

The impact of Cu atoms on the reactivity of ZrO₂ oligomers

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Abstract A theoretical study on (ZrO₂)_n (*n*=1–5) and Cu/ZrO₂ oligomers is presented, DFT/B3LYP/6-31G** calculations along with Lanl2DZ pseudopotentials on metallic centers have been used to predict ionization potentials and electron affinities, chemical potentials and bandgaps indicating that the reactivity reaches reasonably constant values at *n*=5. The effect of copper atoms adsorbed on (ZrO₂)_n is discussed and the reactivity of oligomers of ZrO₂ and Cu/ZrO₂ are compared, results indicate that Cu activates the systems by localizing the specific nucleophilic and electrophilic reactivity.

Keywords Zirconia · DFT · Copper · Theoretical

Introduction

Oxide-supported transition metals have received much attention due to their utility in automotive catalysis and other catalytic processes, [1–3] the use of an oxide as a support material for transition metals has clear economic

benefits, because it reduces the amount of costly noble metals (e.g., Rh, Pt) that need to be used in functioning catalysts. Also, metal islands and particles often show enhanced catalytic activity beyond that of the bare metal, [4] and the ability of the support material to provide oxygen to chemical reactions can significantly enhance many catalytic mechanisms.

Zirconia (ZrO₂) is a promising and technologically important support medium in catalysis, it exhibits many desirable structural and electronic properties, and has been used in many applications, in particular as catalyst support for transition metals such as Cu [1–3]. Zirconia-supported copper exhibits high activity for the catalytic promotion of NO_x reduction by CO (forming N₂ and CO₂) [5–7]. Moreover it is active on CO₂ hydrogenation, [8–10] water-gas-shift and combustion, [8–10] methanol synthesis, [11–13] and CO oxidation [14].

The activity of copper supported on zirconia (Cu/ZrO₂) has been discussed to be originated from an interaction between copper and zirconia, and correlates well with the presence of highly dispersed Cu species on the ZrO₂ surface, and it persists until copper atoms agglomerate into large particles. This interaction resulted in a better Cu dispersion and surface area than CuO or ZrO₂ alone [15]. A density functional theory (DFT) calculation revealed the electron transfer between Cu and Zirconia and the weakened surface hydroxyl on zirconia surface, [16] but the mechanism and the role that Cu plays in those reactions is still unknown.

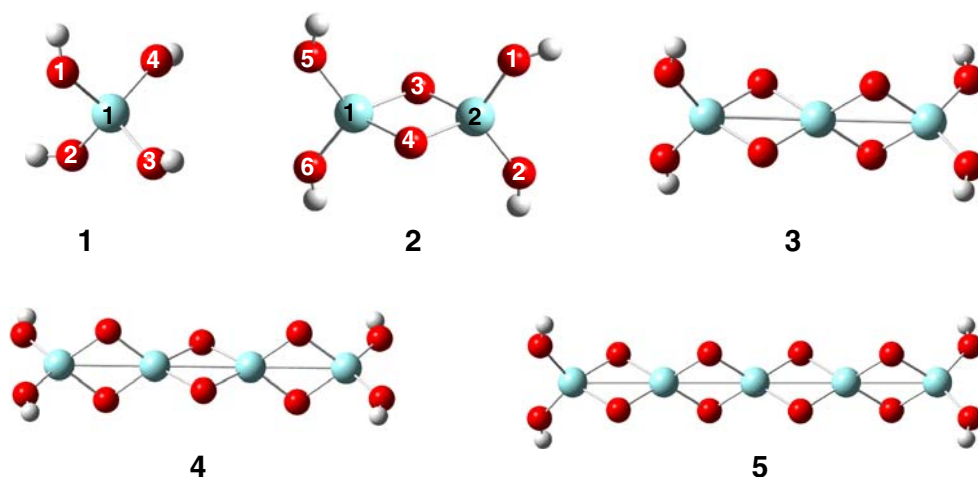
In this paper we report DFT/B3LYP/6-31G** calculations of linear zirconia oligomers. Energetic and electronic properties are calculated in order to characterize the patterns followed by several different properties, as the number of units increases. Linear oligomers, built up using ZrO₂ as building block, are shown in Fig. 1 thus giving rise to the series of linear zirconia oligomers 2–5. Structures 1 and 2

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Fig. 1 (a) Structures of ZrO_2 (1), $(\text{ZrO}_2)_2$ (2), $(\text{ZrO}_2)_3$ (3), $(\text{ZrO}_2)_4$ (4)



were used in turn to mimic the zirconia-copper interaction, the resulting composite structures are displayed in Fig. 2.

