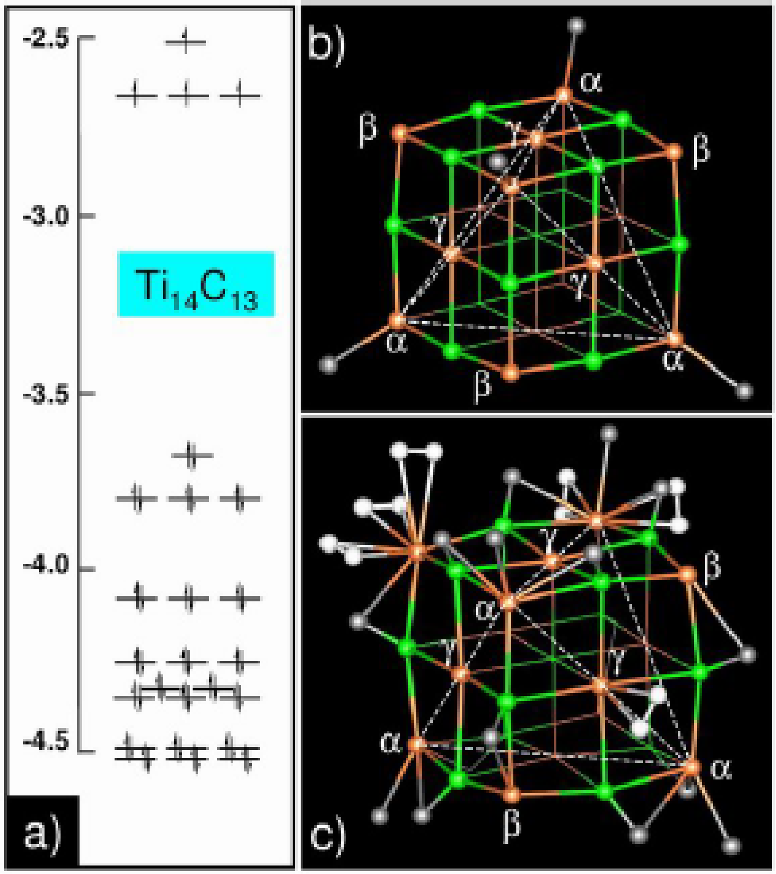
H Storage in Other Organometallic Systems

Metallocarbohedrenes (MetCar)



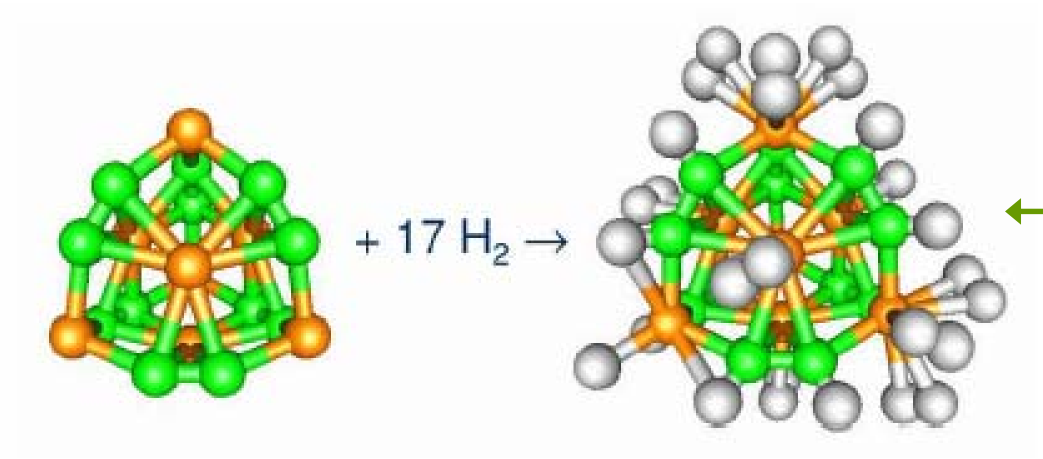
β-Ti	γ-Ti	C	Ti
15.5	31.8	61.7	137
dihydrogen		hydride	

Titanium Carbide Nanocrystals



α-Ti	β-Ti	γ-Ti	C	Ti
18.3	19.3	17.4	126.4	85.9
	36.7		(kJ/mol-H_2)	

