Tuning Activity of Transition Metal Carbides by Surface Metal Alloying: Case of Study of CO_2 Capture

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CO_2 is one of the main actors in the greenhouse effect and its removal from the atmosphere is becoming an urgent need. Recently, it has been theoretically predicted that **transition metal carbides** (TMC) are able to **capture**, **store** and **activate** CO_2.[1] To further improve the capacity of adsorption of these materials atomic knowledge of the CO_2 adsorption is essential. In the present work, we explore the effect of **doping** the **TiC surface** by **Cr, Hf, Mo, Nb, Ta, V, W, Zr**.

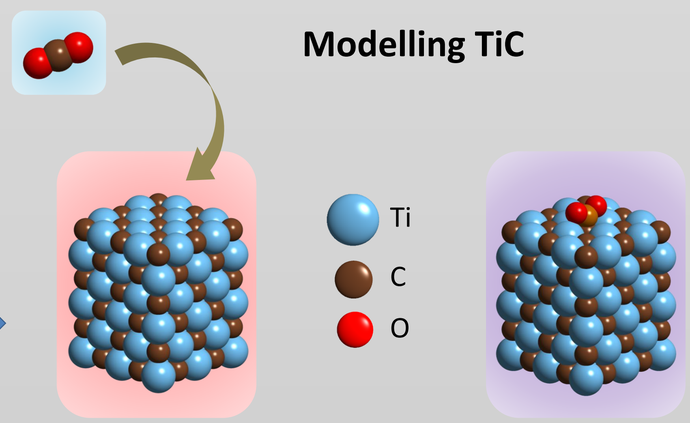
Modelling and Computational Details

Adsorption Energy

$$E_{ads}=E_{CO_2/surf}-(E_{CO_2}+E_{surf})$$

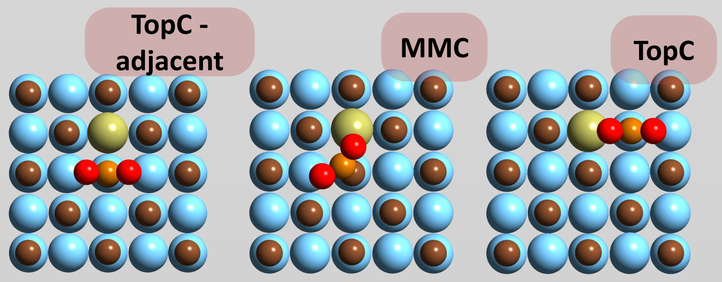
$(2\sqrt{2}\times 2\sqrt{2})R45°$ slab model

Surface (001)



