Influence of the zeolite support on the catalytic properties of confined metal clusters: a periodic DFT study of O\textsubscript{2} dissociation on Cu\textsubscript{n} clusters in CHA

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The catalytic properties of sub nanometer Cu\textsubscript{n} clusters are modified by interactions with the inorganic supports used for their stabilization. In this work the reactivity towards O\textsubscript{2} dissociation of Cu\textsubscript{5} and Cu\textsubscript{7} clusters confined within the cavities of CHA zeolite is theoretically investigated by means of periodic DFT calculations. Increasing the of Al content in the zeolite framework not only modifies cluster morphology, but also leads to a decrease in the electronic density available on the supported Cu\textsubscript{n} clusters, which in turn leads to higher activation energies for O\textsubscript{2} dissociation. Together with cluster size and shape, the Si/Al ratio in the zeolite support appears as a potential parameter to finely tune the stability and oxidation properties of Cu-based catalysts.

Introduction

Sub nanometre metal clusters composed by just a few atoms exhibit electronic, optical, and catalytic properties different from those of larger nanoparticles and bulk metals, which are mostly associated to the accessibility of their low coordinated atoms and to a molecular-like electronic structure with discrete energy levels and localized orbitals. The catalytic properties of metal clusters depend strongly on their size and shape, and are altered by interactions with protecting ligands or inorganic supports. Understanding the nature and extent of these modifications is key to potentially achieve a fine tuning of their catalytic performance.1-8 Copper is an abundant, cheap and nontoxic metal, so copper clusters are promising materials for various applications such as biosensors, therapeutic agents and efficient catalysts.9-11 Previous theoretical and experimental work in our group has demonstrated that the ability of copper clusters to dissociate O\textsubscript{2}, and the subsequent reactivity of the resulting adsorbed O atoms, is closely linked to the size and morphology of the cluster. The activation energy for O\textsubscript{2} dissociation on planar (2D) Cu\textsubscript{5} clusters is much higher than on 3D Cu\textsubscript{5} or Cu\textsubscript{7} clusters, making them more resistant against oxidation.12,13 Moreover, the reactivity of bi-coordinated O atoms adsorbed at the edges of planar (2D) Cu\textsubscript{5} clusters is different from that of O atoms three-coordinated on Cu facets, with direct implications in the reaction mechanism and selectivity achieved in propene epoxidation, CO oxidation, and partial methane oxidation to methanol.14-16 For practical application, it is necessary to stabilize metal clusters either with protecting ligands in solution or by supporting them on solid organic or inorganic matrices, which could provoke changes in their electronic structure and therefore modify their catalytic behaviour. Graphene-based materials, metal-organic frameworks (MOFs), metal oxides and microporous solids have been used as supports for metal nanoparticles and clusters,2,4-8,17-26 and there are numerous examples where the behaviour of the metal is modified due to the interaction with the support. Thus, strong interactions between Cu clusters and perovskite support were theoretically and experimentally confirmed in Cu\textsubscript{2}O\textsubscript{3}/SrTiO\textsubscript{3} nanocomposite catalysts for CO oxidation and NO reduction;15 enhanced activity and improved stability for low T CO oxidation were reported for calcined Cu clusters supported on CeO\textsubscript{2} nanorods;23 the amount of highly dispersed Cu\textsuperscript{0} and Cu\textsuperscript{+} species necessary to catalyze the Water Gas Shift reaction was optimized in Cu/SiO\textsubscript{2} catalyst;24 the catalytic performance of Cu/ZrO\textsubscript{2} catalysts in the CO\textsubscript{2} hydrogenation to methanol was enhanced by increasing the number of Cu-ZrO\textsubscript{2} interface sites;25 and even the crystallographic phase of ZrO\textsubscript{2} in Cu/ZrO\textsubscript{2} catalysts was found to influence the formation of acetaldehyde and ethyl acetate from ethanol.26 It seems therefore necessary to understand at a molecular level the nature of the interactions between metal clusters and supports. Zeolites are good candidates to investigate the influence of the support on the electronic and catalytic properties of metal clusters. On one hand, their microporous structure composed by Si and O atoms provides an excellent environment to confine small metal clusters and prevent their agglomeration into larger particles. On the other hand, the substitution of Si atoms with Al in the framework generates a net negative charge that must be compensated with species bearing positive charge, such as protons, isolated cations or partially charged metal clusters.17-21 By modifying the amount of Al in the zeolite framework it is possible to modulate the total positive charge on the confined metal clusters, and analyse how this factor affects their reactivity.
In this contribution, we explore by means of periodic density functional (DFT) calculations whether the trends previously reported for $O_2$ dissociation on copper clusters are modified when the clusters are confined within the cavities of a zeolite with the CHA structure (see Figure 1). For this purpose, we consider three different clusters, planar Cu$_5$-2D, three-dimensional Cu$_5$-3D and three-dimensional Cu$_7$-3D, stabilized within the cages of CHA models containing an increasing amount of framework Al atoms ($n_{Al} = 0$, 1 and 2). Then, we investigate the adsorption and dissociation of molecular $O_2$ on each of the nine resulting Cu$_n$-CHA systems using dispersion-corrected DFT calculations, and analyse the possible correlations between optimized geometry, charge transfer and activation energy barriers. We find that the presence of Al atoms in the zeolite framework modifies the geometrical structure and the ability of the supported Cu$_n$ clusters to dissociate $O_2$, making them more resistant against oxidation and good candidates for challenging oxidation reactions at experimentally significant Si/Al ratios.

