Analogy between homogeneous and heterogeneous catalysis by subnanometer metal clusters: ethylene oxidation on Ag trimers supported on MgO(100)

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Abstract

An analogy between homogeneous catalysis and heterogeneous catalysis by very small, subnanometer-size metal clusters (or heterogeneous ultrananocatalysis) is proposed. We start from the idea that the catalytically active species in heterogeneous ultrananocatalysis are ligand/cluster/support complexes generated *in situ* under reaction conditions in the high coverage régime, and make a parallel between such species and the metal complexes of homogeneous catalysis. To this aim, we use first-principles simulations and focus on a specific example selecting as catalytic complex a $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ compound which has been suggested to form during the CO oxidation reaction catalyzed by silver trimer (Ag_3) deposited on the regular $\text{MgO}(100)$ surface. We investigate whether such a complex can be used as a catalyst in a different reaction: the partial oxidation of ethylene to ethylene oxide (or EtO_x reaction). The EtO_x catalytic cycle over $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ is determined, and it is found that it presents an overall reaction energy barrier of 0.9 eV. A detailed Molecular Orbital (MO), charge and fragment analysis is then conducted on the species involved in the catalytic cycle, highlighting the similarities of the given catalytic chemistry with homogeneous analogues. The proposed analogy between homogeneous and heterogeneous catalytic aggregates seems promising to widen the spectrum of heterogeneous catalyst design and realize synergistic investigations with accumulated knowledge on homogeneous systems.

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Devising sufficiently active and selective catalysts is one of the challenges of XXI-century chemistry [1]. In this respect, catalysis by metal complexes in the homogeneous phase (solution) has proved significantly successful in achieving a high degree of activity and especially selectivity, by exploiting the freedom in the choice of ligands and the fine tuning of the electronic structure of the complexes, together with a crucial understanding of reaction mechanisms from both experimental and theoretical insight, see e.g. Refs. [2-7]. In addition to activity and selectivity, the catalyst's usefulness in practical applications obviously depends on other variables, such as its mesoscopic features and the accessibility of catalytic sites, since microscopic reactive processes must be combined with mass transport over mesoscopic length scales to determine the final efficiency in throughput of chemical products. As it deals with gas phase reactants and transformations at the solid/gas interface, heterogeneous catalysts present obvious advantages with respect to homogeneous ones, since diffusion coefficients of reactant and product species in the gas phase are orders of magnitude larger than in solution. A natural strategy explored in recent years has then been to combine the advantages of both systems by grafting metal complexes onto a solid surface [8-11]. Here we take an alternative path. We focus on heterogeneous ultrananocatalysis, i.e., in which the catalysts are subnanometer (or ultranano) species made of very small (up to 10-20 atom) metal or metal-oxide clusters deposited on a semi-conductive (in general oxide) support [12-15], and we discuss the possibility of drawing an analogy between homogeneous and heterogeneous ultrananocatalysis. Such an analogy has been advanced in pioneering work by Thomas and co-workers [16]. The novelty here lies in that this analogy is based on the concept of ligand/metal-cluster/support catalytic species. Computational investigations based on systematic sampling [17] have in fact recently shown that the catalytically active species in several examples of ultrananocatalysis are not the bare metal clusters, but rather composite ligand/metal-cluster/support complexes which are spontaneously formed *in situ* under the given reaction conditions in the high-coverage regime [18-19], thus leading to the hypothesis that this corresponds to a mechanism generally operative in heterogeneous ultrananocatalysis. Here we advocate these complexes as the natural analogues of homogeneous catalysts, and support this contention by focusing on one specific example and by conducting a detailed Molecular Orbital (MO), charge and fragment analysis of both the catalyst and the reaction intermediates evolving along a given catalytic cycle. We additionally discuss transferability, i.e., the possibility of creating a catalytic species under conditions of a given reaction and using the species so prepared in a different catalytic reaction. The specific example we choose to develop the proposed analogy is ethylene partial oxidation to ethylene oxide ($\text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O}$, or EtoO_x for simplicity) catalyzed by a $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ catalytic species. This catalytic complex has been recently proposed to be