The energy and the electronic properties, which are related to the reactivity of these systems, were analyzed in detail. We have also investigated the behavior of these properties when these structures reach the so called surface bulk condition ($n \rightarrow \infty$, where n is the number of zirconia units involved) in order to get the behavior of a hypothetical catalytic surface. The properties we report here are the ionization potential (IP), electron affinity (EA) and the chemical potential (μ) which measures the escaping tendency of electrons from equilibrium [17]. The latter is related to the electron transfer from sites of high to low μ . The energy gap between HOMO and LUMO frontier orbitals (ε) has also been studied and an analysis of local properties derived from μ as the local Fukui function [18] is provided.

This paper is organized as follows: the next section is devoted to the definition of the concepts used in the analysis of the various systems and the computational details are presented. Section 2 is devoted to the discussion of the results and in Sect. 3 some conclusions are drawn.

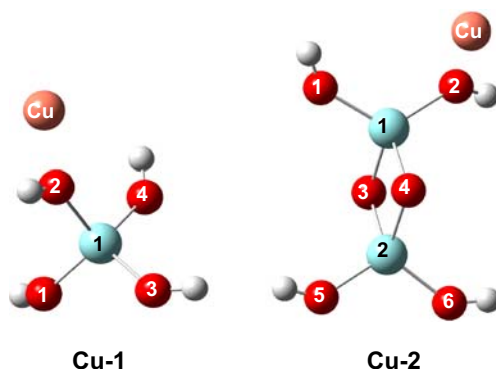


Fig. 2 Structures of Cu-1 and Cu-2

Theoretical background and details of calculation

Global Reactivity Indexes Within the conceptual framework of DFT, the chemical potential of a system of N particles, with total energy E and subject to the external potential $v(\vec{r})$, is defined as [19]

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi. \quad (1)$$

In Eq. (1) χ is the electronegativity [20–25]. The use of the finite difference approximation and Koopmans's theorem [26] leads to the following working expressions for μ :

$$\mu \approx -\frac{1}{2}(IP + EA) \approx \frac{1}{2}(\varepsilon_L + \varepsilon_H), \quad (2)$$

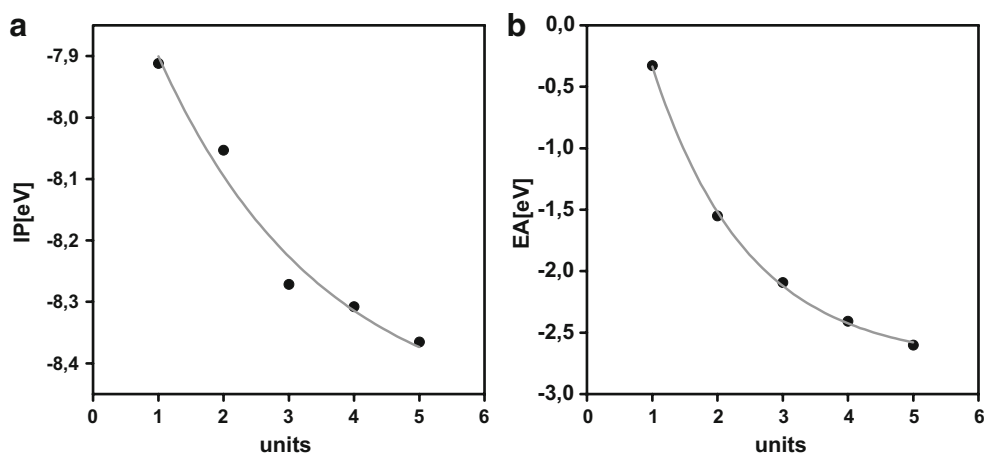
where IP is the first ionization potential, EA is the electron affinity, ε_L and ε_H are the energies of the lowest unoccupied and the highest occupied molecular orbitals, LUMO and HOMO.

On the other hand, since the conductivity of an electronic system is related to the energy gap $\varepsilon = \varepsilon_L - \varepsilon_H$, this property has also been explored in zirconia and in the composite system with copper.