![Figure 1. Optimized structures of Cu$_{n}$-2D, Cu$_{n}$-3D and Cu$_{n}$-3D clusters, isolated and confined within CHA models containing 0, 1 and 2 framework Al atoms. Si and O are depicted as red and yellow wires, Cu and Al are depicted as brown and light green balls.](Image)

**Experimental**

Periodic density functional theory (p-DFT) were performed using the VASP 5.2 code$^{27,28}$ and the PBE functional$^{29}$ including Grimme’s D3 correction$^{30}$ for dispersion interactions. The valence density was expanded in a plane wave basis set with a kinetic energy cutoff of 600 eV, and the effect of the core electrons in the valence density was taken into account by means of the projected augmented wave (PAW) formalism.$^{31}$ All calculations are spin-polarized, and in all cases all structures converged to a doublet state with only one unpaired electron. Electronic energies were converged to 10$^{-6}$ eV and geometries were optimized until forces on atoms were <0.01 eV/Å. Integration in the reciprocal space was carried out at the Γ k-point of the Brillouin zone.

The zeolite chabazite, with the CHA structure, was modelled by means of a hexagonal unit cell with lattice with parameters $a = b = 13.8026$ Å, $c = 15.0753$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, containing 36 T atoms (Si or Al) and 72 O atoms. Three zeolite framework compositions with increasing number of Al atoms ($n_{Al} = 0$, 1 and 2) and three copper clusters with different size and morphology, (Cu$_5$-2D, Cu$_5$-3D and Cu$_7$-3D), were considered, giving rise to nine different catalytic systems. For each system, the copper cluster was initially placed in the centre of the CHA cage and in the proximity of the 8-ring window connecting two cages. Figure 1 shows the most stable structures obtained after geometry optimization.

In all calculations, the positions of all atoms in the system were fully optimized without restrictions. Transition states were characterized by frequency calculations to confirm that the imaginary frequency corresponds to the desired reaction coordinate. The Hessian matrix and vibrational frequencies were calculated using density functional perturbation theory (DFPT)$.^{32}$ Transition states were located using the DIMER algorithm.$^{33,34}$ Atomic charges were calculated using the NBO approach.$^{35}$ The MOLDEN$^{36}$ and ChemCraft$^{37}$ programs were used throughout the work to visualize the systems and their frequencies.