obtained during CO oxidation to CO₂ over Ag trimers deposited on the MgO(100) surface [18]. Silver nanoparticles are able to promote alkene partial oxidation [20], and Ag trimers deposited onto an ultrathin amorphous alumina film has been investigated in previous work, demonstrating the good activity of this ultranano catalytic system [14]. In the present work we focus on a simpler support such as the MgO(100) surface which can be taken as an idealized but reasonably good model of simple oxides [17,21]. The choice of a regular surface as a substrate simplifies our theoretical analysis by providing a known (and simple) atomistic structure for the oxide, thus avoiding a statistical treatment which is necessary for amorphous systems. Since the catalytic complex considered here – i.e., Ag₃(CO₃)/MgO(100) – is derived from those obtained under the conditions of a different reaction (CO oxidation to CO₂), the present proposal can be seen as a form of *in situ* catalyst pretreatment prior to the actual catalytic run of interest and is the natural counterpart of what usually done in the preparative step of ‘real-world’ heterogeneous catalysis. Moreover, since CO₂ is actually a side-product of alkene oxidation [14], it can be hypothesized that a Ag₃(CO₃) complex similar to that here investigated can indeed correspond to the real catalytically active species over a different substrate [14].

The article is organized as follows. Sec. 2 describes the computational details, Sec. 3 the results and discussion, and Sec. 4 summarizes our conclusions.

2. Computational Details

Density-functional theory (DFT) calculations and post-processing analyses are performed using the plane-wave Quantum Espresso package [22]. The Perdew-Burke-Ernzerhof (PBE) [23] exchange-correlation functional is used together with ultrasoft pseudopotentials [24] and energy cutoffs of 40 Ry and 320 Ry for the selection of plane wave describing the wave function and electron density, respectively. Spin-unrestricted calculations are performed, using 3x4 cells with 2 MgO layers (kept frozen during structural optimizations), 17 Å of empty space between replicated cells and a Brillouin zone sampled at the Gamma point. Reaction barriers were calculated using a nudged elastic band (NEB) transition state algorithm based on the Broyden scheme and 5 intermediate images [25]. Charge analysis is conducted by employing a Lowdin scheme [26].

3. Results and Discussion

We start from one of the main results of a previous study [18], in which the oxidation of CO to CO₂ over Ag trimers supported on the MgO(100) surface was computationally investigated, finding that

$\text{Ag}_3/\text{MgO}(100)$ under very general CO oxidation conditions transforms into a $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ composite compound which is then able to efficiently catalyze the oxidation of CO. In the present work, we try to extend this result and consider the possible use of the $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ catalytic complex as a catalyst in the reaction of partial oxidation of ethylene to ethylene oxide:

where Et (or C_2H_4 or $\text{CH}_2=\text{CH}_2$) represent ethylene, while EtO (or $\text{C}_2\text{H}_4\text{-O}$) represent ethylene oxide. In Sec. 3.A we then investigate the catalytic cycle:

and estimate its efficiency, while in Sec. 3.B we will conduct a MO, charge and fragment analysis of the involved species, trying to understand the reasons behind the chemistry described in Sec. 3.A, and drawing a parallel with metal complexes of homogeneous catalysis. Note that in Eq. (2) we start from 3 ethylene molecules because as it will be clear in Sec. 3.A the catalytic complex of the EtO_x reaction is actually a $\text{Ag}_3(\text{CO}_3)(\text{Et})/\text{MgO}(100)$ compound.

3.A The catalytic cycle for EtO_x over $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$

In Fig. 1 we depict the full catalytic cycle for the partial oxidation of ethylene to ethylene oxide corresponding to Eq. (2). Energy differences, denoted as ΔE and measured in eV, correspond to a decrease (negative values) or increase (positive values) of the total energy of the system between steps, while E_b values denote energy barriers and are also measured in eV. In general, we neglect roto-vibrational contributions to free energies and reaction energy barriers, assuming that these compensate at room temperature. Instead, the translational free energy of Et, O_2 , and EtO in the gas phase in standard conditions and assuming ideal-gas behavior are: 0.59, 0.52, and 0.66 eV, respectively, and will be combined in the following with electronic energies to obtain free energies. The initial step of the catalytic sequence is pretty straightforward. The $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ complex is in fact able to co-adsorb an Et molecule and an O_2 molecule (Fig. 1a), with adsorption energies sufficiently large to balance the loss of entropic translational contributions for both

