Supporting Information: Ab Initio Investigation of the Formation Mechanism of Nano-interfaces between 3d- Late Transition-Metals and ZrO₂ Nanoclusters

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1 Introduction

This supporting information (SI) includes different isomers of transition-metal clusters, TM₄ and TM₈, and their infrared spectra. For the putative global minimum configurations (pGMCs), we compare our binding energy (E_b) results for TM_n with the available literature data. Besides, all the configurations obtained for TM_n/(ZrO₂)₁₃, with TM = Fe, Co, Ni, or Cu, and n = 1,4, and 8 are included. The relative energy, ΔE , is shown above the structures.

2 Gas-Phase Structures



Figure S1: The stable isomers of TM₄ clusters, with their respect IR spectra. The relative total energy, ΔE_{tot} , is related with the pGMC structure, and the dihedral angle, α , allows the sign different structures.

		TM_4			TM_8	
	E_b (eV)	E_b ? (eV)	$\Delta E_b (\%)$	E_b (eV)	E_b ? (eV)	$\Delta E_b (\%)$
Fe _n	-2.12	-2.03	4.43	-2.95	-2.86	3.15
Co _n	-2.17	-2.17	0.00	-2.97	-2.96	0.34
Ni _n	-2.13	-2.12	0.47	-2.84	-2.83	0.35
Cu _n	-1.61	-1.59	1.26	-2.16	-2.14	0.93

Table 1: The binding energies, E_b , for TM_4^{pGMC} and TM_8^{pGMC} compared to Ref [1].



Figure S2: The stable isomers of Fe₈ clusters, with their respect IR spectra. The relative total energy, ΔE_{tot} , is related with the pGMC structure.



Figure S3: The stable isomers of Co_8 clusters, with their respect IR spectra. The relative total energy, ΔE_{tot} , is related with the pGMC structure.



Figure S4: The stable isomers of Ni₈ clusters, with their respect IR spectra. The relative total energy, ΔE_{tot} , is related with the pGMC structure.



Figure S5: The stable isomers of Cu₈ clusters y ith their respect IR spectra. The relative total energy, ΔE_{tot} , is related with the pGMC structure.

3 (ZrO₂)₁₃ Cluster



Figure S6: The infrared spectra for $(ZrO_2)_{13}^{pGMC}$. The most intense vibrational modes are highlighted for further analysis in the adsorption studies.



Figure S7: The projected density of states (pDOS) for the $(ZrO_2)_{13}$ cluster. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and their near orbitals are shown. The dashed lined is at the HOMO.

4 Atomic Structure Configurations: ESD Algorithm

The initial set of 10^6 configurations was randomly generated and reduced to a smaller set using a Euclidean Similarity Distance (ESD) algorithm implemented in-house. In this algorithm, every system composed of N atoms is represented by a vector, $\mathbf{x}(x_1,x_1,x_1...x_N)$, containing the distances between every atom and the systems center of gravity. These vectors are used to compute normalized Euclidean distances:

$$S(\alpha, \beta) = \frac{\sum_{i=1}^{N} (x_{i,\alpha} - x_{i,\beta})^2}{\sum_{i=1}^{N} x_{i,\alpha}^2 + x_{i,\beta}^2},$$
(1)

which are employed as a measure of the similarity between two systems α and β . Using this metric we can set a cutoff parameter S_{cut} , and only consider the most dissimilar systems by selecting the cases where $S(\alpha, \beta) > S_{cut}$.



5 The $TM_n/(ZrO_2)_{13}$ Structures

Figure S8: The optmized structures for (a) $Fe_1/(ZrO_2)_{13}$; and $Fe_4/(ZrO_2)_{13}$. The numbers above the structures are the relative energy (ΔE , in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein red, blue, and magenta colors indicate, respectively, the configurations obtained from Fe_4^{HEC} , Fe_4^{pGMC} , and the crossover between the structures. Yellow, green and red spheres indicate iron, zirconium and oxygen species.



Figure S9: The optimized structures for $Fe_8/(ZrO_2)_{13}$. The numbers above the structures are the relative energy, ΔE , in meV, and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein blue, red, green, and magenta colors indicate, respectively, the configurations obtained from Fe_8^{pGMC} , Fe_8^{1-HEC} and Fe_8^{2-HEC} , and the crossover between the structures. Yellow, green and red spheres indicate iron, zirconium and oxygen species.



Figure S10: The optmized structures for (a) $Co_1/(ZrO_2)_{13}$; and (b) $Co_4/(ZrO_2)_{13}$. The numbers above the structures are the relative energy (ΔE , in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein red, blue, and magenta colors indicate, respectively, the configurations obtained from Co_4^{HEC} , Co_4^{pGMC} , and the crossover between the structures. Dark blue, green and red spheres indicate cobalt, zirconium and oxygen species.