Modelling TiC

Binding Modes



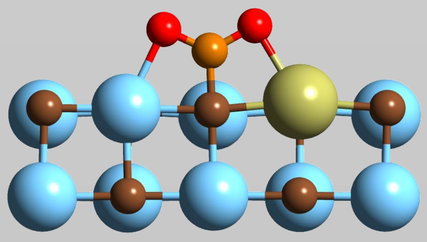
Background

DFT
xc functional
PBE

Program: **VASP**

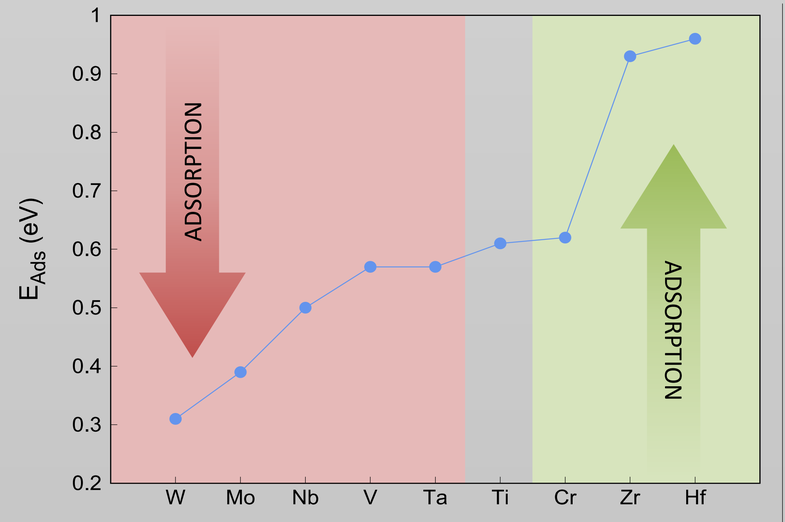
Results and Discussion

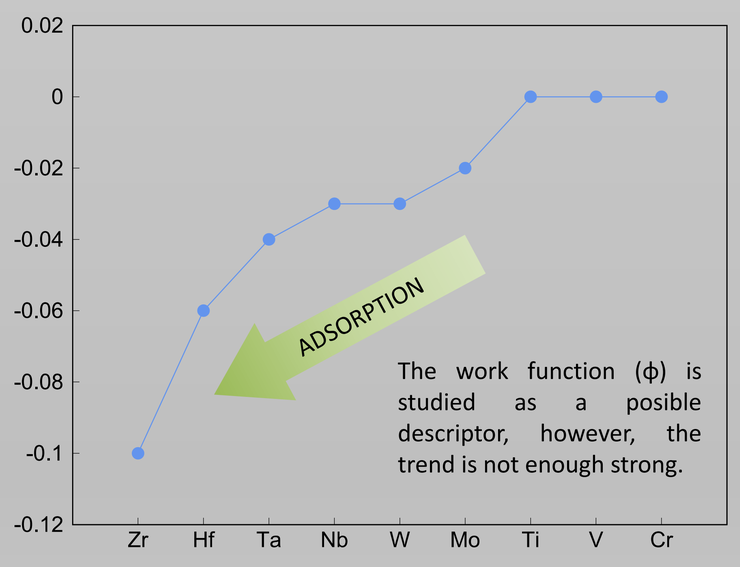
CO_2 adsorption		
Dopant	**Binding mode**	**E_{ads} (eV)**
Ti	-	-0.61
Cr	TopC-adj	-0.62
Hf	TopC	-0.96
Mo	TopC-adj	-0.39
Nb	TopC	-0.50
Ta	TopC	-0.57
V	TopC-adj	-0.57
W	TopC-adj	-0.31
Zr	TopC	-0.93



Relaxed structure of the most favorable adsorption case. The CO_2 remain activated on the surface, its geometry is: Carbon – Carbon distance around 1.48 – 1.50 Å, Oxygen – Carbon distance elongated until 1.28 – 1.30 Å. Oxygen – Carbon – Oxygen angle reduced from 180° to 126 - 129°.