species. The co-adsorbed molecules then produce an oxametallacycle intermediate exhibiting a six-atom cycle [O-O-C-C-Ag-Ag], see Fig. 1b, which further evolves a free EtO molecule, leaving behind an adsorbed O adatom (see Fig. 1c) according to a mechanism proposed in previous work [27]. An alternative path [17] foresees breaking of the O-O bond prior to O reaction with Et: this path however is not favored in the present case as it presents a higher energy barrier (results not shown). Interestingly, the situation becomes more complicated once the O-O bond is broken and an oxygen adatom is left on the cluster. The resulting $\text{Ag}_3(\text{CO}_3)(\text{O})/\text{MgO}(100)$ complex of Fig. 1c can in fact directly react with an incoming ethylene molecule from the gas phase in a Eley-Rideal mechanism (i.e., without pre-adsorption of ethylene on the complex), but the thermodynamically favored situation sees an Et molecule adsorbed on the Ag trimer on the other side with respect to the O adatom, see Fig. 1d. In this intermediate the Et and the O adatom are too distant to react. Co-adsorption of a further Et molecule then shifts the O adatom from the hollow position to a bridge position, see Fig. 1e. A rotation of the Et molecule on the carbonate side brings this to react with the O adatom by creating a five-atom [O-C-C-Ag-Ag] oxametallacycle (see Fig. 1f) which easily evolves to a second gas-phase Et-O: the step [1f $\rightarrow$ 1g] is endothermic by only 0.24 eV, which energy penalty is compensated by the gain in translation free energy of EtO. It can be noted that the catalytic complex in this cycle is the $\text{Ag}_3(\text{CO}_3)(\text{Et})/\text{MgO}(100)$ species, not the original $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ species. The rate determining step in this catalytic cycle is the reaction: [1e $\rightarrow$ 1f] or $[\text{Ag}_3(\text{CO}_3)(\text{Et})_2(\text{O})/\text{MgO}(100) \rightarrow \text{Ag}_3(\text{CO}_3)(\text{O})/\text{MgO}(100) + \text{EtO}]$. A significant energy barrier of 0.90 eV must be overcome for Et to rotate over the Ag trimer, pick up the O adatom and produce the second EtO molecule. A major component of the reaction energy barrier (about 0.5 eV) is spent to simply rotate Et and get it closer to the O adatom to promote their reaction, suggesting that a judicious alloying of Ag with other metals with a lesser oxygen affinity might decrease this barrier, which is higher than that found for the EtO_x reaction on the bare $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ complex [17]. Additionally, if the preference for alkene/O-adatom spatially separated configurations holds also e.g. for propylene, we may conjecture that it can disfavor the process of H abstraction from propylene by the O adatom which in the analysis of Ref. [17] was suggested as the step leading to acrolein rather than propylene oxide. If this is the case, $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ might be a less active but more selective catalyst in propylene partial oxidation.

3.B MO, charge and fragment analysis of the species involved in the catalytic cycle

In this section we conduct an analysis of the species involved in the EtO_x process and catalytic cycle described in Sec. 3.A in terms of Molecular Orbitals (MO), electron density decomposition,

and constituting fragments, trying to achieve a better understanding of the observed catalytic chemistry. This type of analysis is usual in the field of homogeneous catalysis by metal complexes, so that it will allow us to draw a parallel with the present field of heterogeneous ultrananocatalysis. In Fig. 2, isosurfaces of spin density characterizing the most characteristic intermediates of the catalytic cycle are shown, while in Fig. 3 a MO analysis is used to achieve a deeper understanding of the bonding interactions between the catalyst and the ligand species.

