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Fundamental studies of hydrogen storage and catalysis

Balakrishnan Naduvalath
University of Nevada Las Vegas, naduvala@unlv.nevada.edu

Fundamental Studies of Hydrogen storage and catalysis

Balakrishnan Naduvalath

Department of Chemistry, UNLV

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Group members/Collaborators

UNLV

Dr. T. J. Dhilip Kumar (Chemistry)

Dr. Tarakeshwar Pilarisetty (Chemistry)

Dr. Philippe Weck (Chemistry)

Dr. Eunja Kim (Physics)

External Collaborators

Dr. Hansong Cheng (Air Products & Chemicals, Inc.)

Prof. Robert Forrey (Penn State)

Prof. Boris Yakobson (Rice University)

Industrial partner

UTC

Overview

- Catalyst
  - Size effects
  - Alloying
  - Catalyst support
- Hydrogen storage
- Design of novel nanomaterials

Approach

$$H\Psi = E\Psi$$

- First principles calculations
- Density functional theory
- Allows detailed prediction of electronic structure and ground state properties

Hydrogen storage systems

- Liquid/compressed hydrogen
- Metal hydrides/chemical hydrides
- Sorption systems
  - Metal-organic frameworks (MOFs)
  - Pristine and functionalized C and BN nanotubes, graphitic systems,…

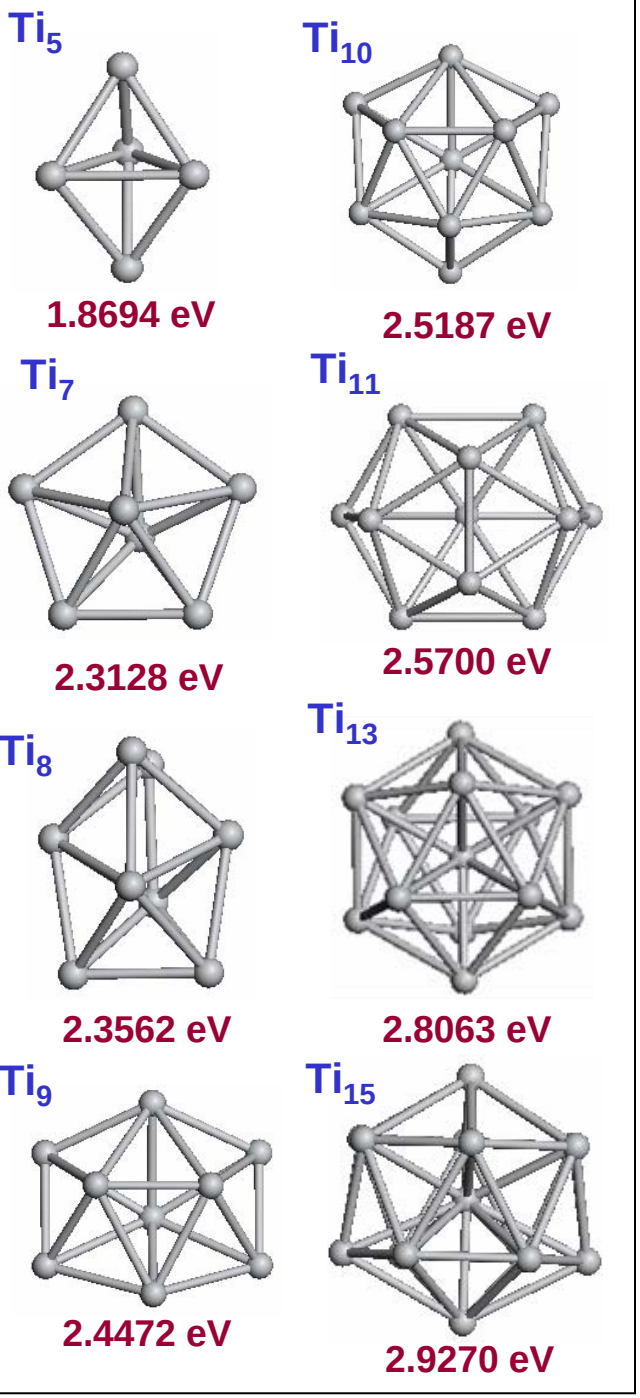
Role of Ti as a catalyst/dopant in hydrogen storage materials

Reversible hydrogen storage in $NaAlH_4$

- $NaAlH_4 \leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \leftrightarrow NaH + Al + 3/2\ H_2$
  - The reverse reaction (hydrogenation) occurs much faster in the presence of small amounts of Ti catalyst (*Bogdanovic et al., J. Alloys and Comp.* ***253****, 1 (1997)*)
  - The mechanism of Ti-catalyzed reversible hydrogen storage is still not understood
- Ti-doped nanostructures have also been proposed as potential hydrogen storage media (*Yildirim and Ciraci, Phys. Rev. Lett.* ***94****, 175501 (2005)*)

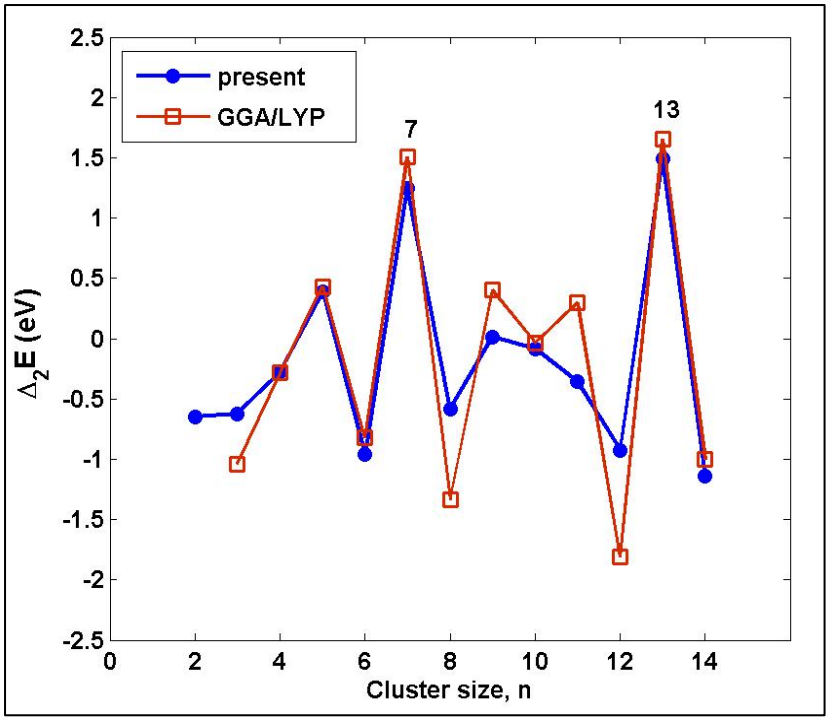
Electronic structure of Titanium clusters