Table 1 Geometrical parameters at B3LYP/6-31** and B3LYP/Lan12dz on $(\text{ZrO}_2)_n$ ($n=1-5$) and $\text{Cu}/(\text{ZrO}_2)_n$ ($n=1,2$) oligomers. Distances in Å and angles in degrees

System	b(Zr-Zr)	b(Zr-O)	b(Zr-Cu)	a(Zr-O-Zr)	a(Cu-Zr-O)
1		1.99			
2	3.02	1.99		98.8	
3	3.02	2.00		98.4	
4	3.02	2.00		98.4	
5	3.02	2.00		98.4	
1-Cu		1.99	2.1		112.0
2-Cu	3.02	1.99	2.1	98.4	100.0

Fig. 3 EA and IP on the oligomers. All values are in eV



Local reactivity indexes Local reactivity indexes are intimately related to the intrinsic selectivity and/or specificity of chemical systems. The key concept in selectivity is the Fukui function that is defined as: [17, 18, 27]

$$f(r) = \left(\frac{\partial \rho}{\partial N} \right)_{v(r)} = \left(\frac{\delta \mu}{\delta v(r)} \right)_N \quad (3)$$

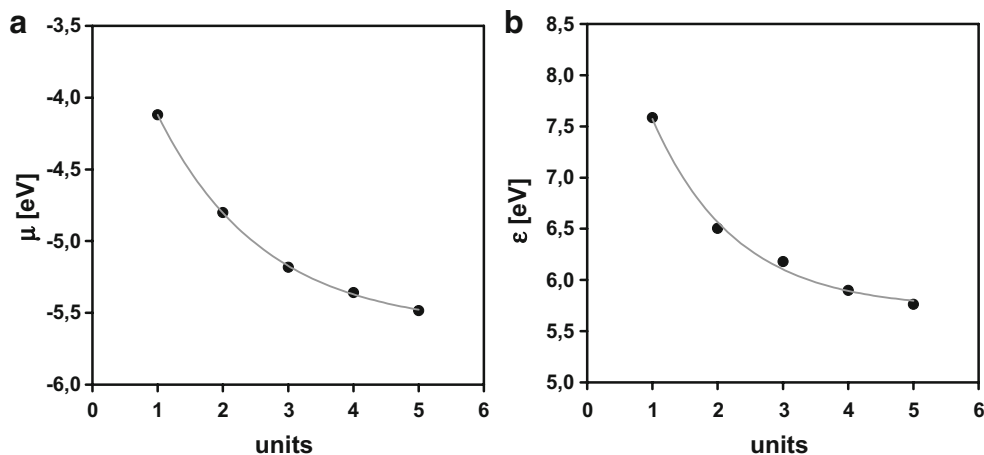
Although an analytic expression for the Fukui function is not available, its evaluation is usually done by using the frozen orbital approximation, that leads to the electrophilic and nucleophilic Fukui functions [28, 29]:

$$f^-(r) \approx |\phi^h(r)|^2 \Rightarrow f_k^- = \int_k f^-(r) dr \approx |\phi_k^h|^2 \quad (4)$$

$$f^+(r) \approx |\phi^l(r)|^2 \Rightarrow f_k^+ = \int_k f^+(r) dr \approx |\phi_k^l|^2 \quad (5)$$

where $|\phi^h(r)|^2$ and $|\phi^l(r)|^2$ are the densities of HOMO and LUMO frontier orbitals, k indicates the site where Fukui index is condensed. Equations 4 and 5 reveal that a highly electrophilic/nucleophilic center is a site presenting a high value of the associated Fukui function.

Fig. 4 μ and ε on the oligomers. All values are in eV



Computational details All calculations were performed using the Gaussian 03 package [30]. All the systems considered in this work, were fully optimized at the B3LYP/6-311G** level [31, 32]. The zirconium and copper atoms were calculated using Lanl2DZ pseudopotentials [33–35]. All minimum energy structures shown in Figs. 1 and 2 were confirmed by the absence of imaginary frequencies.