We start from a discussion of a silver trimer in the gas phase, taken for simplicity in an equilateral triangle configuration belonging to the D_{3h} point symmetry group (we neglect for the sake of simplicity distortions due to the Jahn-Teller effect). Of special importance for metallic bonding are the 3 Ag s -orbitals, which combine to give a bonding A_{1g} and two antibonding E_g MOs [28]. Fig. 3a shows a plot of the A_{1g} orbital and of the two anti-bonding E_g MO of Ag_3 . Since the d -orbitals are fully occupied (the atomic configuration of a Ag atom is $d^{10}s^1$), bonding in neutral Ag_3 is assured by the s -electrons, 2 of which will occupy the bonding A_{1g} MO while one will occupy one of the two anti-bonding E_g MOs. Partial occupancy of anti-bonding MOs explains the relatively low cohesion energy and the fluxionality (the ease with which the bond angle can be changed) of Ag_3 in the gas phase (plus a smaller component due to the Jahn-Teller effect). The cohesion energy of Ag_3 is 2.56 eV, while it is 4.68 eV for Ag_3^+ from our computational approach (Ag_3^+ is a cation, but it has 2 electrons in the A_{1g} bonding MO while the E_g anti-bonding MOs are empty). In passing, we note that this analysis also explains why O_2 dissociation is energetically disfavored on Ag_3 whereas it is favored on Au_4 and larger clusters [17,29]: the reason is that two unpaired electrons are necessary to interact with two O adatoms, whereas Ag_3 only has one.

The picture does not change much when Ag_3 is adsorbed on the regular MgO(100) surface: covalent and charge transfer effects are minor in the Ag_3 /MgO(100) interaction [30]; the spin density shown in Fig. 2a (the system is a doublet) has a strong anti-bonding s -character on the Ag atoms, confirming that the electronic density is not much perturbed by the oxide substrate.

The situation radically changes, instead, when the $Ag_3(CO_3)$ /MgO(100) complex is formed. In fact, the CO_3 carbonate group absorbs one electron from Ag_3 transforming into a CO_3^- anion which efficiently interacts with the resulting Ag_3^+ cation. As shown in the spin-density plot of Fig. 2a (the system is still a doublet), the spin density is now mainly localized on the three O atoms of the carbonate group with minor residual components on the two vicinal Ag atoms. This electron transfer, which is already present in the gas phase leading to a large Ag_3/CO_3 interaction energy of 4.36 eV, also has the effect of strongly reinforcing the interaction of CO_3^- and Ag_3^+ with the MgO(100) surface as these charged species favorably interact with the electric field generated by the MgO(100) surface (it can be recalled that Ag_3 sits on top of O anions of MgO, while the O

atoms of the carbonate sit on top of Mg cations). A Lowdin analysis confirms the previous arguments: the Lowdin charges in $\text{Ag}_3/\text{MgO}(100)$ are 10.71, 10.81 and 10.86, whereas they are 10.39, 10.65 and 10.73 in $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$. This explains why $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ is a more robust ultrananocatalyst with respect to $\text{Ag}_3/\text{MgO}(100)$: (i) the metallic bond is stronger because of a lesser anti-bonding contribution (the electron in the anti-bonding MO has been partially removed), (ii) the interaction with the surface is also stronger because of ionic interactions, thus disfavoring cluster diffusion and sintering, and (iii) the Ag_3 cluster is further held together against disaggregation by the bidentate carbonate ligand. Also the carbonate group is reasonably cohesive in this complex: the energetics of the reaction $[\text{Ag}_3(\text{CO}_3)/\text{MgO}(100) \rightarrow \text{Ag}_3(\text{O})/\text{MgO}(100) + \text{CO}_2]$, is endothermic by 1.47 eV in the gas-phase. The presence of a substantially cationic Ag_3 moiety in the $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ catalytic complex implies that a comparison can be made between the chemical behavior of such species and the knowledge accumulated in the gas phase on free metal clusters (including Ag_3) which always invariably deals with *charged* clusters (often anions, but also cations, see e.g. Refs. [31-32]. An even more punctual parallel can be done with the knowledge accumulated on homogeneous metal complexes: these are usually positively charged, and are held together by a coordinating shell of ligands, including carbonate groups, see e.g. Ref. [33].