Total Capacity @ Full Hydrogen Sorption

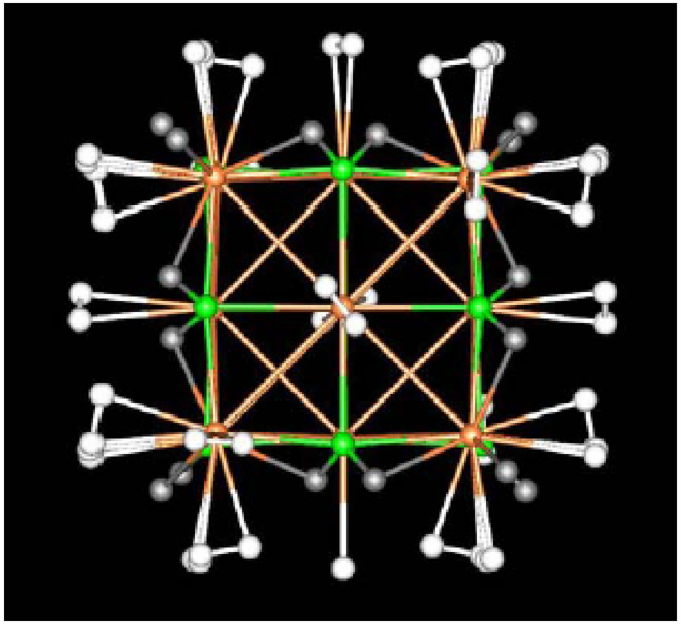


MetCar

6.1 total wt%

Ti carbide nanocrystal

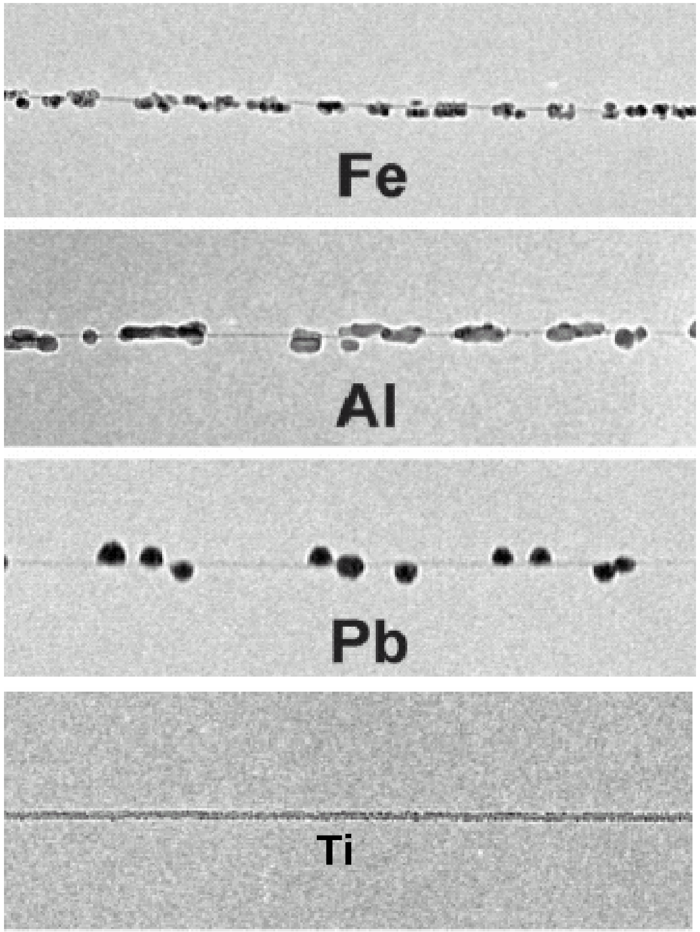
7.7 total wt%



- H sorption may not depend on the TM incorporation details, as long as abundant empty d orbitals are made available

