

Platinum subnanometer clusters adsorbed on oxides like $TiO_2(110)$ are known to play an important role as catalysts for the oxidation process of CO to form CO_2 . The CO adsorption by a Pt_{13} cluster deposited on the reduced rutile $TiO_2(110)$ surface is here investigated by means of density functional theory calculations (DFT), using the VAS code and including the Hubbard term "U" to correct the coulombic interactions in the oxide support. The aim is to provide relevant structural and energetic information of this CO/cluster/substrate system.

Previous studies using this methodology let us determine the equilibrium configurations of isolated Pt_{13} clusters; we find that layered clusters are more stable than the more compact and symmetrical cuboctahedral (Oh) and icosahedral (Ih) isomers. However, when these compact isomers are adsorbed on the oxide rutile surface they experience a strong restructuring, with the Pt cluster getting oxidized and adopting a more layered structure which increases the interaction with the substrate, leading to a high adsorption energy. A recent experimental study based on fast dynamic scanning transmission electron microscopy (STEM) performed for Pt clusters deposited on carbon, showed a strong trend for these clusters to exhibit the fcc bulk structure with cuboidal geometries. In particular, for Pt_{13} , the cuboidal structure consists of a basic fcc cube, with a Pt atom missing at one corner. In this work, we first analyze the stability of this new cuboid configuration for the isolated cluster, to evaluate its relative stability as compared to the layered and Oh structures, previously studied by us. Then, we characterize the cluster/substrate interaction for these isomers deposited on the reduced surface: $TiO_2(110)$ plus an oxygen vacancy (TiO_2+Vo), and compare with the Pt_4 -rutile system. The last step is to study the adsorption of CO over the Pt_{13} cluster/substrate system, for the different Pt_{13} cluster geometries considered, and investigating the more favorable sites of adsorption of this molecule. We determine the equilibrium geometries, energies of adsorption, charge transfer effects and the electronic density of states, and discuss these results in connection with the possible oxidation of CO by an oxygen of the substrate.

MOTIVATIONS

- Pt clusters → used as catalysts of chemical reactions like electro-oxidation of CO, catalytic conversion of vehicle gases, chemical conversion of ethane.
- They are deposited over oxide substrates to get established and avoid their sinterization.
- The system $Pt_n/TiO_2(110)$ is an efficient catalyst for the WGS (water gas shift) reaction: $CO + H_2O \rightarrow CO_2 + H_2$ at low temperatures.
- The oxidation of CO to CO_2 represents an intermediate step for most of the proposed mechanisms of the WGS.
- Most accepted redox mechanism: the CO is adsorbed on the Pt cluster being oxidated to CO_2 by oxygen atoms of the surface support. To favour the CO oxidation, it is convenient that the catalyst be in a reduced state [1].

