

Innovation for Our Energy Future

Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study

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H Binding Energy in Various Storage Hosts





Binding Energy Impacts System Design



A large binding energy will lead to energy penalties during charge & discharge, prohibit on-board recharging, and reduce the system capacities (space for heat exchangers)



Outline

- Enhanced H₂ binding in boron-doped fullerenes *Phys. Rev. Lett.* 96, 016102 (2006)
- Kubas complex of (transition metal-H₂) in organometallic molecules *Phys. Rev. Lett.* 94, 155504 (2005)
- Ti_mC_n nanocrystals: embedded metal atoms to
 avoid clustering *Chem. Phys. Lett.* 425, 273 (2006)

Objective: Establishing the theoretical underpinning for molecular H_2 adsorption in the 10-50 kJ/mol energy range.



A Few Words about First-Principles Methods

 We used a combination of the density functional theory within LDA or GGA approximation and the quantum Monte Carlo method

 The only input is the atomic numbers and the approximate atomic geometries from which the energy minimum is searched by a force minimization

• We develop models only to interpret the results, never to dictate the calculations by any adjustable parameters.

Why Molecular Hydrogen?



- No noticeable barrier for adsorption
- No additional barrier for desorption other than the adsorption energy
- Maintain the integrity of H₂ in the entire process

→ superb adsorption/desorption kinetics.

H₂ Binding to Light Element-Doped C₃₆

Bare C_{36} : 0.065 eV (1 eV \cong 100 kJ/mol)





Perhaps the largest curvature existing

- Weak molecular binding to fullerenes regardless of the curvature
- Endohedral doping does not help, whereas substitutional may, but need to find out which impurity and why.

H₂ Binding Mechanism: Electronic Picture

Chemical Binding

Boron

Beryllium



By electronically mixing the occupied H₂ state with the *empty p_z* state of the dopant, the system gains electronic energy.

H₂ Binding Mechanism: Bond Picture

 Charge-density change due to H₂ adsorption can tell if bond forms between the H₂ and dopant

solid contour = accumulation; dashed contour = depletion

More charge transfer
 from H₂ to C₃₅B, but the
 transfer from H₂ to C₃₅Be
 is much more *localized* in
 the "bond" region



• H_2 binding energy = 0.39 eV for B & 0.65 eV for Be.

Multi B (Be) Sites on C₆₀ & Their H₂ Binding

 (Multi) boron-doped C₆₀ has been experimentally demonstrated, and hence it can be used to test our theory



• Binding energy is nearly a constant for Be, but drops a lot for B at higher H concentration due to less localized p_z orbital

Recent NMR and inelastic neutron scattering studies of Bdoped nanotubes indicate the existence of boron enhancement.

Key Results from Metal Doping

- light-metal doping can in principle enhance the binding energy of H₂, but it requires the following conditions to be simultaneously satisfied:
- (a) Presence of **nonbonding** orbital like the p_z state to accommodate the H_2 molecule (site availability)
- (b) The state needs to be **empty** with adequate energy level position with respect to that of the σ level of H_2 (enabling energy gain by hybridization)

(c) Highly localized charge transfer (maximizing bond charge) Phys. Rev. Lett. 96, 016102 (2006)

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Can We Generalize the Key Findings ?

- Is there any other dopant, beyond just the light-metal atoms, that can provide, on a per atom basis, more abundant nonbonding and localized orbitals ?
- \rightarrow Yes, transition metal (TM) atoms

At least in their nanocluster form, a significant number of the d-orbitals may have not been used up for the chemical bonding.



The Kubas Complexes



In 1984, Kubas experimentally discovered the molecular complexes, in which transition metal atom binds molecular hydrogen through a three center-two electron interaction

• A backdonation of electrons from metal *d* orbital to empty $H_2 \sigma^*$ orbital was implicated for the observation.

Organometallic Molecule with Carbon Ring



Scandium & Cp Ring: The Binding Mechanism

Configurations

Sc + Cp

one electron transfer -> Coulombic

 $ScCp + H_2$

coupling between two nearly degenerate states

 $ScCpH_2 + H_2$

coupling between two states energetically distant



Consecutive H₂ Loading to a Removable 6.7 wt%



Consecutive H₂ Binding to 3d Metal-Cp Complex



Full width open bar for dihydride (2H) Half width open bar for monohydride (H) Solid bars for dihydrogen (H₂) <<<



The 18-Electron Rule for H Sorption on TM

In all cases, we have $n_v + N_H + 5 = 18$ where

- n_{v} : number of s + d electrons of the TM atom
- N_H : number of the H atoms a TM can bind
- **5**: number of the π electrons in the Cp ring

	Sc	Ti	V	Cr	Mn	Fe	Со	Ni
$egin{array}{c} n_v \ N_H \end{array}$	3	4	5	6	7	8	9	10
	10	9	8	7	6	5	4	3

Phys. Rev. Lett. 94 (April), 155504 (2005)



A Problem: Polymerization of CpTM Complexes



 After the removal of H₂, the CpTM complexes are likely to form polymerized chains due to their mutual Coulomb attraction, thereby loosing the ability to retake molecular hydrogen



Cp[ScH₂] chain

What Can One Do?

One can assemble the organometallic molecules into more stable forms

- (1) TM-coated buckyball or nanotubes;
- (2) TM-decorated polymers;
- (3) TM-decorated metalorganic frameworks;
- (4) organometallic supra molecules;
- (5) metal carbide nanocrystals;
- (6) or whatever that may work.