Figure S11: The optimized structures for $\text{Co}_8/(\text{ZrO}_2)_{13}$. The numbers above the structures are the relative energy (Δ E, in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein blue, red, green, and magenta colors indicate, respectively, the configurations obtained from $\text{Co}_8^{\text{pGMC}}$, $\text{Co}_8^{1-\text{HEC}}$ and $\text{Co}_8^{2-\text{HEC}}$, and the crossover between the structures. Dark blue, green and red spheres indicate cobalt, zirconium and oxygen species.



Figure S12: The optmized structures for (a) $Ni_1/(ZrO_2)_{13}$; and (b) $Ni_4/(ZrO_2)_{13}$. The numbers above the structures are the relative energy (ΔE , in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein where red, blue and magenta colors indicate, respectively, the configurations obtained from Ni_4^{HEC} , Ni_4^{pGMC} , and the crossover between the structures. Grey, green and red spheres indicate nickel, zirconium and oxygen species.



Figure S13: The optimized structures for Ni₈/(ZrO₂)₁₃. The numbers above the structures are the relative energy (ΔE , in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein blue, red, green, and magenta colors indicate, respectively, the configurations obtained from Ni₈^{pGMC}, Ni₈^{1-HEC} and Ni₈^{2-HEC}, and the crossover between the structures. Grey, green and red spheres indicate nickel, zirconium and oxygen species.



Figure S14: The optmized structures for (a) $Cu_1/(ZrO_2)_{13}$; and (b) $Cu_4/(ZrO_2)_{13}$. The numbers above the structures are the relative energy (ΔE , in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein red, blue and magenta colors indicate, respectively, the configurations obtained from Cu_4^{HEC} , Cu_4^{pGMC} , and the crossover between the structures. Light blue, green and red spheres indicate copper, zirconium and oxygen species.



Figure S15: The optimized structures for $Cu_8/(ZrO_2)_{13}$. The numbers above the structures are the relative energy (ΔE , in meV), and in parenthesis the effective coordination number (ECN, in next near neighbors - NNN), wherein blue, red, green and magenta colors indicate, respectively, the configurations obtained from Cu_8^{pGMC} , Cu_8^{1-HEC} and Cu_8^{2-HEC} , and the crossover between the structures. Light blue, green and red spheres indicate copper, zirconium and oxygen species.

6 Definition for Geometrical Parameters for $TM_n/(ZrO_2)_{13}$

The geometrical parameters were obtained based on the effective coordination number (ECN) concept,? considering the fact that a particular atom i is strongly bonded to each j closer atom in the structure and, hence, a weighted function is used to capture even small changes in the atomic environment, for example, when there is an adsorption as our case. Thus, the ECN for a particular atom is given by

$$\text{ECN}_{i} = \sum_{j} exp \left[1 - \left(\frac{d_{ij}}{d_{av}^{i}} \right)^{6} \right], \qquad (2)$$

where d_{ij} is the distance between atoms *i* and *j*, while the average bond length for a particular atom (d_{av}^i) is defined as,

$$d_{av}^{i} = \frac{\sum_{j} d_{ij} exp\left[1 - \left(\frac{d_{ij}}{d_{av}^{i}}\right)^{6}\right]}{\sum_{j} exp\left[1 - \left(\frac{d_{ij}}{d_{av}^{i}}\right)^{6}\right]},$$
(3)

from which is possible to observe that d_{av}^i requires a self-consistent resolution, within the initial d_{av}^i value being defined by the smallest distance between *i* and *j* atoms. In this project, the convergence is reached once $|d_{av}^i(\text{new}) - d_{av}^i(\text{old})| < 10^{-4}$ Å. Finally, the average ECN for a structure containing *N* atoms is calculated as

$$ECN = \frac{1}{N} \sum_{i=1}^{N} ECN_i$$
(4)

From previous definitions, the number of bonds between TM and O in the $TM_n/(ZrO_2)_{13}$ is directly given, N^{TM-O} , while the shortest distance between these atoms is d_{min}^{TM-O} . With the aim to consider the changes in the $(ZrO_2)_{13}$ cluster size due to the adsorption, we also calculated its radius variation. Once the zirconia cluster is not a perfect sphere, we calculated the average radius by

$$Rav = \frac{r_c + \frac{d_{max}}{2}}{2},\tag{5}$$

where r_c is the distance of the farthest atom from the geometric center, and d_{max} is the largest distance between two atoms in the structure.