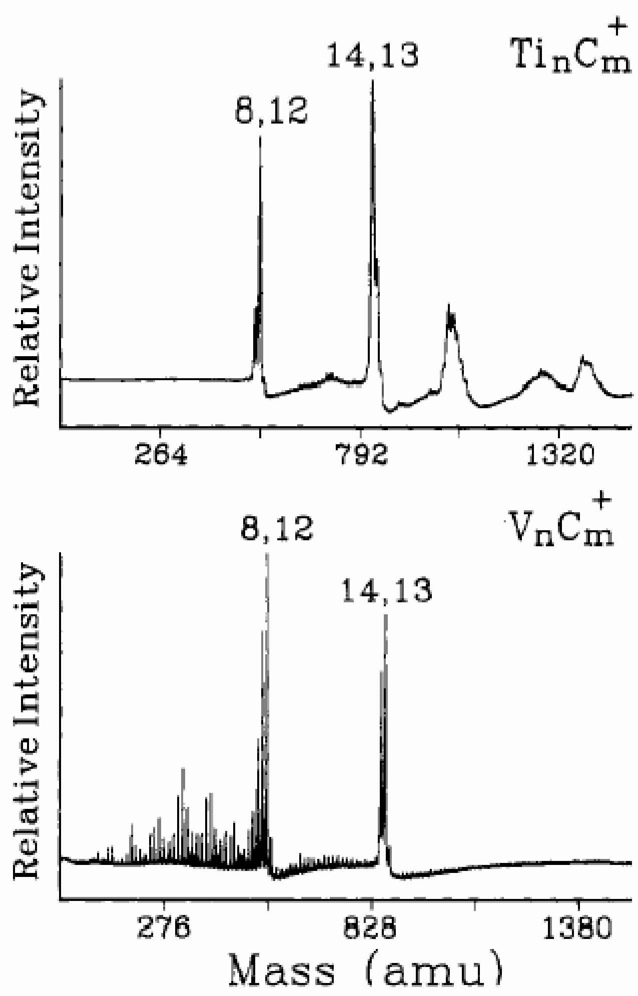
Experimental Relevance

- Metal-coated nanotubes



Zhang & Dai, APL 77, 3051 (2000)

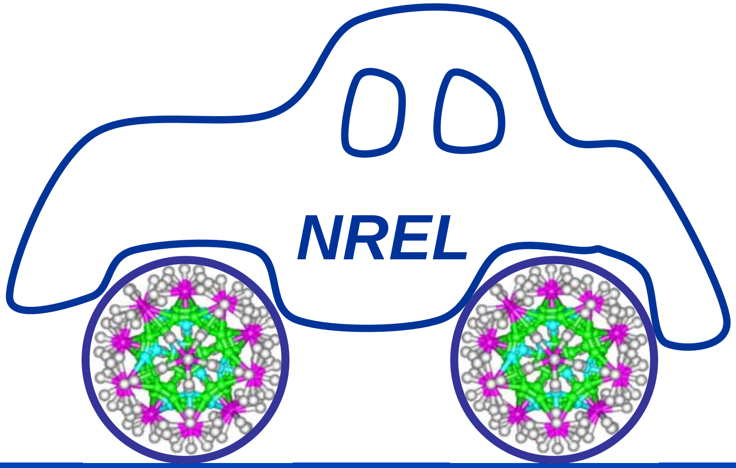
- MetCars & nanocrystals



Pilgrim & Duncan, JACS 115, 9724 (1993)

Conclusion

- Transition metal (TM) empty orbitals are good "containers" for non-dissociated H_2
- Buckyballs and other carbon-backbone materials could be superior for separating TM atoms for H storage
- Sc, Ti, V have more empty *d*-orbitals, strong binding to the carbon backbones, and nearly ideal binding energies with H_2



References

1. Zhao, Kim, Dillon, Heben, and Zhang, Phys. Rev. Lett. **94** (April), 155504 (2005) TM coated C_{60}
2. Yildirim and Ciraci, Phys. Rev. Lett **94** (May), 175501 (2005) TM coated carbon nanotubes
3. Kim, Zhao, Williamson, Heben, and Zhang (submitted) Light metal doped fullerenes
4. Zhao, Dillon, Kim, Heben, and Zhang (submitted) MetCar and nanocrystals

Methods: Spin-Polarized First-Principles Calculations

- VASP package

  G. Kresse *et al.*, http://cms.mpi.univie.ac.at/VASP

- Ultrasoft pseudopotential
- Generalized gradient approximation (GGA) with PW91 exchange-correlation functional

  Perdew *et al.*, PRB **46**, 6671 (1992)

- Supercell approach with cell dimension = (25 Å)^3
- Plane wave basis with cutoff energy = 400 eV

- Results are checked using Projector Augmented Wave (PAW) method and PBE exchange-correlation

  Perdew, Burke, Ernzerhof, PRL **77**, 3865 (1996)