H_2 dissociation on transition metal carbide surfaces

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Introduction

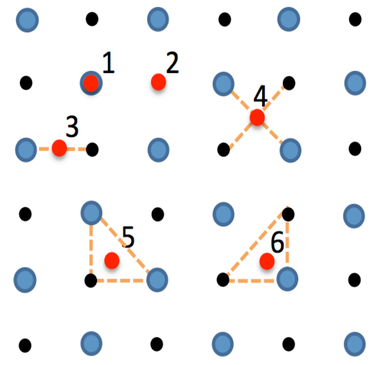
The project deals with the H_2 adsorption and dissociation into H + H on the (001) surfaces of various transitions metal carbides (TMCs; TM=Ti, V, Zr, Nb, Mo, Hf, Ta), all displaying the NaCl crystallographic structure.

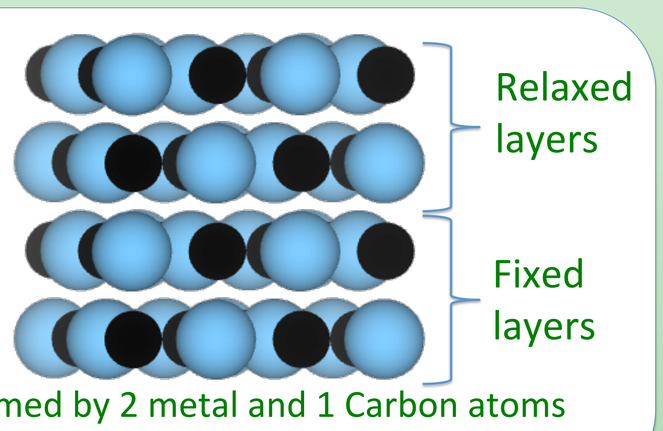
Computationals details

- DFT calculations
- VASP code[1]
- PBE functional[2]
- Climbing Image Nudge Elastic Band (Cl-NEB) method[3]

Models

- Supercell of (2×2)
- 64 atoms (32 C and 32 M)
- 2 fixed and 2 relaxed layers.
- 6 sites explored for H ads.
- 19 sites explored for H_2 ads.





(M-top, 1), (C-Top, 2), Bridge (3), 4-fold hollow (4), 3-fold hollow formed by 2 metal and 1 Carbon atoms (MMC, 5), and 3-fold hollow formed by 2 Carbon and 1 metal atoms (CCM, 6).

H_2 adsorption on TiC

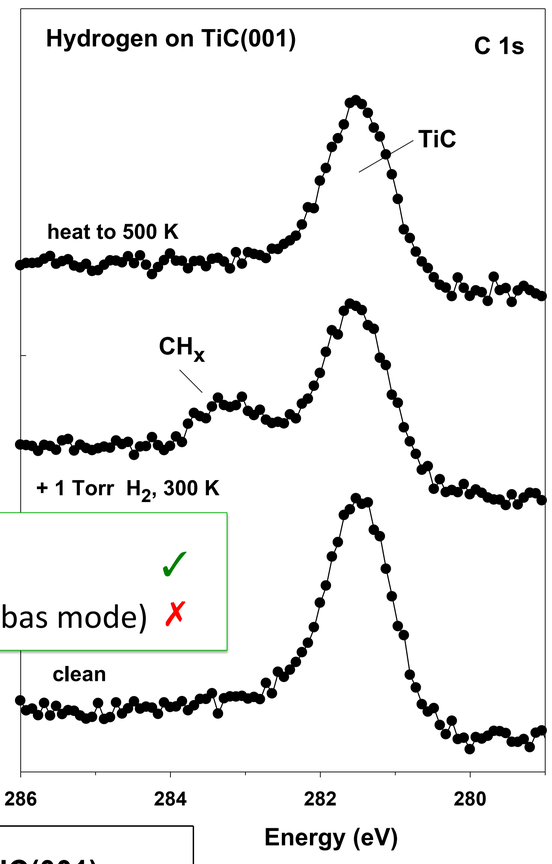
Adsorption on (001) TiC surface: How it happens?