OBJECTIVES

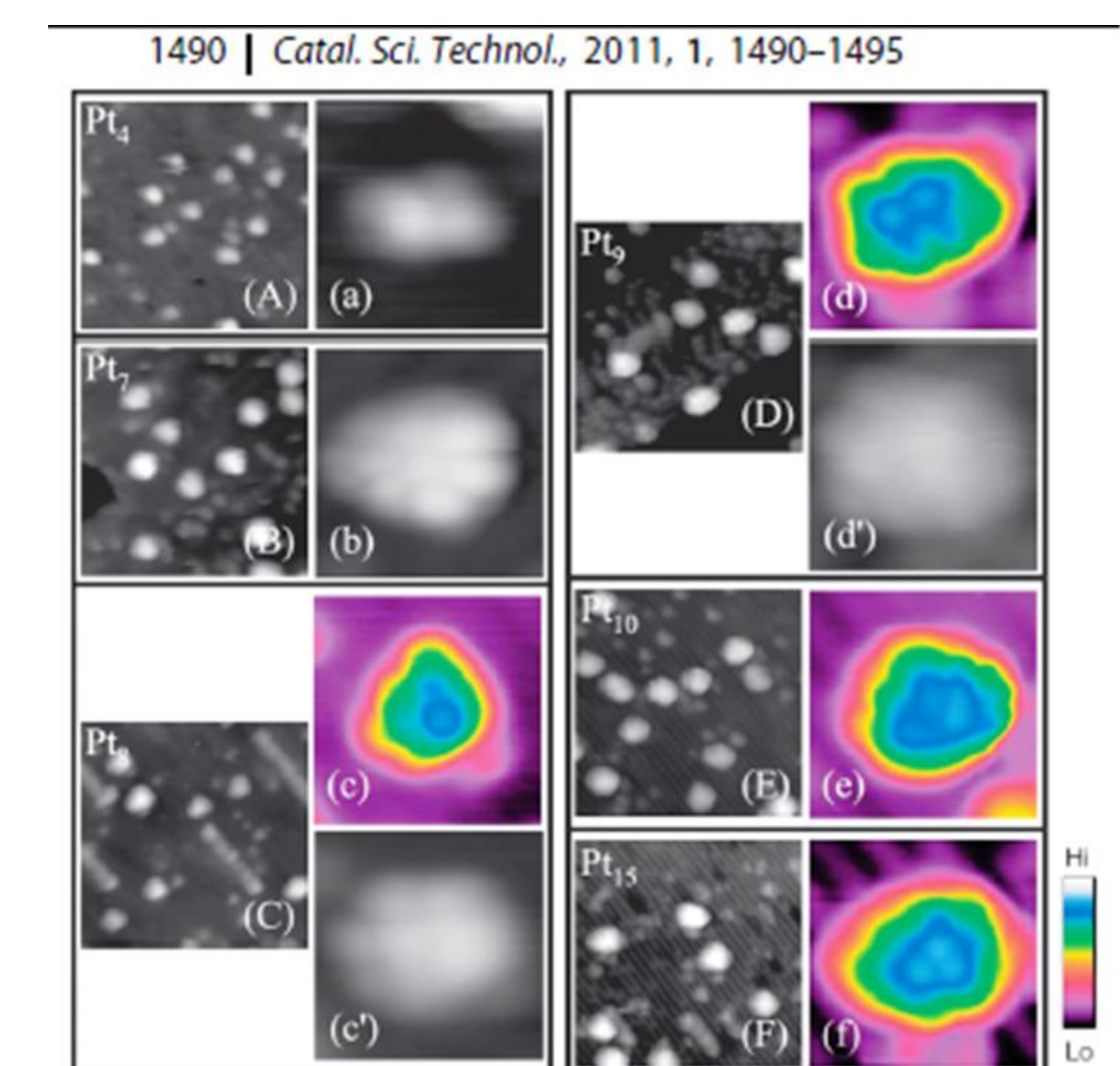
- Model by ab initio DFT method the CO molecule adsorbed over three different isomers of Pt_{13} clusters deposited on the reduced $TiO_2(110)$ surface.
- Characterize the adsorption process by evaluating: adsorption energies, equilibrium configurations and charge transfer effects

CALCULATION METHOD

- Ab initio spin polarized DFT calculations.
- VASP Code (Vienna Ab initio Simulation Package) [3] and the projected augmented plane wave (PAW) method [4].
- Correlation and exchange potentials: generalized gradient approximation (GGA) PW91 [5].
- Cut-off kinetic energy for the expansion of plane waves: $E_{cut} = 450$ eV.
- Hubbard term to correct the Coulomb interaction between d electrons of Ti: $U = 8$ eV [6].
- Convergence criterion for the energy: 0.1 meV, forces: $f < 0.01$ eV / at.
- Harmonic approximation by the finite displacement method to determine the vibrational density of states (VDOS)
- Cohesive energy per atom in the cluster [7]: $E_B = E_{atom} - E_{cluster} / n$
- Charge Bader analysis is used to quantify charge transfer effects: ΔQ expressed in units of the electron charge.
- Rutile $TiO_2(110)$ surface: slab with layers of Ti and O atoms with a vacuum of 12.9 Å along the [110] direction; periodic supercell of (4 x 1 x 2). k-point mesh : 3x1x3.
- The reduced $TiO_2(110)+Vo$ surface is obtained by removing a bicoordinated oxygen atom of the surface.
- The CO molecule was placed close to the most reduced Pt atom of the cluster
- The CO adsorption energy of the CO molecule on the $Pt_{13}/TiO_2(110)$ system was calculated as:

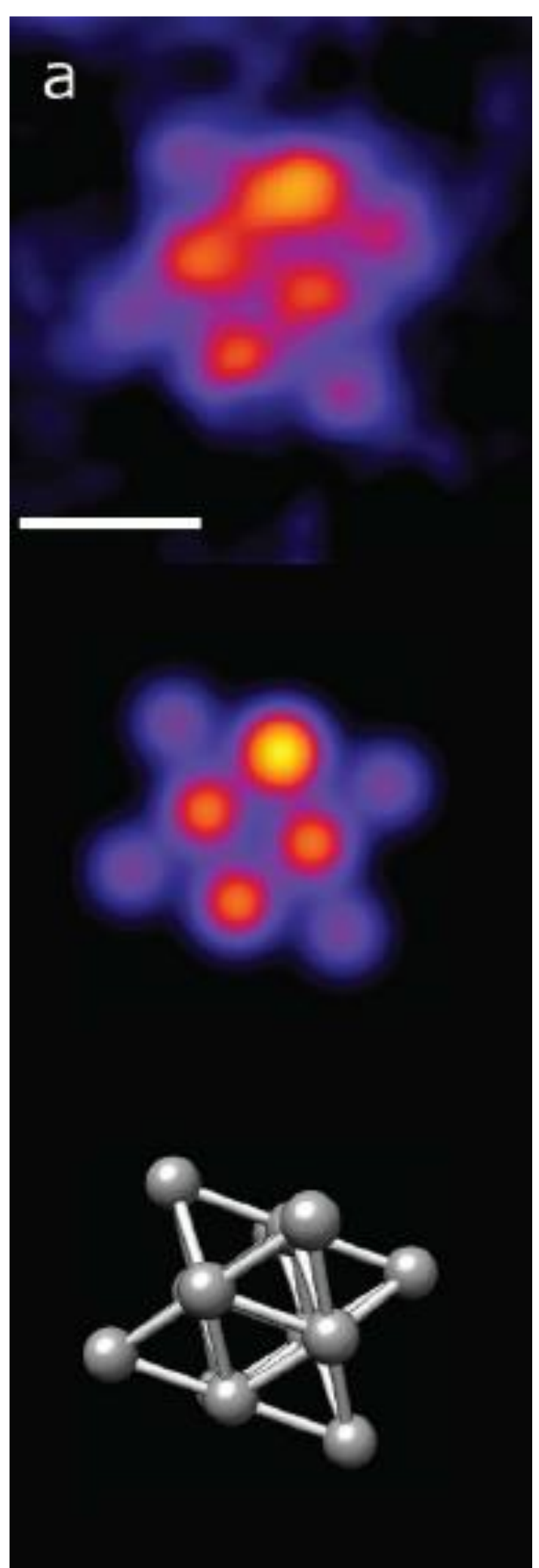
$$E_{ads} = E_{CO-Pt_{13}/TiO_2} - (E_{CO} + Pt_{13}/TiO_2)$$