- Ti_n clusters evolve on **Pentagonal** growth pattern.
- $\Delta_2 E$ indicates Ti_7 and Ti_{13} clusters are highly stable which agrees well with the experimental **CID** rates.



Second Energy Difference

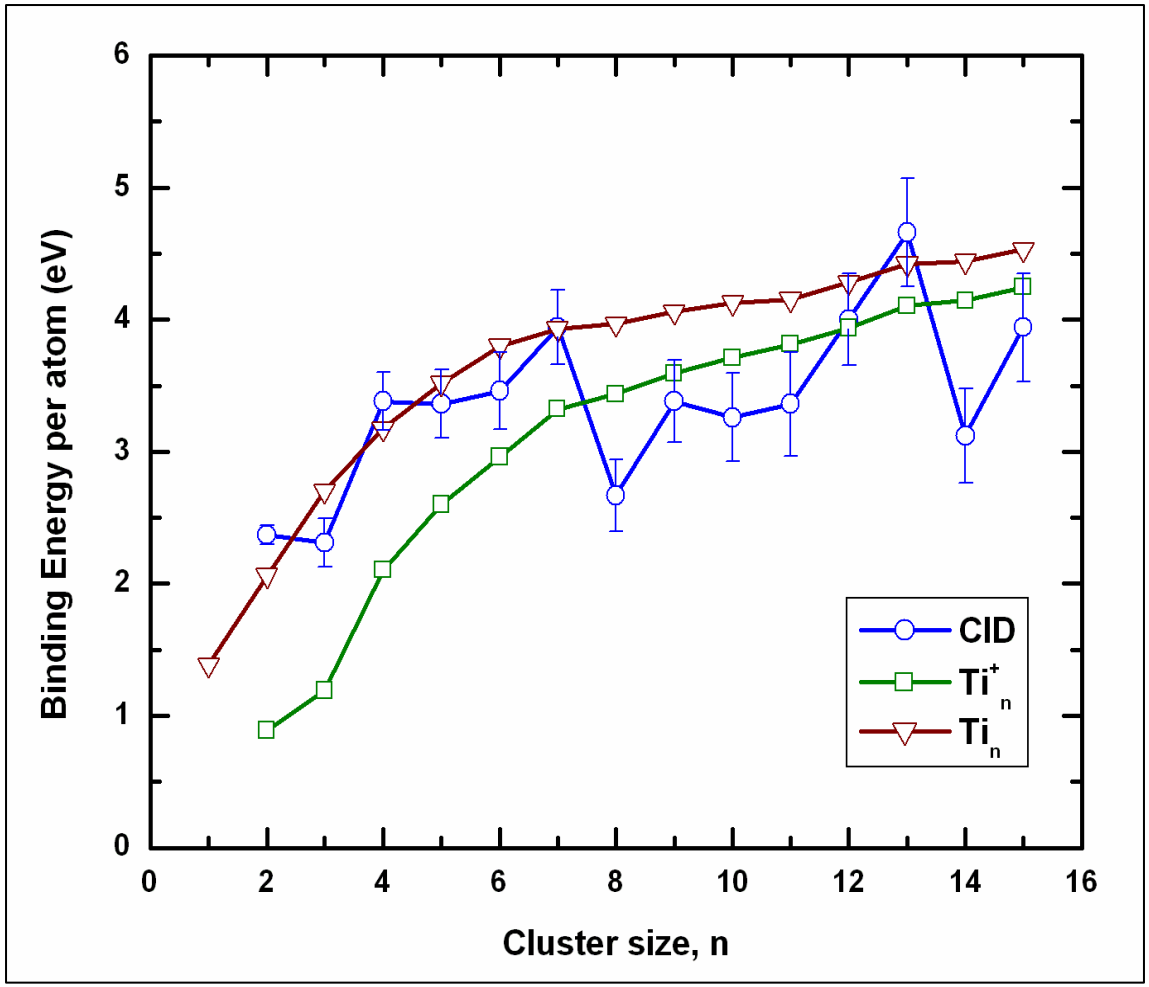
$$\Delta_2 E = E(n+1) + E(n-1) - 2E(n)$$



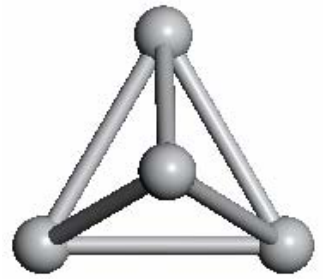
Energetics of small Titanium clusters

Binding Energy

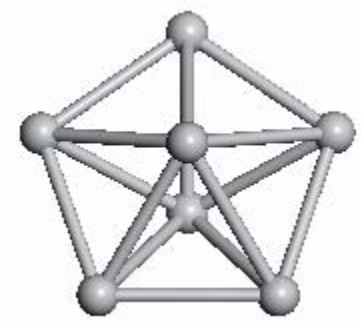
$$\Delta E_{BE} = \left[E(Ti_n) - nE(Ti_n) \right] / n, \quad (n = 2,3,..15)$$