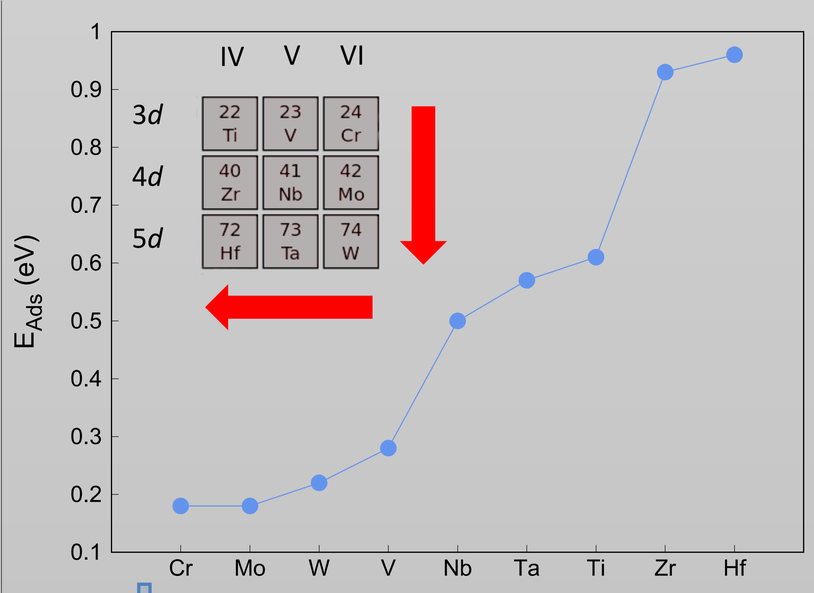
General analysis



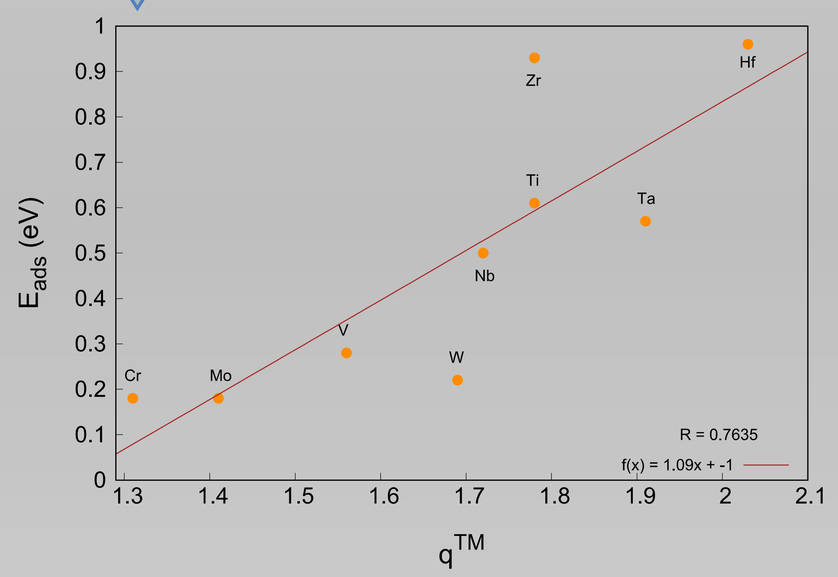


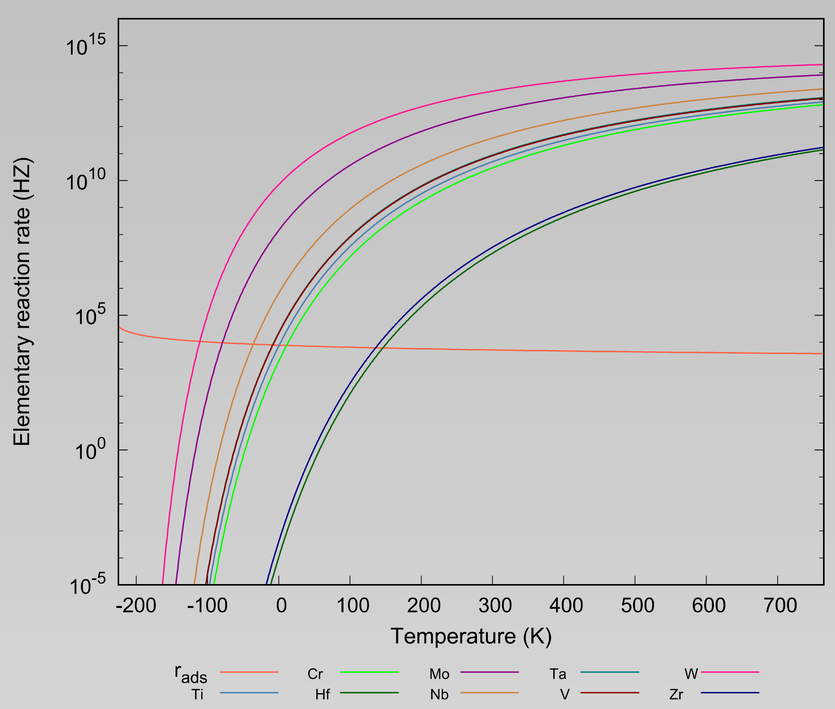
The work function (ϕ) is studied as a posible descriptor, however, the trend is not enough strong.

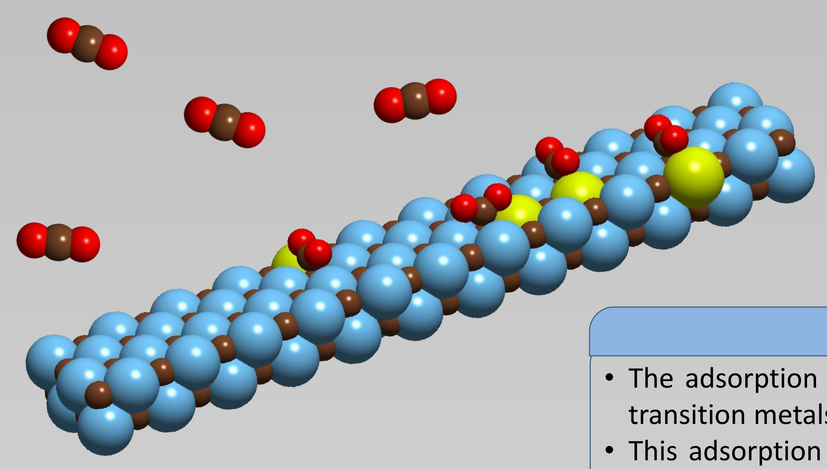
TopC analysis



Bader's *atoms-in-molecules* analysis permits to correlates the influence of transferred charge and the adsorption energy.







Adsorption/desorption rates can be obtined throw the **Transition State Theory (TST)** and the **partition functions** of the free and the adsorbed CO_2 molecule.

Conclusions

- The adsorption energy of TiC can be **enhanced by doping** the surface with early transition metals.
- This adsorption process can be categorized as an **Lewis acid-base reaction**, from that the charge transfer affects strongly the adsorption properties. A big charge transfer is indicative of a strong adsorption.
- TiC can be easily tuned to obtain the **desired properties.**
- The CO_2 can be used after the adsorption for some other utilities, **CO_2 Capture and Usage (CCU)** such methanol obtention through its hydrogenation.[2]

References

[1] Kunkel, C.; Viñes, F.; Illas, F. *Energy Environ. Sci.* **2016**, 9, 141-144.
[2] Porosoff, M. D.; Kattel, S.; Li, W.; Liu, P.; Chen, J. G. *Chem. Commun.* **2015**, 51, 6988-6991.

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