Pt cluster structures: experimental information



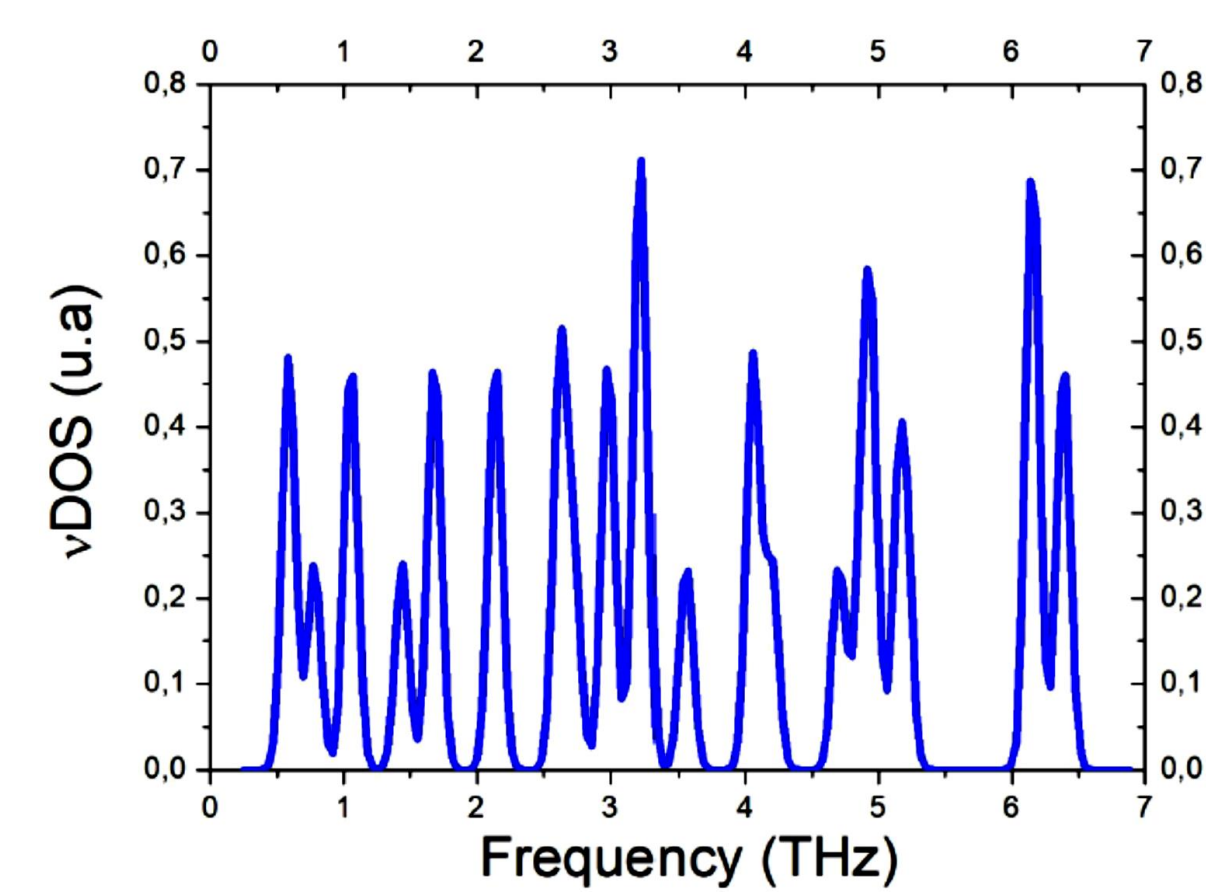
For small Pt_n clusters planar structures are observed: transition 2D-3D for $n \sim 8$

Scanning transmission electron microscopy images (STEM) show cuboid Pt_{13} structures deposited over carbon substrate [3]