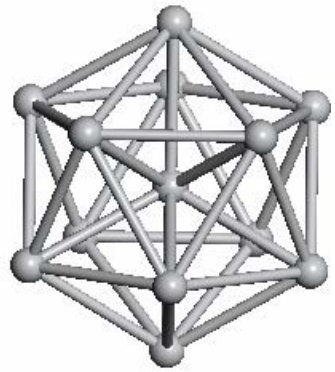
Dissociative Chemisorption of H_2 On Titanium clusters



Ti_4



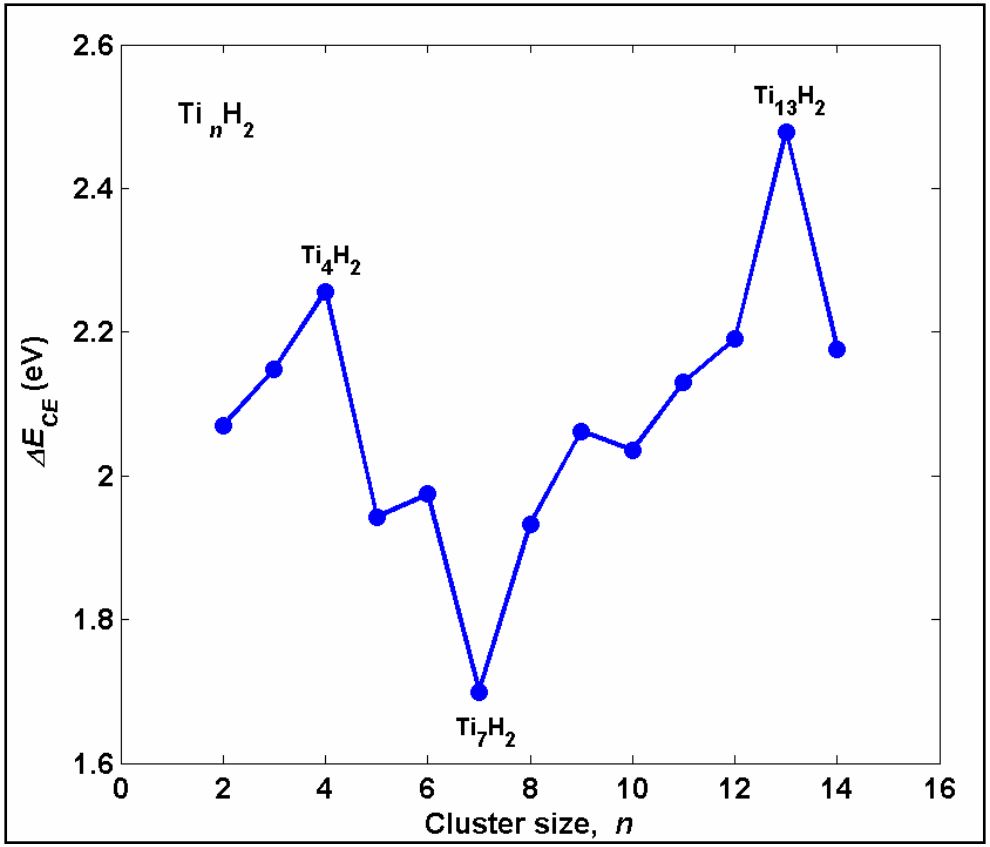
Ti_7



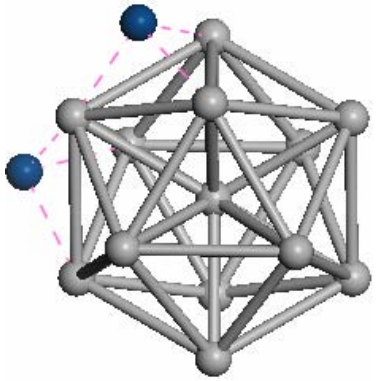
Ti_{13}

H_2 Dissociative Chemisorption Energy

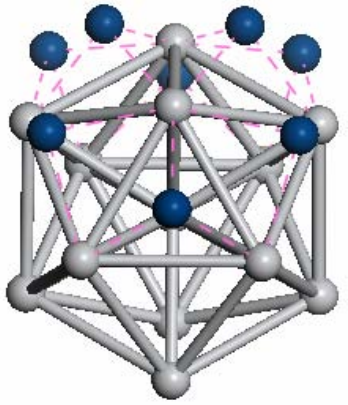
$$\Delta E_{\mathrm{CE}} = E_{\mathrm{Ti}_n} + E_{\mathrm{H}_2} - E_{\mathrm{Ti}_n\mathrm{H}_2}$$



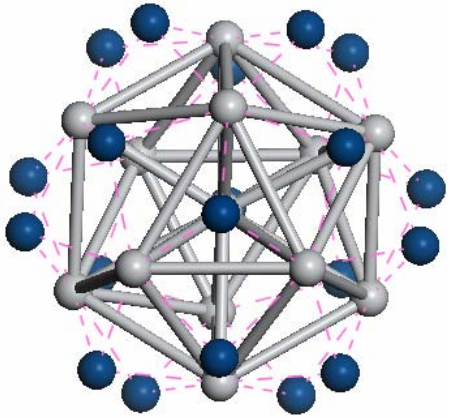
Dhilip Kumar et al. J. Phys. Chem. C **111**, 7494 (2007)