As shown in the previous section, the $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ complex easily adsorbs an Et and an O_2 species, see Fig. 1a. Due to the residual electron density on the silver atom next to the carbonate group, see Fig. 2b, where the Et is adsorbed, the interaction between the Et and the Ag_3 cluster is not too strong and the oxametallacycle of Fig. 1b is easily formed, followed by the formation of a gas-phase Et-O species. The O adatom left on the catalyst further oxidizes the Ag_3 cluster: for example, the Lowdin charges on the Ag atoms are further reduced to 10.30, 10.28 and 10.30, respectively. Moreover, as shown in the spin-density plot of Fig. 2c (this system is also a doublet), the presence of the O adatom enhances the *d*-character of the residual unpaired spin density on the silver atoms, proving that a depletion of the *d*-shell is also effective. The electron-deficient (or strong Lewis acid) $\text{Ag}_3(\text{CO}_3)(\text{O})/\text{MgO}(100)$ compound can adsorb a further Et molecule on the apex Ag atom which is the farthest from the O anions of the MgO surface, and produce a species in which the spin density is basically localized on the carbonate, the O adatom, and a *d*-orbital of the Ag atom farthest from Et, as shown in Fig. 2d. As a consequence of the enhanced oxidation of the silver cluster due to the synergic effect of the carbonate group and the O adatom, a strong interaction between the $\text{Ag}_3(\text{CO}_3)(\text{O})/\text{MgO}(100)$ and the Et molecule is established, whose origin we now describe in more detail. The anti-bonding *s*-band of Ag_3 is depopulated and can therefore accept electron density from the π -bond of Et (the donor, see left side of Fig. 3b) and back-donate *d*-band electrons into the anti-bonding π^* -orbital of Et, see right side of Fig. 3b [34]. Back-donation

slightly lengthens the C=C double bond of Et (C-C distances are 1.33 Å and 1.37 Å in free and adsorbed Et, respectively). This π -donation/ π^* -back-donation interaction is similar to that occurring in Pt_n-Et complexes [34,35], with a similar necessity of depopulating the *s*-band of the metal system to allow π -donation from the Et molecule. Such a strong Et/Ag₃ interaction is the reason why a direct reaction of the adsorbed Et with the O adatom to form EtO is disfavored. However, after the adsorption of an Et molecule, the complex can easily adsorb another Et molecule. The latter species adsorbs on the silver atom next to the carbonate group, due to steric reasons: the top-most Ag atom is in fact saturated, whereas the bottom-most one is too close to and interacting with the oxide substrate. In analogy with the adsorption of the first Et molecule, due to the residual spin density present on the Ag atom next to the carbonate group (see spin density plot in Fig. 2d) and to the proximity to the O adatom, the formation of a five-ring oxameallacycle is energetically favorable, as shown in Fig. 1e. However, the stability of this intermediate is an issue for the efficiency of the EtO_x reaction, as the detachment of EtO must now go through an appreciable rearrangement and thus a sizable energy barrier of 0.9 eV.

In concluding this section, we note that a MO or orbital-scheme analysis coupled with orbital occupation arguments as considered here seems appropriate to develop the analogy between homogeneous and heterogeneous ultrananocatalysis. This type of analysis has been widely used in the case of metal complexes, producing insight and understanding [2-7,35]. In the specific case of C₂H₄ interacting with Ag₃ compounds, the necessity for the metal *s*-band to be depopulated in order to accept electron density from the π -bond of Et (the donor) and the possibility of back-donating *d*-electrons into the anti-bonding π^* -orbital of Et can moreover suggest ways of fine tuning the Et/cluster interaction by judicious alloying so as to decrease the barrier of the rate determining step.

4. Conclusions

In the present work we draw an analogy between homogeneous and heterogeneous ultrananocatalysis, i.e., catalysis by subnanometer or ultrananometal clusters. We ground this analogy on the concept of ligand/metal-cluster/support catalytic complex in heterogeneous ultrananocatalysis [18-19], suggesting that such species represent the natural analogues of homogeneous catalysts metal complexes in a heterogeneous setting. These species in fact, formed *in situ* and under reaction conditions, share with their homogeneous analogues many of the basic fundamental chemical bond concepts, so that for example they can be subjected to a similar theoretical understanding, as shown by the MO, charge and fragment analysis expounded in Sec. 3.B. In passing, one can note that – once formed under given conditions – these species can be

robust enough to be used not necessarily for the same process, but to catalyze a different reaction under different conditions. In the present work indeed the $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ catalytic complex generated by CO oxidation on $\text{Ag}_3/\text{MgO}(100)$ is explored as a catalyst for the ethylene partial oxidation (or EtO_x) reaction.