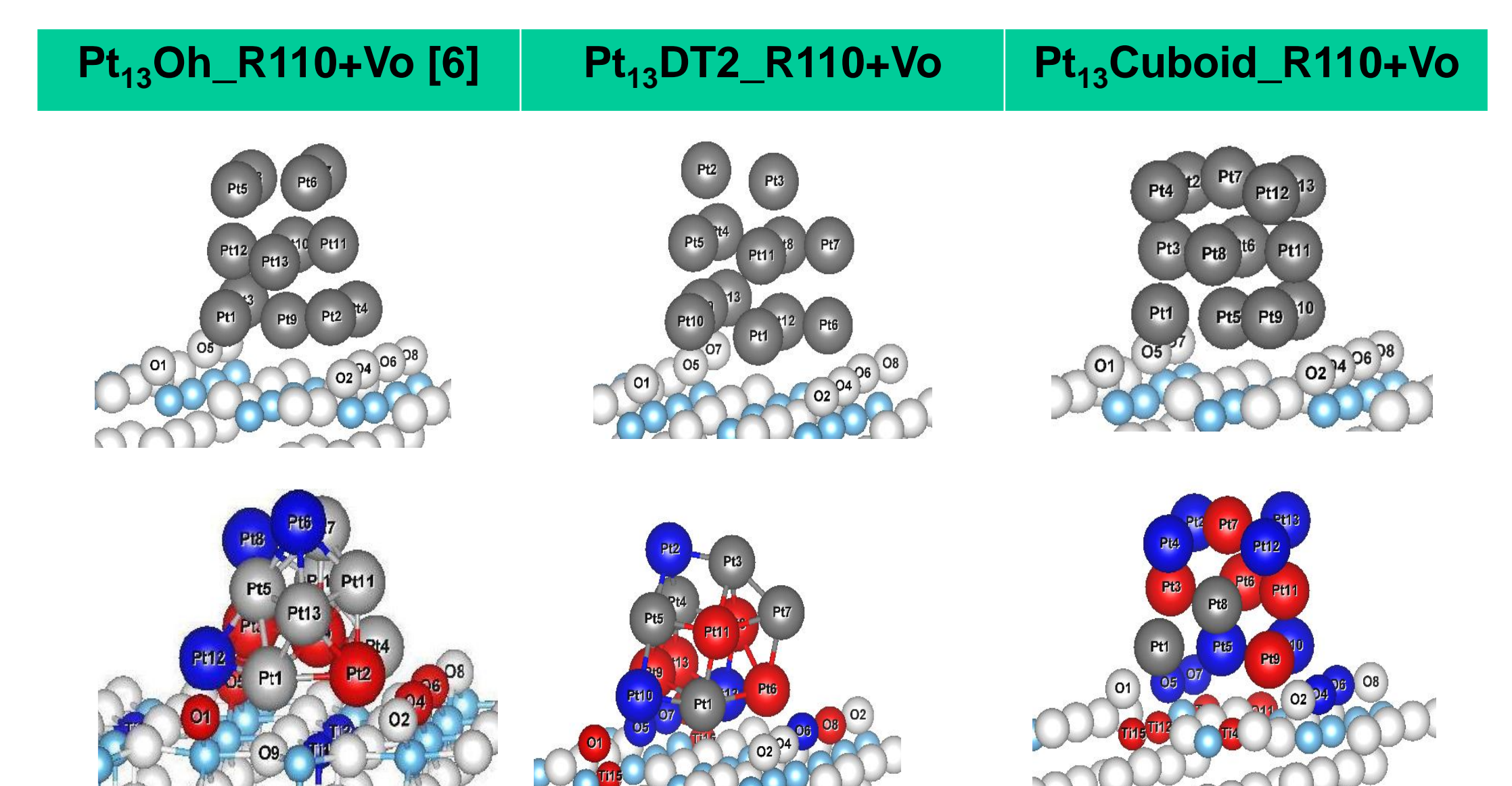
Equilibrium structures selected for the Pt_{13} cluster

Clusters	E_{coh} (eV/atom)	μ (μ_B /atom)	$\langle d \rangle$ (Å)
$Pt_{13}Oh$	-3.63	0.48	2.68
$Pt_{13}Cuboid$	-3.84	0.33	2.59
$Pt_{13}DT2$	-3.86	0.31	2.61
Pt-bulk	-5.51	0.00	2.81



The calculated vibrational density of states indicate that the cuboid Pt_{13} cluster is stable.