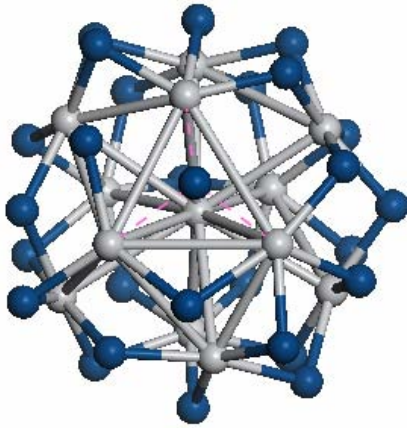
$Ti_{13}H_2$



$Ti_{13}H_8$



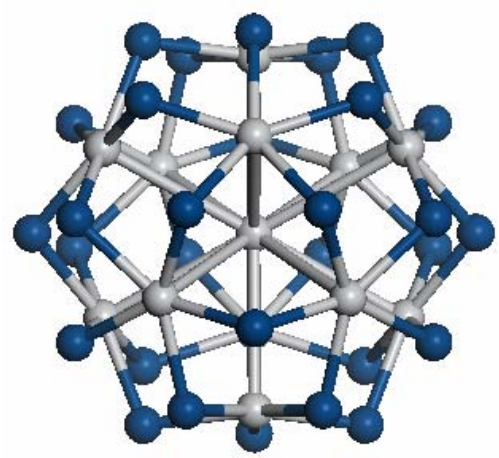
$Ti_{13}H_{20}$



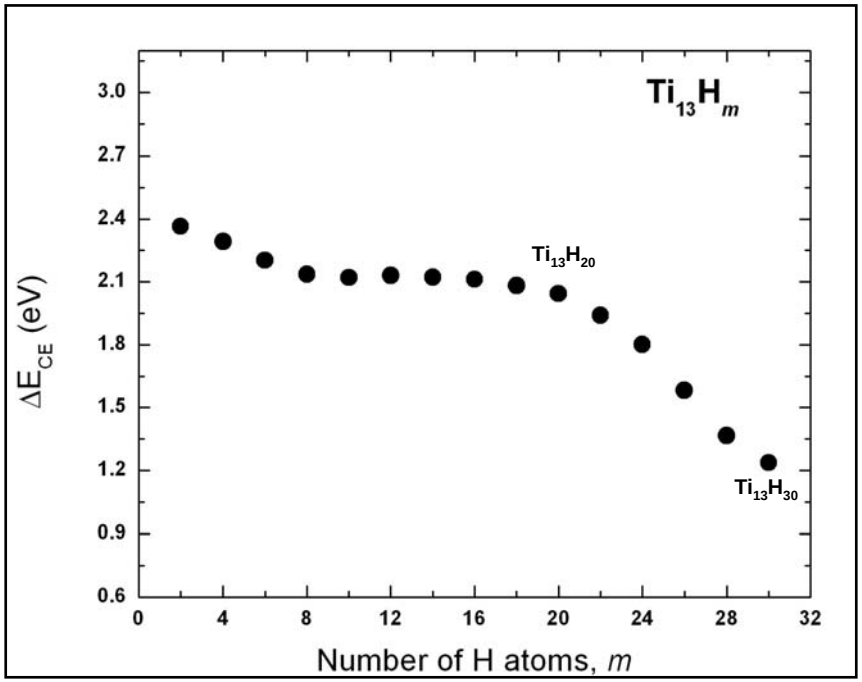
$Ti_{13}H_{28}$

Average Dissociative Chemisorption Energy

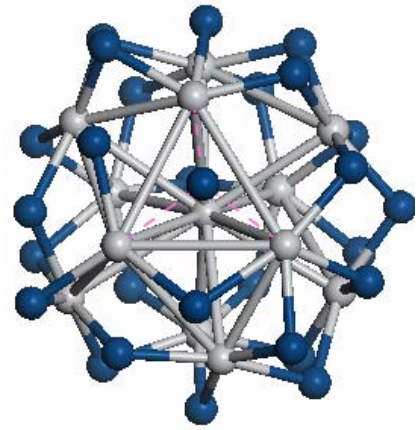
$$\Delta E_{CE} = (2/m)(E_{Ti_{13}} + (m/2)E_{H_2} - E_{Ti_{13}H_m}) \qquad (m = 2, 4, 6, \ldots)$$