Adsorption on C-Top
Adsorption on Ti-Top
Kubas modes?

Computational studies + Experimental studies → What happens

C 1*s* XPS spectrum

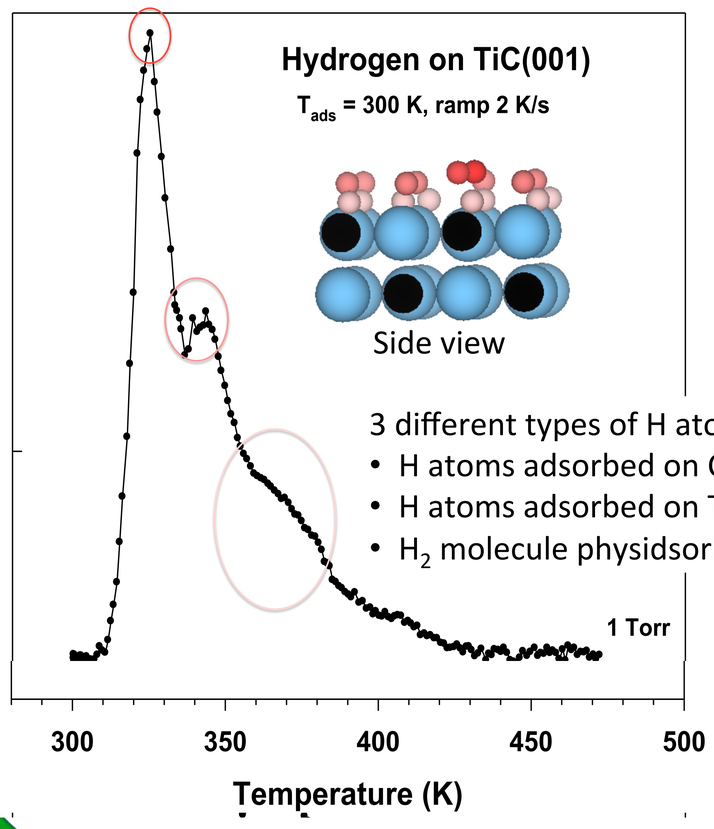
Show 2 types bondings
- C-Ti
- C-H_x



Computational studies + C 1*s* XPS spectrum → CH ✓, CH_2 (kubas mode) ✗

Thermal desorption study: types of H

Thermal desorption spectrum



H_2 exposed to 1 Torr for 5 minutes

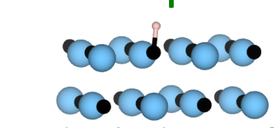
3 different types of H atoms:
- H atoms adsorbed on C-Top
- H atoms adsorbed on Ti-Top