**Results and discussion**

**Confined Cu$_n$ clusters**

Figure 1 shows the most stable isomers of isolated Cu$_2$-2D, Cu$_3$-2D and Cu$_3$-3D, together with their optimized geometries when they are confined within the cavities of CHA models containing 0, 1 and 2 framework Al atoms. Interaction of Cu$_5$ clusters with the pure silica CHA framework (0Al model) is weak and does not lead to any relevant geometry deformation of the confined clusters. The shortest Cu-O$_2$ distances are 2.387, 2.097 and 2.281 Å in Cu$_5$-2D, Cu$_5$-3D and Cu$_7$-3D, respectively, and the three clusters become positively charged by less than 0.2 e (see Table 1). The substitution of one Si atom by Al (1Al model) generates a net negative charge in the zeolite framework that is compensated by the appearance of a positive charge of ~0.8 e on the confined clusters (see Table 1). The shortest Cu-O$_2$ distances in the 1Al model decrease to 1.974, 2.067 and 2.125 Å in Cu$_5$-2D, Cu$_5$-3D and Cu$_7$-3D, and the planar geometry of the Cu$_5$-2D cluster is slightly distorted. When two Si atoms in the framework are replaced by Al (2Al model) all copper clusters interact strongly with the framework, forming at least 6 bonds with the shortest optimized Cu-O$_2$ framework distances being 1.984, 1.982 and 2.022 in Cu$_5$-2D, Cu$_5$-3D and Cu$_7$-3D, and the planar geometry of the Cu$_5$-2D cluster is slightly distorted.

In all calculations, the positions of all atoms in the system were fully optimized without restrictions. Transition states were characterized by frequency calculations to confirm that the imaginary frequency corresponds to the desired reaction coordinate. The Hessian matrix and vibrational frequencies were calculated using density functional perturbation theory (DFPT). Transition states were located using the DIMER algorithm. Atomic charges were calculated using the NBO approach. The MOLDEN and ChemCraft programs were used throughout the work to visualize the systems and their frequencies.

**Table 1.** Total atomic charges on Cu$_n$ clusters (q$_{Cu_n}$, in e) and on adsorbed O$_2$ (q$_{O_2}$, in e) calculated for the Cu$_n$ clusters stabilized in CHA zeolite and for structures R, TS and P involved in O$_2$ dissociation.

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<tr>
<th></th>
<th>nAl</th>
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<th>q$_{Cu_5}$ (R)</th>
<th>q$_{Cu_5}$ (TS)</th>
<th>q$_{Cu_5}$ (P)</th>
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<td>2.768</td>
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O₂ adsorption on supported Cuₙ clusters

Molecular O₂ adsorbs on small Cuₙ clusters forming stable complexes in which the O-O bond is activated by charge transfer from the metal cluster to the π* orbital of O₂, facilitating its dissociation to produce adsorbed O atoms. In isolated clusters where all the electrons are available to be transferred the activation of molecular O₂ depends on the cluster size and on the geometry of adsorption on the cluster: the larger the number of Cu-O contacts, the larger the charge transferred to O₂.9,10 When the clusters are supported in a zeolite the availability of electrons to be transferred decreases with increasing the Al content in the framework, adding a new variable to this process.

Figure 2 shows the optimized geometries of the most stable complexes found for O₂ adsorbed on Cu₅-2D, Cu₅-3D and Cu₇-3D clusters confined within CHA models containing 0, 1 and 2 framework Al atoms. Since these structures are the reactant species in the O₂ dissociation process, they are labelled as R in Tables 2 and 3, summarizing calculated charges and optimized OO bond lengths, respectively.

Molecular O₂ adsorbs on Cuₙ clusters forming two or three Cu-O bonds. In the systems not containing Al the geometry of the cluster is not modified after O₂ adsorption, but in the 1Al and 2Al models the clusters undergo important restructuration upon interaction with O₂, usually leading to lower symmetry structures. The Cu₅-2D cluster loses its planarity and in the presence of two framework Al atoms it evolves to a 3D structure not too different from that obtained for Cu₇-3D cluster. In all cases a net transfer of electron density from the catalyst to O₂ occurs, leading to a net negative charge on adsorbed O₂ and a net positive charge on the Cuₙ clusters that follows the trend with Al content reported for the confined clusters without adsorbates (see Tables 1 and 2, and Figure S1). However, not all the electron density lost by the metal clusters ends up in O₂ (see Figure S2). The largest capture of electron density by O₂ occurs in the systems with only one framework Al. Accordingly, the increase in the optimized O-O bond length is also largest in the 1Al models, and the correlation between rOO and neet charge on O₂ follows the trend with Al content reported for the confined clusters without adsorbates (see Figures S3 and S4). The calculated adsorption energies E_ads summarized in Table 4 and plotted in Figure S5 are on average larger in the planar cluster Cu₅-2D than in Cu₇-3D and less favourable on Cu₇-3D, and as a general trend they are more favourable as the charge transferred to O₂ increases (see Figure 3b).