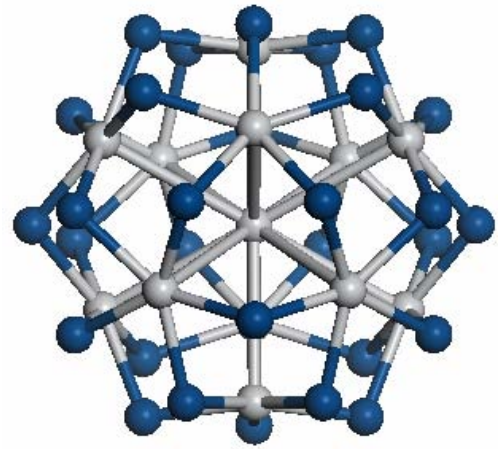
$Ti_{13}H_{30}$



Sequential Hydrogen Desorption Energy

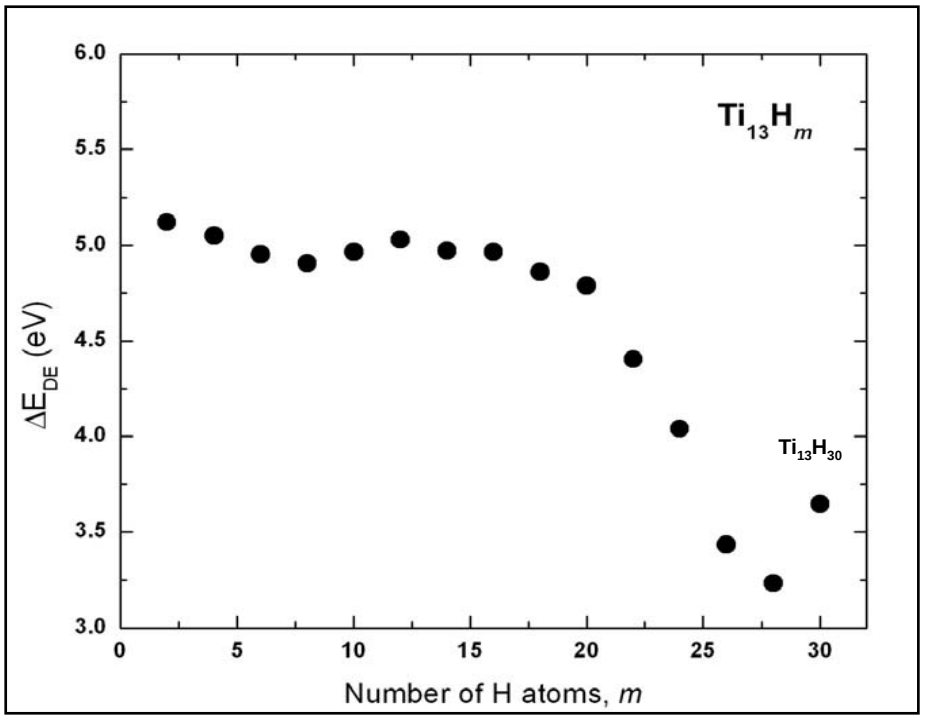


$Ti_{13}H_{28}$



$Ti_{13}H_{30}$

$$\Delta E_{\mathrm{DE}} = E_{\mathrm{H}} + (E_{\mathrm{Ti_{13}H_{\mathit{m}}}} - E_{\mathrm{Ti_{13}H_{\mathit{m-2}}}})/2 \qquad (m = 2, 4, 6, \ldots)$$



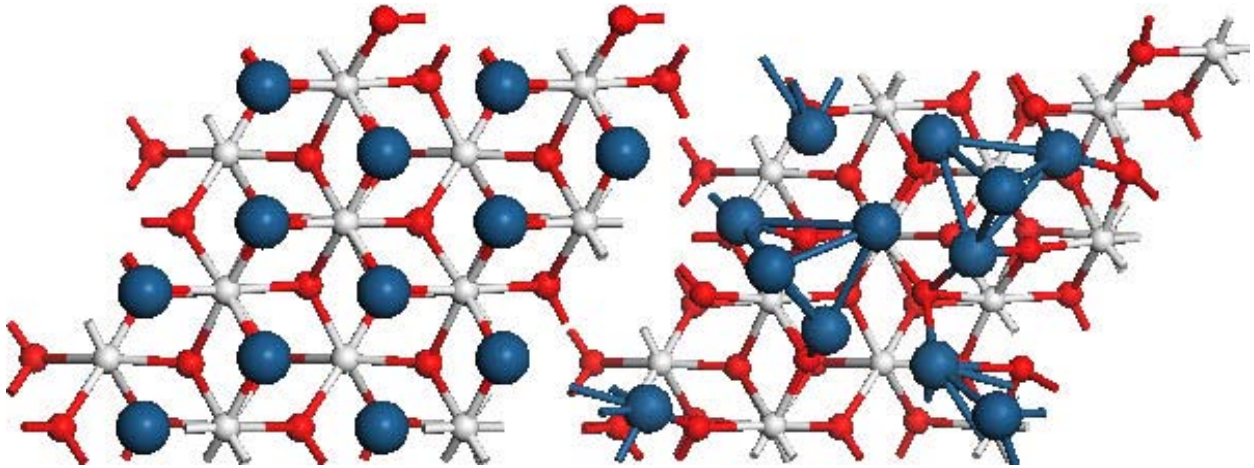
Catalyst-support interaction

Growth of small Pt clusters on α-Al_2O_3 surface investigated
Zhou et al. J. Phys. Chem. C (in press)