The framework here discussed presents several aspects of potential interest. For example, it rationalizes the beneficial effect of trace dopants or promoters – see e.g. Refs. [36-38] – as an integral part of the catalytically active species, thus determining energetics and catalytic efficiency. Also, the high-ligand-coverage here discussed as necessary to produce the catalytic complex parallels the ligand environment in homogeneous metal complexes, in its various properties and functions of protecting, stabilizing, and promoting the coordination shell of the metal clusters.

In the present case of $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$, the analysis conducted in Sec. 3.B suggests reasons why its energy barriers to diffusion and disaggregation are larger than those for the corresponding bare $\text{Ag}_3/\text{MgO}(100)$ species, thus stabilizing this ultrananocluster against sintering. In fact, the electrostatic interaction of Ag_3^+ and CO_3^- with the charge-separated ionic $\text{MgO}(100)$ support appreciably increases diffusion energy barriers. Also, Ag_3 – with its three valence electrons one of which unpaired in an anti-bonding orbital – is very reactive and thus potentially a good catalyst but at the same time is also very liable to disaggregation, whereas in $\text{Ag}_3(\text{CO}_3)$ the unpaired anti-bonding electron is partly adsorbed by the carbonate group making $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ a much more stable catalytic species. The lesser occupation of the Ag anti-bonding s -band which makes $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$ similar to a cationic $\text{Ag}_3^+(\text{CO}_3)/\text{MgO}(100)$ complex, apart from reinforcing the analogy with homogeneous metal catalysts (as a norm exhibiting metal atoms in positive oxidation states), strengthens its interaction with ethylene, facilitating σ -donation of the Et π -bond into the s -orbital system. The rate determining step of the EtO_x cycle is then found when an O adatom and Et molecules are co-adsorbed on the catalytic species. In this co-adsorbed aggregate in fact the stronger interaction between the Et ligands and the metal cluster, apart from weakening the metallic bond, favors an adsorption mode in which O and Et are spatially separated to maximize synergic effects, so that a larger energy barrier must thus be overcome for the complex to undergo the final step of the EtO_x cycle.

In conclusion, apart from the details of the specific example here investigated, the *in situ* formation of an appropriate catalytic complex via catalyst pretreatment and preparation process here discussed may correspond to a general mechanism operative in heterogeneous ultrananocatalysis. If grounded, this idea offers an enormous combinatorial playground for catalyst design and optimization. In this perspective, the accumulated experience from homogeneous catalysis will be highly relevant and useful to understand, device, and engineer heterogeneous ultrananocatalytic species, thus offering

significant opportunities for interdisciplinary collaborations. To make an example, many of the descriptors derived for homogeneous catalysts [3-4] may be brought over and adapted to the heterogeneous setting with appropriate but possibly not too drastic modifications.

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Figure 1. Catalytic cycle for EtO_x reaction over the Ag₃(CO₃)(Et)/MgO(100) complex. ΔE values correspond to differences in electronic energy, whereas E_b values correspond to energy barriers (both values are in eV). Color coding: in the support, white dots correspond to O atoms and yellow dots to Mg atoms; in the ligand/cluster moiety, grey, red, green and blue spheres are used to represent Ag, O, C and H atoms, respectively.

Figure 2. Isosurfaces of electronic spin density (taken at a value of 0.001 a.u.) for the following systems: (a) $\text{Ag}_3/\text{MgO}(100)$; (b) $\text{Ag}_3(\text{CO}_3)/\text{MgO}(100)$; (c) $\text{Ag}_3(\text{CO}_3)(\text{O})/\text{MgO}(100)$; (d) $\text{Ag}_3(\text{CO}_3)(\text{Et})(\text{O})/\text{MgO}(100)$; (e) $\text{Ag}_3(\text{CO}_3)(\text{Et})_2(\text{O})/\text{MgO}(100)$. Color coding as in Fig.1.

Figure 3. Density isosurfaces (at a value of 0.001 a.u.) corresponding to selected Molecular Orbitals (MO). In detail: (a) the A_{1g} (left) and the two E_g (middle and right) orbitals of the gas-phase Ag_3 system; (b) two selected MO of the $\text{Ag}_3(\text{CO}_3)(\text{Et})(\text{O})/\text{MgO}(100)$ complex showing the donation process from the π -bond of Et to the d -band of Ag_3 (left) and the back-donation process from the d -band of Ag_3 into the anti-bonding π^* -orbital of Et (right). Color coding as in Fig.1.

Graphical Abstract