Results and discussion

Geometrical parameters In Table 1 are shown the fully optimized geometrical parameters for zirconia oligomers and Cu/ZrO₂ systems, whose structures are displayed in Figs. 1 and 2. It is interesting to note that the optimized structures are in quite good agreement with X ray data on cubic zirconia, with differences not larger than (0.6 Å) [1, 36] and changing only slightly with the oligomer size (~0.01–0.02 Å). It is also interesting to point out that there are no marked structural distortions as the system grows in size, both for zirconia chains and the copper adsorbed structures. It has been found that as copper is adsorbed on

Table 2 μ and ε at B3LYP/LANL2DZ/6-31** on the smaller zirconia clusters and the effect of copper

System	μ	ε
1	-4.12	3.79
Cu-1	-1.58	0.47
2	-4.80	3.25
Cu-2	-2.03	0.25

zirconia it binds at the oxygen atom, in agreement with previous experimental and theoretical results [1, 8].

Ionization potentials and electron affinities Some properties of oligomeric systems are quite different from those of the monomer or the surface [37]. In fact, the latter correspond to extreme cases that can be visualized as infinitely small and infinitely large polymers. This applies to the evolution of the ionization potentials and the electron affinities as a function of the size and the geometry of the oligomer. Both properties are expected to converge at the “surface bulk limit” that corresponds to a very large number of units ($n \rightarrow \infty$). In this context, the evolution of a property $P(n)$, such as IP or EA, as a function of the number of building units of atomic or molecular aggregates, can be described by the following analytic form: [37]

$$P(n) = P(\infty) + A_p e^{-an}, \quad (6)$$

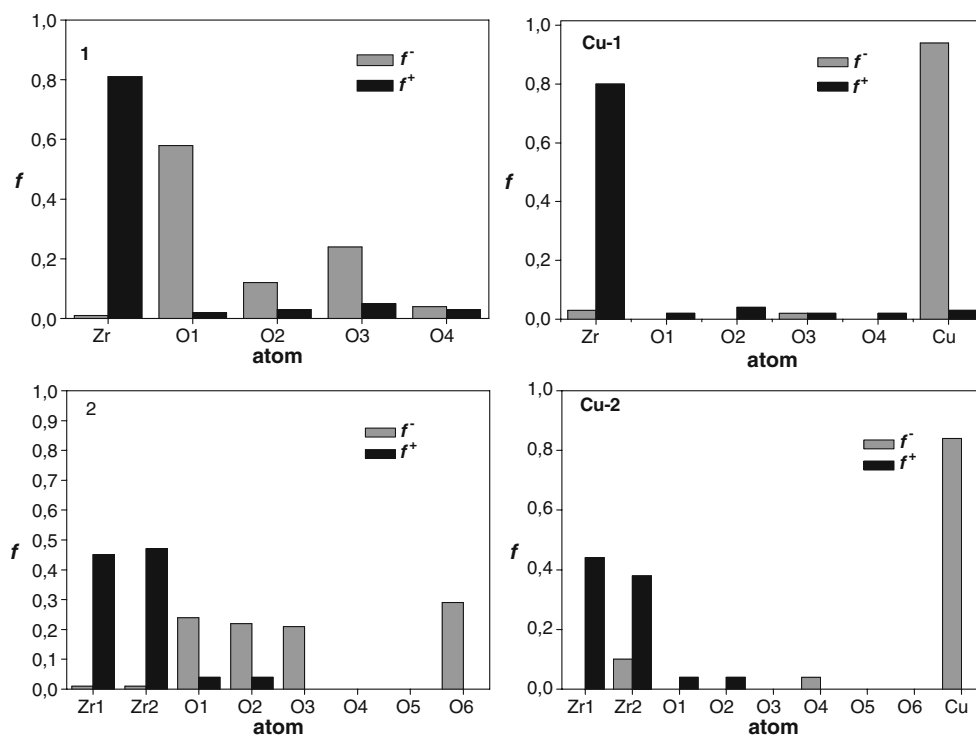
where a takes values of 2/5 and 2/3 for IP and EA respectively; $P(\infty)$ corresponds to the property value in

the surface bulk limit ($n \rightarrow \infty$) and A_p is a fitting parameter. Figure 3 displays the behavior of IP and EA for the five zirconia oligomers we have investigated. Figure 3 (a) shows that EA values decrease slightly as they approach $EA(\infty) = -2.47$, with rather small variations, indicating that these kind of structures are nearly saturated and thus unable to accept electrons. The IP (see Fig. 4 (b)) values show a similar trend, the amount of energy needed to remove an electron as the number of units n grows up, converges rapidly to the surface bulk value is $IP(\infty) = -8.49$ eV.