Table 2. Total atomic charges on adsorbed O₂ (qO₂, in e) calculated for structures R, TS and P involved in O₂ dissociation.

<table>
<thead>
<tr>
<th>nAl</th>
<th>qO₂(R)</th>
<th>qO₂(TS)</th>
<th>qO₂(P)</th>
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<td>Cu₅-2D</td>
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Table 3. Optimized values of the OO distance (rOO in Å) in structures R, TS and P involved in O₂ dissociation.

<table>
<thead>
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<th>rOO(R)</th>
<th>rOO(TS)</th>
<th>rOO(P)</th>
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<td> </td>
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<tr>
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<tr>
<td> </td>
<td>2</td>
<td>1.493</td>
<td>1.841</td>
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</table>

Figure 2. Optimized structures of O₂ adsorbed on Cu₅-2D, Cu₅-3D and Cu₇-3D clusters confined within CHA models containing 0, 1 and 2 framework Al atoms. Si and O are depicted as red and yellow wires, Cu and Al are depicted as brown and light green balls.
O₂ dissociation on supported Cuₙ clusters

The electron density transferred to adsorbed O₂ weakens the OO bond facilitating its dissociation through the transition states depicted in Figure 4. The two O atoms are always interacting with at least two Cu atoms of the cluster, and the optimized OO distances in the TS structures range from 1.82 to 1.94 Å (see Table 3). Additional electron density is transferred to O₂ from the Cuₙ clusters, whose positive charge increases following the trend with Al content described in Sections 3.1 and 3.2.

The activation energies for the dissociation of O₂ on the supported Cuₙ clusters are summarized in Table 4 and plotted in Figure 3c to facilitate its analysis. In the systems without framework Al the trend in activation energies is quite similar to that previously reported for isolated clusters: high activation barriers for planar Cu₅-2D, that decrease when changing to 3D morphology (Cu₅-3D) and with increasing cluster size (Cu₇-3D). In the presence of framework Al atoms, the planar Cu₅-2D cluster rearranges upon interaction with O₂ adopting a 3D structure that, in turn, leads to a lower activation energy for O₂ dissociation. The three Eₜₐₓ values in the 1Al models are similar and really low, 46 and 19 kJ/mol for Cu₅ and 31 kJ/mol for Cu₇ (see Table 4). Finally, moving to the 2Al model with more positively charged Cuₙ clusters results in an increase of all the calculated activation energies, more noticeable in the smaller Cu₅ clusters with less availability of electron density to activate O₂. As previously reported for isolated clusters, there is a correlation between the calculated activation energies Eₜₐₓ and the total charge on O₂ in the reactant species R (see Figure 3d), suggesting that the degree of activation of the OO bond in adsorbed O₂ through electron density transfer to the π* antibonding orbital is what determines the energy that will be necessary to break this bond and dissociate molecular O₂.

After dissociation, the two O atoms tend to occupy positions on the surface of the Cuₙ clusters, either three-coordinated on the facets or bi-coordinated at the cluster edges (see Figure 5). The total positive charge on the Cuₙ clusters increases to values between 2.0 and 3.4 e (see Table 1) and the adsorbed O atoms become negatively charged by -1.0 e. The process is always clearly exothermic, with calculated reaction energies between -230 and -310 kJ/mol (ΔE values in Table 4). The only exception is the product of O₂ dissociation on the Cu₅-3D cluster supported on the 1Al zeolite model. The reaction energy is less favorable, -176 kJ/mol, and the net negative charge on the O atoms is also the lowest, -0.88 e on average on each atom. It could be related to the fact that after O₂ dissociation in this model the two O atoms are bi-coordinated at neighboring edges of the cluster sharing one Cu atom, which is a less stable situation than having at least one three-coordinated O atom as in all other cases (see amplified images in Figure 5).
Figure 5. Optimized structures of two O atoms adsorbed on Cu5-2D, Cu5-3D and Cu7-3D clusters confined within CHA models containing 0, 1 and 2 framework Al atoms. Si and O are depicted as red and yellow wires, Cu and Al are depicted as brown and light green balls.