Wetting vs clustering

Pt-monolayer on α-Al_2O_3 surface

Pt-cluster on α-Al_2O_3 surface

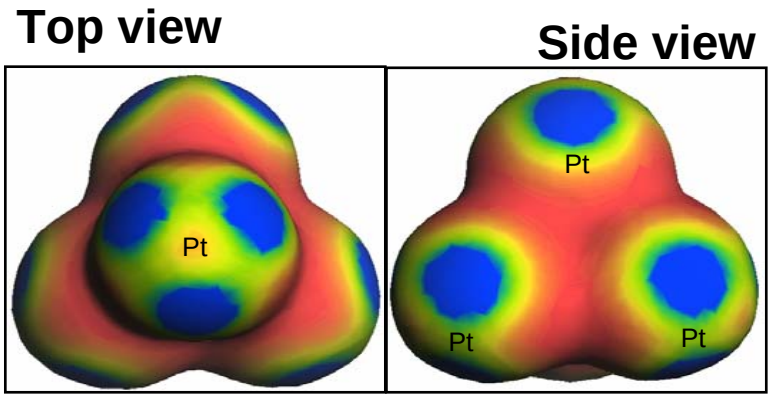


Clustering preferred over wetting

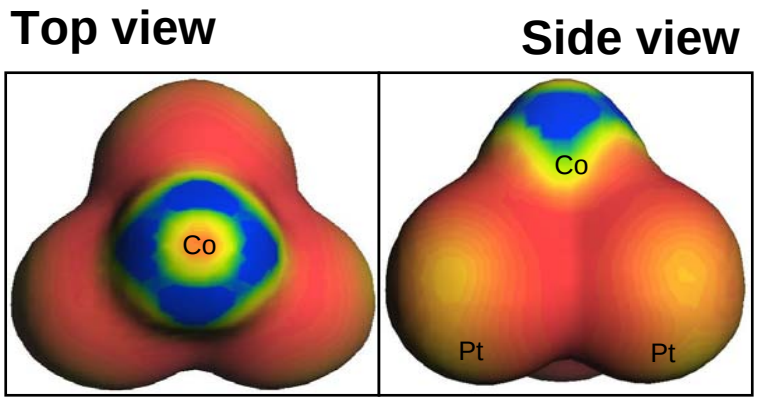
Effect of Alloying

Electrostatic Potential Map

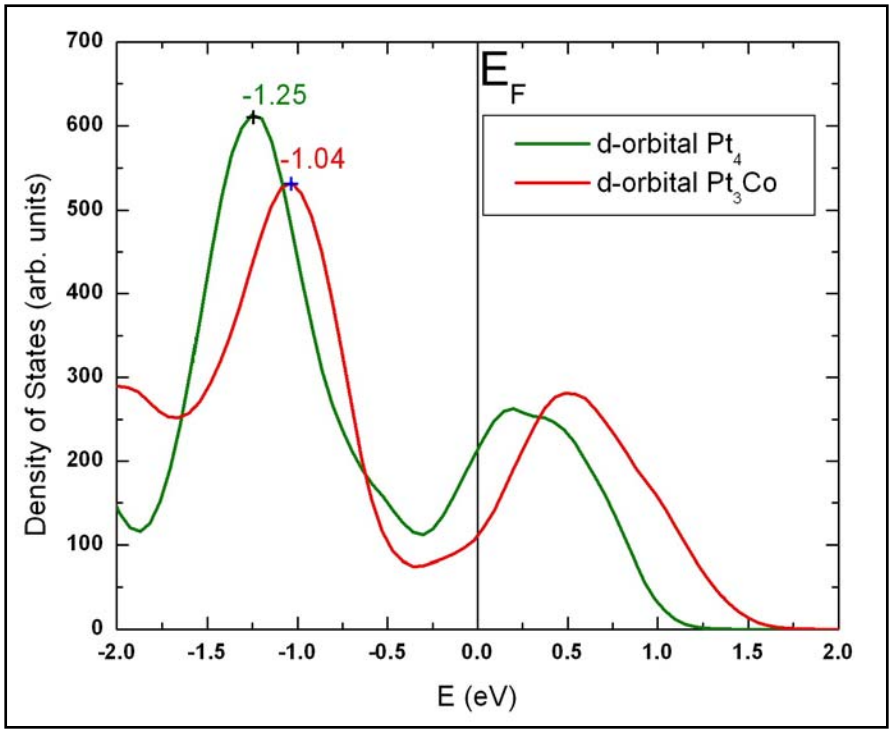
(a) Pt_4



(b) Pt_3Co



Total Density of States of Pt_4 and Pt_3Co



Position of the d-band relative to the Fermi-level has important consequences to the catalytic activity.

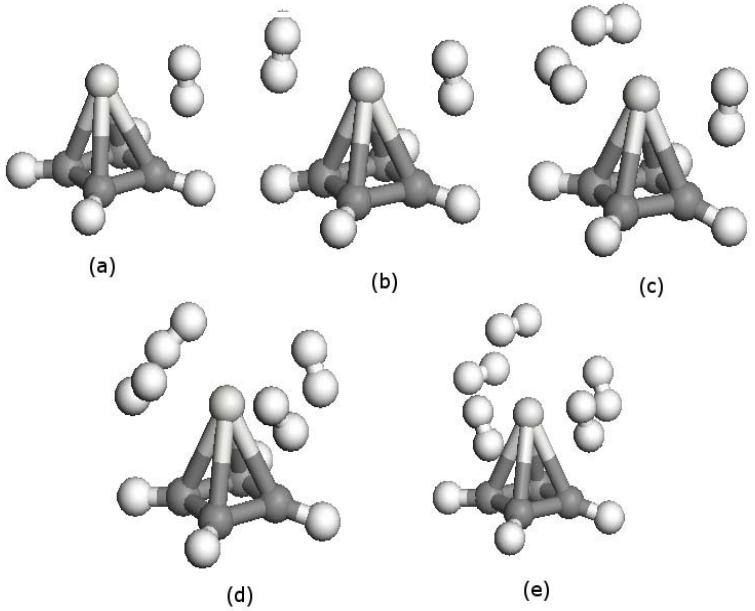
Transition-metal bonded organic systems as building blocks for hydrogen storage materials

- Hydrogen storage capacity of model organometallic systems consisting of **Sc**, **Ti** and **V** transition-metal atoms bound to C_mH_m rings (m=4-6).
- Calculations were performed using the density functional theory (GGA, PW91).
- The maximum retrievable H_2 uptake predicted is **9.3 wt %** using **ScC_4H_4**, slightly better than the **9.1 wt %** hydrogen using **TiC_4H_4** and much larger than the **7.2 wt %** hydrogen with **VC_4H_4**.
- Average binding energies:

  $ScC_4H_4(H_2)_n$: **0.33 eV/H_2**

  $TiC_4H_4(H_2)_n$: **0.64 eV/H_2**

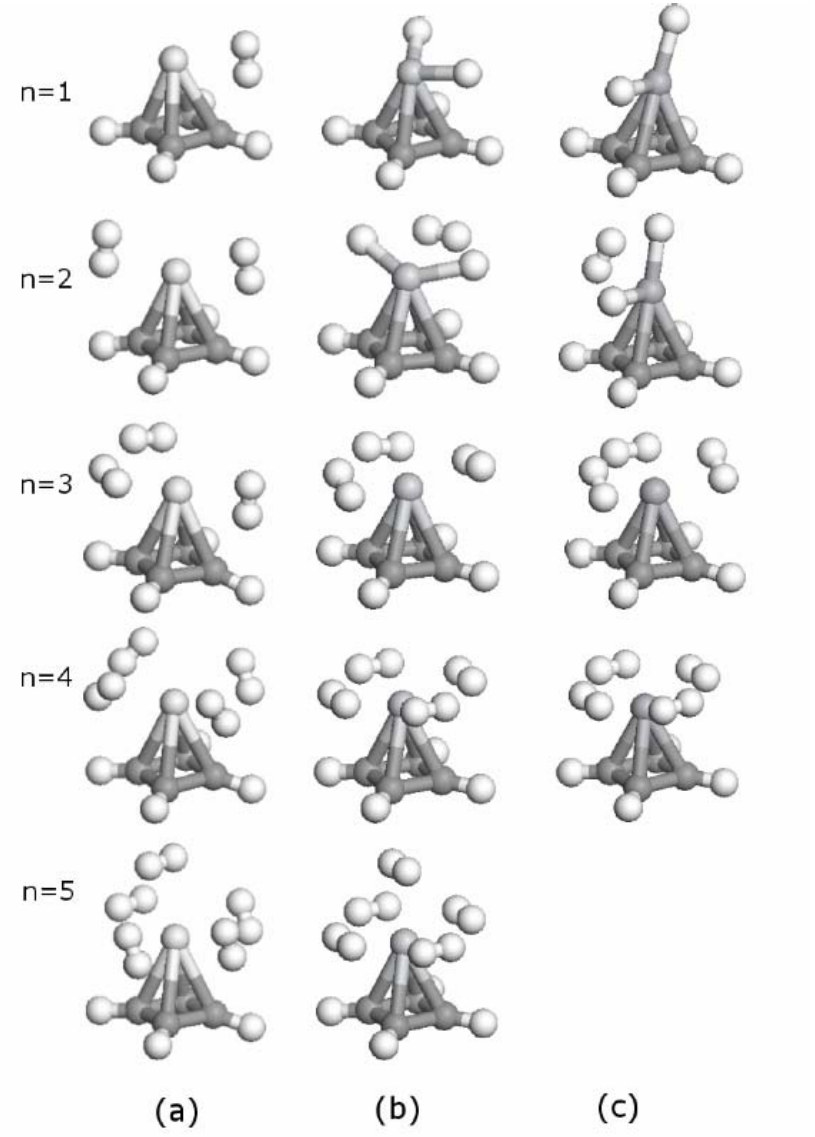
  $VC_4H_4(H_2)_n$: **0.77 eV/H_2**



Optimized geometries of $ScC_4H_4(H_2)_n$ (n=1-5)

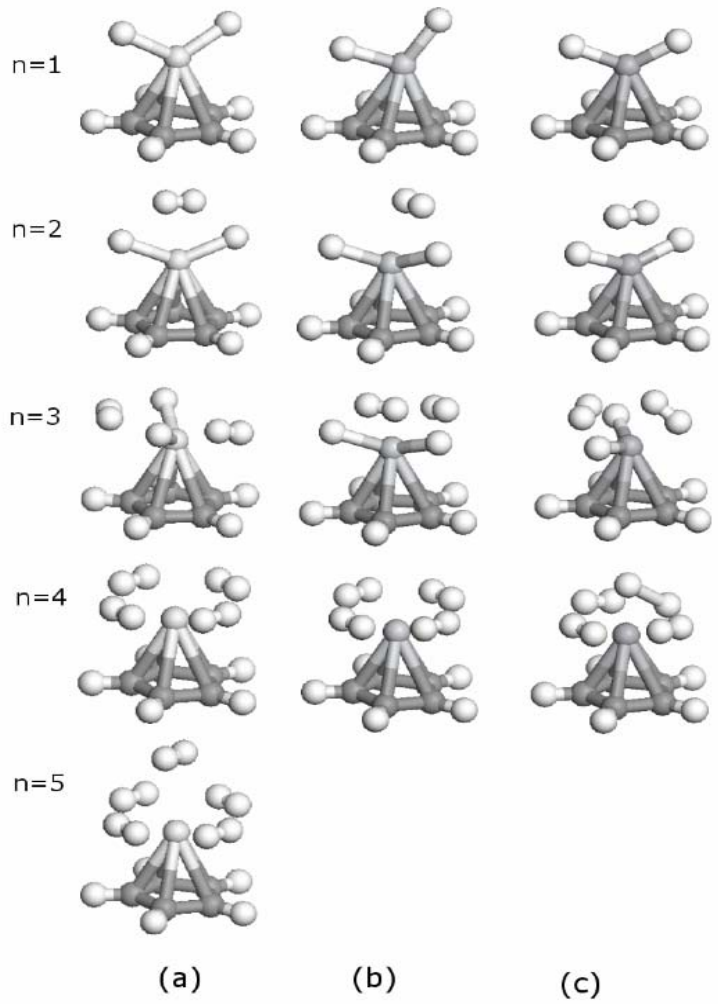
Weck et al. J. Chem. Phys. 126, 094703 (2007)