Pt_{13} clusters deposited on $TiO_2(110)+Vo$



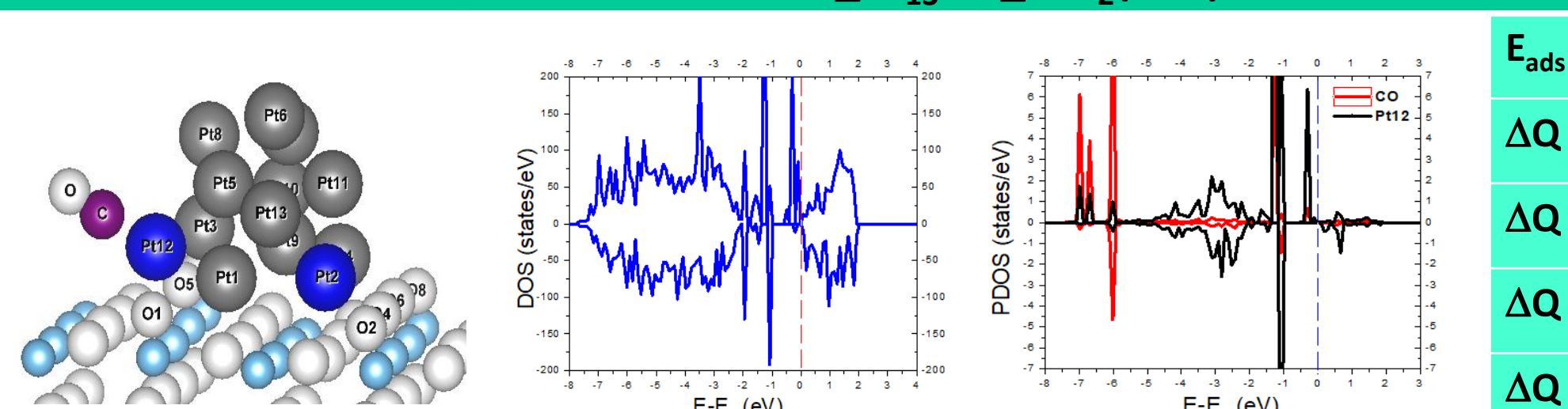
Blue: reduced atoms; Red: oxidized atoms

System	E_{ads} (eV)	ΔQ [e]	ΔQ (cluster) [e]
$Pt_{13}Oh_{TiO_2(110)+Vo}$	-9.39	-0.46 (Pt12)	+0.02
$Pt_{13}DT2_{TiO_2(110)+Vo}$	-5.84	-0.45 (Pt10)	+0.24
$Pt_{13}Cuboid_{TiO_2(110)+Vo}$	-3.50	-0.18 (Pt5)	+0.02

* Most reduced Pt atom

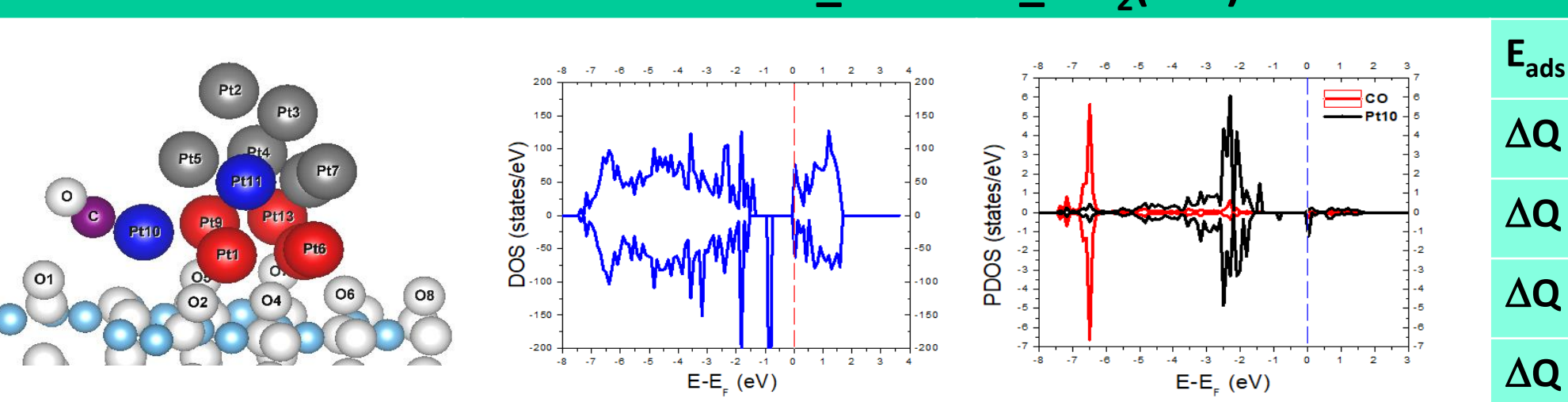
CO adsorption on $Pt_{13}/TiO_2(110)+Vo$