**Successive dissociation of multiple O2 molecules on supported Cu7**

After the dissociation of the first O2 molecule all clusters have increased significantly their positive charge, reaching values larger than 3.3 e in the systems with two framework Al atoms (see qCu, (P) values in Table 1). Taking into account that electron density transfer to adsorbed O2 is key to promote its dissociation, the possibility to avoid the undesired overoxidation of Cu7 clusters by supporting them on zeolites with the proper amount of Al was investigated. For this purpose, a second O2 molecule was adsorbed on the product P structure obtained for Cu7-3D, labelled Cu7-3D-2O in Figure 7 and Table 5. As expected, less electron density is transferred to O2 in this system, only -0.384 e (see Table 5), leading to a shorter optimized OO bond length, 1.388 Å, and to a higher activation energy for O2 dissociation, 152 kJ/mol. This value is similar to that obtained for the planar Cu5-2D cluster in the 0Al model, 134 kJ/mol, probably because of the similar geometry obtained for the adsorbed O2 molecule at the edge of the cluster and for the transition state with the two O atoms sharing the same two Cu atoms forming the cluster edge (see Figure 6). In addition, at difference with all the other systems studied in this work, the dissociation of O2 on the Cu7-3D-2O cluster is endothermic by 63 kJ/mol, and the negative charge on the resulting adsorbed O atoms is small, ~-0.4 e.

To make this study systematic, the adsorption and dissociation of an O2 molecule on Cu7 clusters containing one, three and four additional O atoms, labelled Cu7-3D-O, Cu7-3D-3O and Cu7-3D-4O in Figure S4 and Table 5, was also investigated. Again, the charge transferred to O2 is less than -0.4 e, the optimized OO bond lengths are between 1.36 and 1.38 Å, the calculated reaction energies are positive or only slightly negative, and the activation energies are higher than 100 kJ/mol with the only exception of the Cu7-3D-4O system, probably due to the low stability of the reactant structure. These results indicate that deep oxidation of zeolite-supported Cu7 clusters by successive dissociation of O2 molecules is disfavoured both kinetically and thermodynamically, making zeolites a promising support to stabilize metallic Cu.

Table 5. Total atomic charges on adsorbed O2 (qO2, in e) and optimized values of the OO distance (rOO, in Å) in structures R, TS and P involved in O2 dissociation, and calculated adsorption (Eads), activation (Eact) and reaction (ΔE) energies (in kJ/mol) for O2 dissociation on Cu7-3D clusters with increasing amount of adsorbed O stabilized in a CHA zeolite model with 2 framework Al atoms.

<table>
<thead>
<tr>
<th>Cu7-3D</th>
<th>Cu7-3D-O</th>
<th>Cu7-3D-2O</th>
<th>Cu7-3D-3O</th>
<th>Cu7-3D-4O</th>
</tr>
</thead>
<tbody>
<tr>
<td>qO2 (R)</td>
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<td>-0.384</td>
<td>-0.339</td>
</tr>
<tr>
<td>qO2 (TS)</td>
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<td>-0.641</td>
<td>-0.584</td>
</tr>
<tr>
<td>qO2 (P)</td>
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</tr>
<tr>
<td>rOO (R)</td>
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<td>-287</td>
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<td>ΔE (kJ/mol)</td>
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<td>131</td>
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</table>

Figure 6. Optimized structures of reactant R, transition state TS and product P of O2 dissociation reaction on (a) Cu7-3D-2O in CHA with 2 framework Al and (b) Cu7-2D clusters in CHA with 0 framework Al atoms. Si and O are depicted as red and yellow wires, Cu and Al are depicted as brown and light green balls.

**Conclusions**

The present computational study shows that the stabilization of Cu7 clusters within Al-containing zeolites modify their charge and morphology, and, as a consequence, their reactivity towards O2. The
total positive charge on the Cu clusters increases with the number of Al atoms in the zeolite framework. O₂ adsorption and its subsequent dissociation into two O atoms requires an additional transfer of electron density from the catalyst to the O₂ and O species, leaving the Cu clusters highly charged after the reaction takes place. As a consequence, deep oxidation of zeolite supported Cu clusters by successive adsorption and dissociation of additional O₂ molecules is unlikely, which can be exploited to stabilize metallic oxidation state under oxidizing conditions, necessary for some challenging reactions.

**Author Contributions**

M. B. and A. C. directed the study. M. G. carried out the DFT calculations, supervised by M.B. All the authors discussed the results and contributed to the preparation, writing and revision of the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**