H_2 Chemisorption on M-C_4H_4 systems



Sc-C_4H_4 Ti-C_4H_4 V-C_4H_4

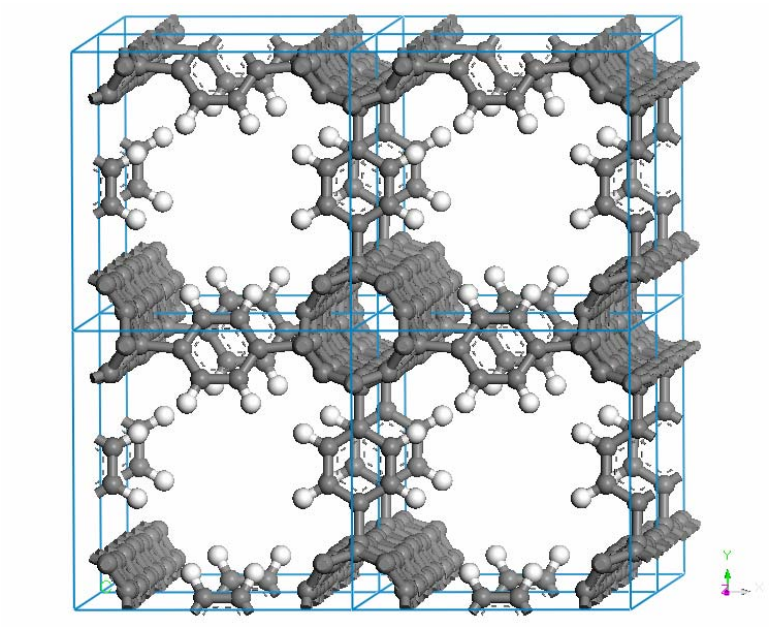
H_2 Chemisorption on M-C_5H_5 systems



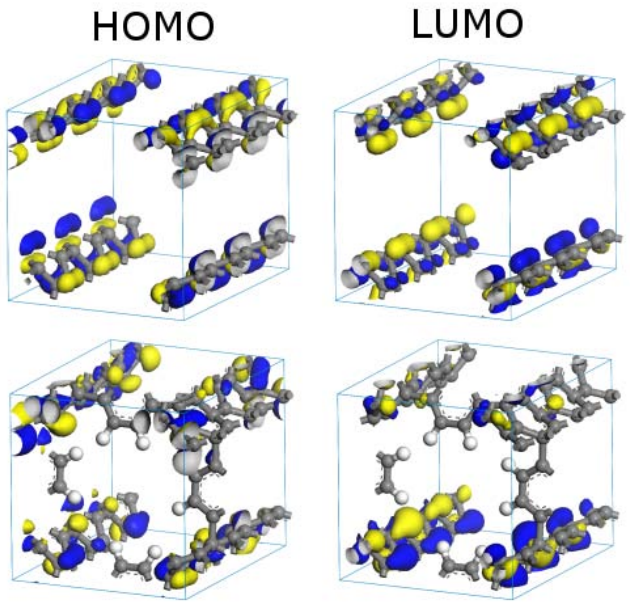
Sc-C_5H_5 Ti-C_5H_5 V-C_5H_5

Carbon nanoframeworks tailored for hydrogen storage

- Novel class of 3-D materials consisting of small diameter single-walled carbon nanotubes (SWCNTs) functionalized by organic ligands are proposed, as potential hydrogen storage media.
- Nanoframeworks consisting of (5,0) and (3,3) SWCNTs constrained by phenyl spacers are constructed.

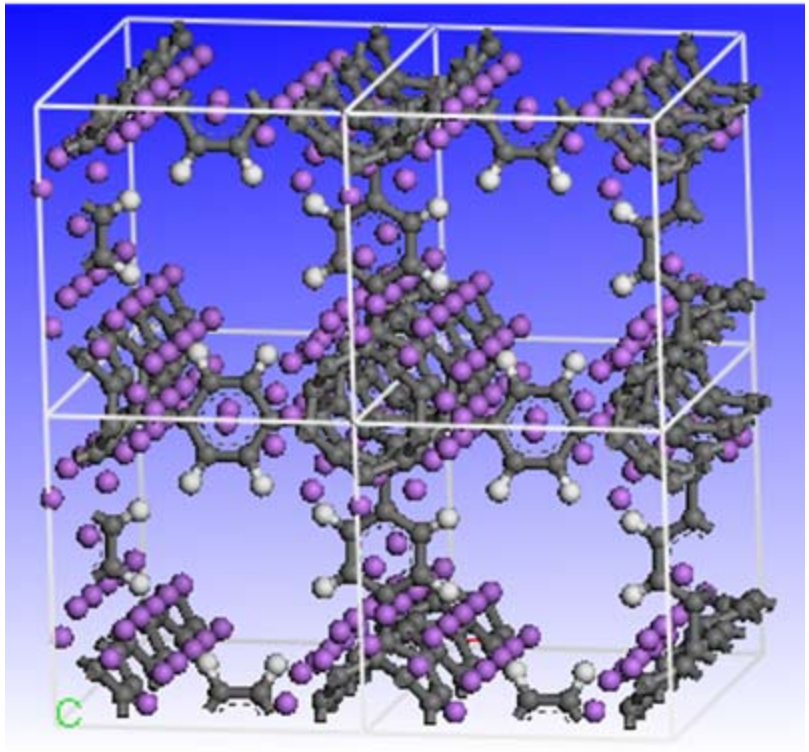


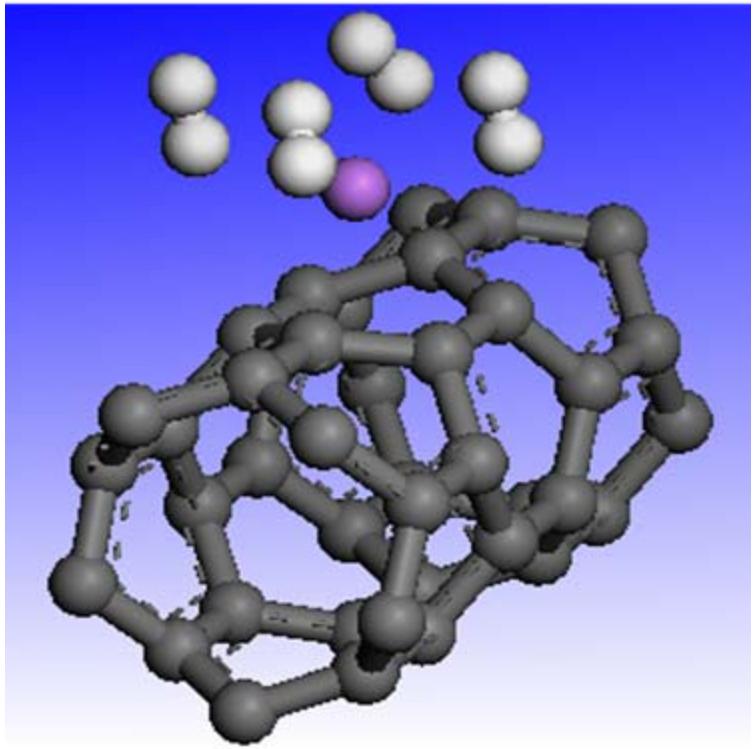
Optimized nanoframework structure consisting of (5,0) SWCNTs constrained by phenyl spacers. The unit cell is shown in blue.



HOMO (left) and LUMO (right) of pristine (5,0) SWCNTs (top) and the framework (bottom) consisting of (5,0) SWCNTs and phenyl ligands.

Hydrogen uptake on Li-decorated nanoframework





Work in progress!