CO- $Pt_{13}Oh_{TiO_2(110)+Vo}$



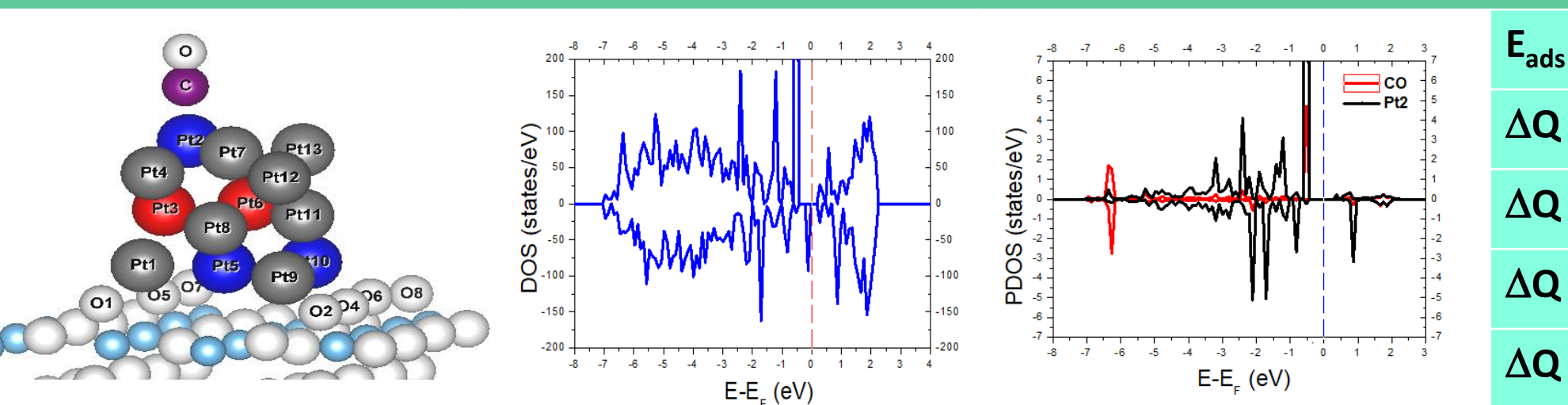
E_{ads} (eV)	-3.76
ΔQ (Pt12) (e)	-0.47
ΔQ (CO) (e)	-2.4
ΔQ (cluster) (e)	0.52
ΔQ ($TiO_2(110)+Vo$) (e)	-0.32

CO- $Pt_{13}DT2_{TiO_2(110)+Vo}$



E_{ads} (eV)	-1.75
ΔQ (Pt10) (e)	-0.18
ΔQ (CO) (e)	-2.34
ΔQ (cluster) (e)	0.10
ΔQ ($TiO_2(110)+Vo$) (e)	-0.07

CO- $Pt_{13}Cuboid_{TiO_2(110)+Vo}$



E_{ads} (eV)	-3.50
ΔQ (Pt2) (e)	-0.26
ΔQ (CO) (e)	-2.35
ΔQ (cluster) (e)	0.26
ΔQ ($TiO_2(110)+Vo$) (e)	-0.11

In blue: reduced atoms; In red: oxidized atoms

Conclusions

- When comparing the isolated Pt_{13} clusters, the DT2 and cuboid are more stable than the $Pt_{13}Oh$ one. However, when the clusters are deposited on the reduced rutile surface, the stability is reversed, being the Oh cluster the most stable one.
- Also for the CO adsorption over the reduced $Pt_{13}/TiO_2(110)$ system, the $Pt_{13}Oh$ configuration is preferred.
- Comparing the adsorption of CO on smaller clusters (Pt_4), a higher adsorption energy is obtained for the 13 atom cluster [6].
- For the CO adsorption the 3D configurations of Pt_{13} clusters seem to be more favourable as compared to layer ones, as previously observed for the Pt_4 case [6].

References

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- [6] Maldonado et al., Molecular Catalysis (2017)
- [7] Maldonado et al., Journal of Physics and Chemistry of Solids. (2019)

Acknowledgments

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