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Molecular geometries and relative stabilities of titanium oxide and gold-titanium oxide clusters

Rohan J. Hudson, Alexander Falcinella, Gregory F. Metha *

Department of Chemistry, University of Adelaide, South Australia 5005, Australia

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ABSTRACT

Titanium oxide and gold-titanium oxide clusters of stoichiometry M_xO_y ($M_x = Ti_3$, Ti_4 & $AuTi_3$; $y = 0 - (2x + 2)$) have been investigated using density functional theory. Geometries of determined global energy minimum structures are reported and other isomers predicted up to 0.5 eV higher in energy. The Ti_3O_n geometries build upon a triangular Ti_3 motif, while Ti_4O_n stoichiometries template upon a pseudo-tetrahedral Ti_4 structure. Addition of a gold atom to the Ti_3O_n series does not significantly alter the cluster geometry, with the gold atom preferentially binding to titanium atoms over oxygen atoms. Adiabatic ionization energies, electron affinities and HOMO/LUMO energies increase in magnitude with increasing oxygenation. The HOMO-LUMO energy gaps reach the bulk anatase band gap energy at stoichiometry $(Au)Ti_mO_{2m-1}$, and increase above this upon further oxygen addition. The most stable structural moieties are found to be a cage-like, C_{3v} symmetric $Ti_4O_{6/7}$ geometry and a Ti_3O_6 structure with an η^3-bound oxygen atom.

1. Introduction

Titanium oxide (TiO_2), or 'titania', is a white, powdery solid in the bulk phase [1] which has found applications as a pigment [2], photocatalyst and photocatalyst support [3–11], photovoltaic cell component [12–14] and organic pollutant filter [15]. Its photoactive behavior arises from titania's relatively low band-gap energy of 3.0–3.2 eV, which allows for absorption of near-ultraviolet wavelengths from incident solar radiation.

Absorption of such photons by titania generates an 'exciton' electron/hole pair [16], which may subsequently react with other species to initiate photochemical processes [17]. The efficiency of such reactions are often limited by exciton recombination, which may be minimized through charge transfer to an electron-accepting dopant species, separating the electron/hole pair [16]. Transition metal species are commonly deposited upon titania for this purpose; in particular, nanoparticles of noble metals such as platinum and gold possess unoccupied molecular orbitals below the titania conduction band, allowing for thermodynamically favorable electron transfer [18–20]. Deposition of gold nanoparticles and atomically-precise clusters upon titania are of particular interest due to their unusual reactivities and catalytic properties when compared to the typically inert bulk gold metal [4–8,21–24]. The mode of gold binding to the metal oxide support has been shown to significantly influence its reactive behavior [25]; hence, an understanding of the electronic gold-titania bonding interaction is vital to predict and design efficient gold/titania photocatalysts.

Atomically precise clusters have previously been used to model catalytic and metal-metal interactions on various solid-state metal oxide surfaces, including vanadium oxide [26], molybdenum oxide [27] and rhodium-holmium oxide [28] to name only a few. It is then logical to extend this to model the surface effects upon titanium dioxide surfaces. To this end, extensive study of atomically-precise titanium oxide Ti_mO_n and transition metal substituted $M_xTi_mO_n$ clusters has been undertaken in recent years. Multiple experimental studies have observed gas phase cationic and neutral titanium oxide clusters through ion sputtering and laser vaporisation of both titanium metal and oxide targets [29–36]. However, the vast majority of research into small titania clusters have been computational in nature, typically using density functional theory (DFT) methods. The molecular structures of Ti_n, stoichiometric Ti_nO_{2n} and approximately stoichiometric Ti_nO_m ($m = 2n \pm 2$) clusters have been extensively studied by DFT calculations at a range of theory levels [29,37–45]. Metal atom substitution upon these clusters has been less comprehensively studied; however, the deposition of nickel, vanadium, cobalt and platinum atoms upon $(TiO_2)_n$ clusters was calculated by Cakir and Gülseren [46] and Verkhovtsev et al. [47]. More recently, Himeno et al. investigated the energy minima geometries of the cationic gold-substituted

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* Corresponding author.
E-mail address: greg.metha@adelaide.edu.au (G.F. Metha).

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titania clusters $Au_mTi_6O_n$, for $m = 1,2$ & $n = 12, 13$ [23]. He and co-workers also modelled the reaction mechanisms of CO oxidation and methane activation upon $Au(TiO_2)_yO_z^-$ ($y = 2, 3$; $z = 1, 2$) cluster anions [36,48]. However, this previous work has predominantly focused upon metal substitution of clusters at or close to $(TiO_2)_n$ stoichiometry; to the best of our knowledge, the effect of metal atom substitution upon an entire series of non-stoichiometric titanium oxide clusters has not yet been undertaken.

In this work, the geometric structures and relative stabilities of the Ti_nO_{2n+2} cluster oxide series' for $n = 3$ & 4 are investigated by density functional theory. The adiabatic detachment energies of the anionic and neutral species are determined for each stoichiometry, as well as the highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) energy gap predicted by these calculations. Relative stabilities of each cluster are examined through the calculation of molecular binding energies. This is then extended to the gold-substituted $AuTi_3O_n$ series for $n = 0$–10, in order to investigate the structural and electronic effects of gold atom binding to clusters of titania.