From Cp-TM Complex to TM-Coated Buckyball



• Organizing the Cp-TM-H clusters into a buckyball can help to eliminate dipole-induced polymerization



$12-ScH_2$ Loaded C₆₀: 7.0 wt% H₂



 $C_{60}[\text{ScH}_2]_{12} \xrightarrow{48H_2} C_{60}[\text{ScH}_2(H_2)_4]_{12}$

 Very similar binding energies to those of a Cp ring for the hydrides and the H₂ molecules

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12-ScH Loaded C₄₈B₁₂: 8.8 wt% H₂



One more electron is transferred from each Sc to the corresponding pentagon, which enhances both the Sc-C₆₀ binding and the hydrogen storage capacity.

Will the TM Coated Fullerenes Disintegrate?



First-Principles Molecular Dynamic Simulation of $C_{48}B_{12}$ [ScH]₁₂



T = 727°C, t = 10 ps, Δt = 0.4 fs (= 25,000 time steps)

 See no sign of disintegration of the coated fullerenes, nor TM clustering.



Enhanced H₂ Binding to Ti-Coated Carbon Nanotubes Yildirim and Ciraci, PRL 94 (May), 175501 (2005)



FIG. 3 (color online). Two high-density hydrogen coverage on a Ti-coated (8, 0) nanotube.

Enhanced H₂ Binding to Cr Atom Gagliardi and Pyykko, JACS 126, 15014 (2004)



62 kJ/mol-H₂ (exothermic)

1174 J. Chem. Theory Comput., Vol. 1, No. 6, 2005



Figure 3. The structure of ZrH₁₆@C₆₀.



Figure 4. The structure of two TiH₁₆ inside C₁₁₄.

Gagliardi

Enhanced H₂ Binding to Ni-Coated C₆₀

Shin, Yang, Goddard III, and Kang, APL **88**, 053111 (2006)



FIG. 3. (Color online) Hydrogenated Ni-dispersed C_{60} . Three hydrogen molecules could be adsorbed to a Ni atom. Carbon, nickel, and hydrogen atoms are shown in silver, yellow, and black, respectively.

First H₂ adsorption is 77.7 kJ/mol; 6.8 wt %

Metal Clustering Could Be a Problem

Sun, Wang, Jena, and Kawazoe, JACS **127**, 14582 (2005)





2.07 eV/Ti

0.0 eV/Ti

Thermodynamically, a clustered phase is noticeably more stable.

However, there are also other possibilities ...



In B doped fullerene, clustering energy is substantially smaller, and Sc prefers to coat nano-surfaces evenly.

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Embedding Transition Metal Atoms into Carbon Network

Zhao, et al., Chem. Phys. Lett. 425, 273 (2006)



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Experimental Observations: Ti_8C_{12} and $Ti_{14}C_{13}$



Guo et al., Science 255, 1411(1992)

Pilgrim and Duncan, JACS **115,** 9724 (1993)

Ti₈C₁₂: Total Hydrogen Capacity of 6.1 wt%



 $Ti_8C_{12}H_2$



 $Ti_8C_{12}H_{34}$

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	# of H atoms	$E_b (eV/H_2)$
Hydrides on Ti:	2	1.43
Hydrides on C:	12	0.64
Dihydrogen (H ₂):	10	0.17-0.33

 $+ 16 H_2 =$

Ti₁₄C₁₃: Total Hydrogen Capacity of 7.7 wt%

 $+ 19 H_2 =$



 $Ti_{14}C_{13}H_4$



	# of H atoms	$E_b (eV/H_2)$
Hydrides on Ti:	4	0.89
Hydrides on C:	12	1.31
Dihydrogen (H ₂):	10	0.18-0.38
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Lee, Choi, and Ihm Combinatorial Search for Enhanced H₂ Binding in Polymers PRL 97, 056104 (2006)





(a) *Cis*-polyacetylene, (b) and (c) *Trans*-polyacetylenes, (d) Polypyrrole,
(e) and (f) Polyaniline; The transition
metal is Ti

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Summary

 First-principles calculations establish a unified Kubas-type mechanism for enhanced H₂ binding on metal atoms on carbon hosts: *Non-bonding, empty, and localized metal states*

B-doped fullerenes & TM coated buckyballs are among the potential systems to first try experimentally

 Metal clustering is a challenge but may be avoidable by a better choice of the host systems

In any case, it is unlikely and probably unnecessary that the ultimate H_2 adsorbate system is thermodynamically stable; kinetic stability is more likely and, in most applications, enough

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Methods of Calculations

 First-principles density functional theory within the LDA approximation for light elements
 Validated by Quantum Monte Carlo calculations

- GGA approximation for 3d transition metals
 Validation by comparing calculated Kubas molecule
 with experiment
- Ultrasoft pseudopotentials and projector augmented wave method; converged results.

How Reliable Are the $C_{35}B$ Results?



• 0.2 eV (QMC) vs. 0.39 eV (LDA) and -0.03 eV (GGA) for H_2 binding to $C_{35}B$

The 0.2-eV QMC energy here represents a significant increase from that of a typical vdW energy of 0.04 eV.

Chemistry of the Ti₈C₁₂



MetCar is full of TM atoms with unsaturated d states, which could be beneficial for H₂ binding, while the carbon backbone serves to stabilize the structure from metal clustering.

A Microscopic Model for the Spillover @ MetaCar



A Diamond Lattice of the MetCars