Therefore, the geometric parameters' variations ($\chi = \text{ECN}, d_{av}$, or R_{av}) were obtained as

$$\Delta \chi = \left(\frac{\chi^{(\text{ZrO}_2)_{13}^{\text{ad}}} - \chi^{(\text{ZrO}_2)_{13}^{\text{pGMC}}}}{\chi^{(\text{ZrO}_2)_{13}^{\text{pGMC}}}}\right) \times 100\%,\tag{6}$$

where $(ZrO_2)_{13}^{ad}$ and $(ZrO_2)_{13}^{pGMC}$ are, respectively, the structures after and before the formation of nano-interfaces.

We also performed structural analysis considering the number of TM atoms in the interface. We consider a TM atom in the interface with the cluster when such atom is directly coordinated with an O or Zr atom from the ZrO_2 cluster. The coordination is obtained considering that two atoms are interacting when the distance between them is smaller than a cutoff radius set to r_{cut} . The r_{cut} is calculated depending on each structure and atom specie to make the absolute value of the difference between the closest and farthest atoms within the radius to be smaller than 37.5 % of the average of the distances between all atoms in the same radius.

7 Vibrational Analysis



Figure S16: The infrared spectra for $TM_n/(ZrO_2)_{13}$ directly compared to the gas-phase TM_n , n = 4 and 8, and $(ZrO_2)_{13}$ clusters.

The infrared spectra for the lowest energy $TM_n/(ZrO_2)_{13}$ configurations were calculated and compared to the TM_n and $(ZrO_2)_{13}$ clusters in Figure S16. The first observation is, beyond to confirm that the lowest energy configurations are true local minima - since there is no imaginary frequencies, that the major contribution to the $TM_n/(ZrO_2)_{13}$ spectra comes from the $(ZrO_2)_{13}$ cluster, as expected. The adsorption of TM_1 atoms occur at the same adsorption site preference, which eliminates the O6 asymmetric stretching (709 cm^{-1}) of $(ZrO_2)_{13}$, while the bending mode related to these atoms is intensified. Also, the increasing in the TM atomic number decreases the vibrational intensity.

8 Hirshfeld Charges Distribution



Figure S17: Atomic distribution of Hirshfeld charges for gas phase $(ZrO_2)_{13}$ cluster.



Figure S18: Atomic distribution of Hirshfeld charges for (a) $Fe_1/(ZrO_2)_{13}$; and (b) $Fe_4/(ZrO_2)_{13}$ lowest energy configurations.



Figure S19: Hirshfeld charges distribution for (a) Zr and O atoms, and (b) Fe and the O atoms in the $Fe_8/(ZrO_2)_{13}$ lowest energy configuration.



Figure S20: Atomic distribution of Hirshfeld charges for (a) $Co_1/(ZrO_2)_{13}$; and (b) $Co_4/(ZrO_2)_{13}$ lowest energy configurations.



Figure S21: Hirshfeld charges distribution for (a) Zr and O atoms, and (b) Co and the O atoms in the $Co_8/(ZrO_2)_{13}$ lowest energy configuration.



Figure S22: Atomic distribution of Hirshfeld charges for (a) $Ni_1/(ZrO_2)_{13}$; and (b) $Ni_4/(ZrO_2)_{13}$ lowest energy configurations.



Figure S23: Hirshfeld charges distribution for (a) Zr and O atoms, and (b) Ni and the O atoms in the $Ni_8/(ZrO_2)_{13}$ lowest energy configuration.



Figure S24: Atomic distribution of Hirshfeld charges for (a) $Cu_1/(ZrO_2)_{13}$; and (b) $Cu_4/(ZrO_2)_{13}$ lowest energy configurations.



Figure S25: Hirshfeld charges distribution for (a) Zr and O atoms, and (b) Cu and the O atoms in the $Cu_8/(ZrO_2)_{13}$ lowest energy configuration.

9 Hirshfeld Charges and HOMO-LUMO gap vs Structural Stability



Figure S26: Relative energies normalized by the number of TM atoms in the interface against the charge accumulated on such TM atoms and against the HOMO-LUMO gaps. The values obtained for the lowest energy configurations are represented by filled symbols, while open symbols represent the high energy systems.



10 Projected Density of States for $TM_n/(ZrO_2)_{13}$

Figure S27: The projected density of states (pDOS) for the lowest energy configurations of $TM_n/(ZrO_2)_{13}$, TM = Fe, Co, Ni, and Cu, and n = 1,4 and 8. A Gaussian broadening of 0.010 eV was used in the plot. Positive and negative numbers of pDOS are related to *up* and *down* states in collinear calculations.

References

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