} Full coverage

- H_2 molecule physidsorbed on Ti-Top

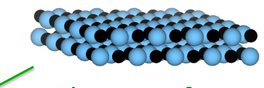
Over full coverage

Adsorption energy on different TMCs



H adsorbed on surface

$$E_{ads} = E_{H/TMC} - (E_H - E_{TMC})$$



Clean surface

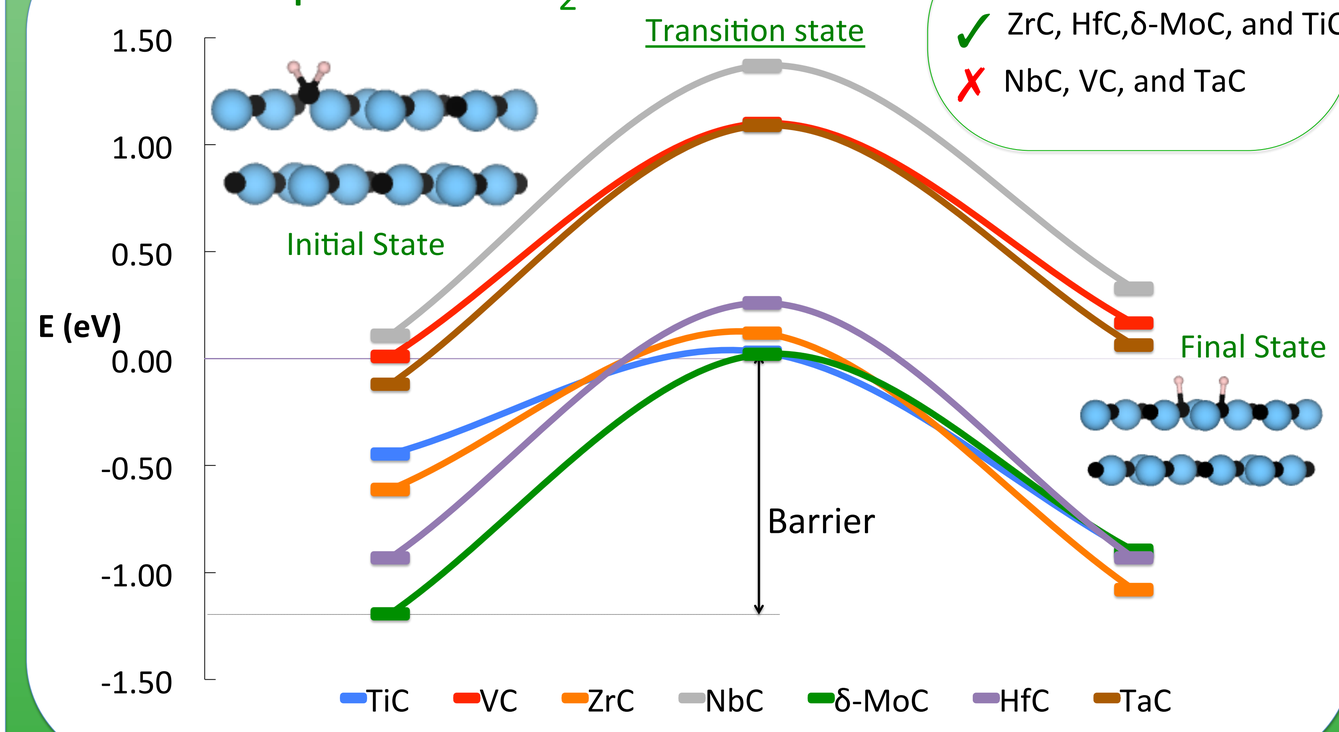
H atom on vacuum

E (eV)	TiC	VC	ZrC	NbC	δ-MoC	HfC	TaC
H	-2.73	-2.13	-2.84	-2.01	-2.93	-2.77	-2.30
H_2	-0.46	0.01	-0.61	-0.07	-1.19	-0.93	-0.12
barrier	0.49	1.09	0.73	1.26	1.21	1.19	1.21

Most stable H adsorption site: C-top, except in TaC, Ta-Top.
Most stable H_2 adsorption site: C-top on TiC, ZrC, δ-MoC, and HfC.
M-top on VC, NbC, and TaC.

Reaction profile of H_2 dissociation

Dissociation
- ✓ ZrC, HfC,δ-MoC, and TiC
- ✗ NbC, VC, and TaC



Conclusions

- H_2 dissociation occurs on (001) TiC surface
- TiC barrier: 0.49 eV. ⇔ The best candidate to produce H_2 dissociation.
- The order to cover the surface was found: First H atoms are adsorbed on C-Top, secondly H atoms are adsorbed on Ti-Top and, finally, H_2 molecules are physisorbed on Ti-Top.
- 3 different H sites are found: H adsorbed on C-Top and on Ti-Top, and H_2 molecules physisorbed on Ti-Top.
- Computational studies were done on other TMCs so to find candidates to perform experimental studies.
- Results show that H_2 dissociation is also thermodynamically favourable on TiC, ZrC, HfC, and δ-MoC.

References

1. *Phys. Rev. B*. **1996**, 54, 11169-11186.
2. *Phys. Rev. Lett.*, **1996**, 77, 3865-3868.
3. *J. Chem. Phys.*, **2000**, 113, 9901

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