Size dependence of μ and ε The use of the analytic form of Eq. (6), for $\mu(n)$ and $\varepsilon(n)$ leads to:

$$\begin{aligned} \mu(n) &= \mu(\infty) + A_\mu e^{-0.6n}, \\ \varepsilon(n) &= \varepsilon(\infty) + A_\varepsilon e^{-0.8n} \end{aligned} \quad (7)$$

the trends followed by $\mu(n)$ and $\varepsilon(n)$ are displayed in Fig. 4. We observe in Fig. 4 (a) that as the number of units increase from n to $n+1$ the chemical potential decreases until reaching $\mu(\infty) = -5.6$ eV and $A_\mu = 2.75$. Similarly, ε decreases reaching $\varepsilon(\infty) = 5.7$ eV ($A_\varepsilon = 4.06$), a value that is in good agreement with experimental data [8] but not small enough to allow electronic conductivity. In the surface bulk limit it is not possible for the electron transport, but doping or substituting with donor/acceptor atoms, such as copper, may induce charge transfer and possibly increase conductivity of the composite system.

Fig. 5 Nucleophilic (f^-) and electrophilic (f^+) Fukui functions at the studied oligomers

Copper and its relation to catalytic properties We have studied so far the electronic properties of zirconia clusters and its size dependence observing that μ and ϵ decrease until reaching constant values at -5.6 eV and 5.7 eV respectively. In order to study the copper influence on ZrO_2 and $(\text{ZrO}_2)_2$ clusters, a copper atom adsorbed on them is considered. The reactivity changes induced by copper are shown in Table 2 where the values of μ , and ϵ for copper adsorbed clusters (**Cu-1** and **Cu-2**) are compared to bare zirconia (1 and 2).

Moreover, when local properties are analyzed to characterize the change of the selectivity of zirconia surfaces the results strongly confirm the change on the electronic structure due to Cu. In Fig. 5 are displayed the f^- and f^+ on the selected oligomers whose structures and atom labels are displayed in Fig. 2, the results show that copper attracts most of the nucleophilic reactivity observed on the oxygen in bare zirconia oligomers. Whereas the electrophilic character remains on Zr atoms. This indicates that the adsorption of Cu on zirconia creates an active site $\text{Zr}-\text{O}\cdots\text{Cu}$ for both oxidation and reduction that can oxidize/reduce species on its surface, as well as present catalytic activity not observed on each element separately.

For example, it has been shown how the presence of copper promotes the activity of the Cu/ZrO_2 system for methanol synthesis starting from CO and H_2 [38–42]. It has been proposed that the role of copper is to dissociate the H_2 molecule to generate the hydrogen spillover, which then will participate on the CO or CO_2 hydrogenation to form CH_3OH on the ZrO_2 surface. Another example of the notable activity of the $\text{Cu}-\text{ZrO}_2$ system is its activity for hydrogen production by methanol steam reforming, infrared studies of Araya et al. show that when H_2O and CH_3OH flow over pure ZrO_2 is less reactive at methanol adsorption than Cu/ZrO_2 [43].

These two examples provide experimental evidence of the strong chemical interaction between Cu and ZrO_2 in a Cu/ZrO_2 system as it has been previously indicated by the theoretical results presented in this work. Further work is now underway to understand in more detail the role of each element in the global reaction mechanism of steam reforming.

Concluding remarks

We have studied different zirconia oligomers through the characterization of their energies, ionization potentials and electron affinities. It has been found that the IP's and EA's are strongly dependent on the number of building blocks involved; their energy stabilizes to reach a constant value with the number of zirconia units. The bandgap obtained at infinite units ($\epsilon(\infty)$) is in good agreement with experimental

values; however, zirconia is not able to transfer electrons, which only occurs in materials with bandgaps smaller than $1\text{--}1.3$ eV [44, 45].

The addition of Cu, increases drastically the charge transfer and decreases the bandgap, this is also confirmed by the exponential fit applied to $\mu(n)$ where it was found that the charge transfer comes from Cu to zirconia. Copper creates dual active sites where it acts as an electron donor whereas the Zr atom that is next to Cu acts as an electron acceptor, explaining the nature of the catalytic activity of this composite material.

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