2. Methods

Geometric optimization and vibrational frequency calculations of all species of interest were undertaken with the *Gaussian 09* software suite [49], using the B3P86 hybrid functional in conjunction with the Stuttgart-Dresden (SDD) basis set [50]. Titanium atoms were treated with an effective core potential (ECP) of the innermost 10 electrons (i.e. the $^{10}[Ne]$ core), while gold atoms were treated with an ECP of 60 core electrons [51,52]. This level of theory has previously been established by our group to show relatively close agreement between computed and experimental molecular parameters of transition metal and lanthanide gas-phase clusters [28,53–56]. Additional calculations were performed using the all-electron basis set cc-pvdz for both titanium and oxygen atoms [57,58] on geometries of $AuTi_3O_n$ ($n = 0$, 6, 10), Ti_3O_n ($n = 0$, 6) and Ti_4O_n ($n = 0$, 6, 10). As no formulation of this basis set exists for gold, the SDD basis set with MWB60 ECP was maintained for gold in these calculations.

Initial geometries of the neutral Ti_3 trimer consisted of differing triangular and linear starting structures. Using the lowest-energy optimized structure of this, multiple initial geometries Ti_4 and $AuTi_3$ were generated through the addition of a titanium or gold atom, respectively. Oxygenated cluster starting geometries were built up from the addition of single oxygen atoms at various potential sites on the previously optimized lowest-energy geometries. To ensure a thorough search of the entire potential energy surface (PES) at each stoichiometry, at least fifteen to twenty unique trial geometries were generated for each cluster of interest. This was deemed acceptable for smaller, less complex structures. The Kick algorithm was employed to randomly generate multiple trial geometries of each $AuTi_3O_n$ stoichiometry for $n = 5$–10 [59]. Atoms of either gold or oxygen were 'kicked' at optimized geometries of Ti_3O_n or $AuTi_3O_{n-1}$ respectively, within a cube of edge length 6 Å. For $n = 5$–8, 50 structures were each generated from addition of a gold or oxygen atom. For $n = 9$ & 10, no corresponding Ti_3O_n optimized geometries were available, and so 100 structures were produced from addition of oxygen atoms at $AuTi_3O_{n-1}$ structures.

A large number of geometric isomers were optimized for all stoichiometries, and only those within 0.5 eV of the lowest energy structure were considered here. For each initial geometry submitted for optimization, the lowest four possible multiplicities (singlet, triplet, pentet and septet for Ti_mO_n; doublet, quartet, sextet and octet for $AuTi_3O_n$) were tested. Calculation of vibrational frequencies ensured that all optimized structures were true minima of the species' PES and not transition states. All lowest-energy structures and those within the 0.5 eV energy range (after zero-point energy correction) were constrained to the highest possible symmetry and re-optimized, to ensure correct determination of each geometry's point group.

Lowest energy structures for each neutral cluster stoichiometry were re-optimized as singly-charged cationic and anionic species, with multiplicities differing from the neutral state by ±1. The adiabatic ionization energies (IE) and electron affinities (EA) were determined as the energy differences between these and the optimized neutral structure, including zero-point energy corrections.

To determine the binding energies of each lowest-energy cluster stoichiometry, the energies of single atoms of oxygen, titanium and gold were calculated using at the same level of theory, with electronic states of $^3P_2$, $^3F_2$ and $^2S_{1/2}$, respectively. The molecular binding energy per atom is calculated as the difference between total cluster energy and the sum of the atomic cluster constituent energies, divided through by the number of atoms within the cluster. The binding energies of oxygen atoms ($^3P_2$ state) and molecular O_2 ($^3\Sigma_g^-$ state) of each cluster, and the gold binding energies of the $AuTi_3O_n$ cluster series, were similarly determined as per equations 1–3, using the lowest energy optimized structure at each stoichiometry.

$$BE_{Atomic\ Oxygen} = E_{Au_xTi_yO_z} - (E_{Au_xTi_yO_{z-1}} + E_O) \tag{1}$$

$$BE_{Molecular\ Oxygen} = E_{Au_xTi_yO_z} - (E_{Au_xTi_yO_{z-2}} + E_{O_2}) \tag{2}$$

$$BE_{Gold} = E_{AuTi_yO_z} - (E_{Ti_yO_z} + E_{Au}) \tag{3}$$

Partial atomic charges were determined for each optimized cluster using Hirshfeld population analysis.

3. Results and discussion

3.1. Effect of an all-electron basis set on titanium and oxygen

Geometries and isomers within 0.2 eV of the global minima of Ti_3O_n, Ti_4O_n and $AuTi_3O_n$ optimized at the B3P86/SDD level of theory are shown in Figs. 1–3. Isomers up to 0.5 eV in energy from the minima geometries are show in Figs. S1–S3 in the Supplementary Information, alongside relative energies of $AuTi_3O_n$ ($n = 0$, 6, 10), Ti_3O_n ($n = 0$, 6) and Ti_4O_n ($n = 0$, 6, 10) re-optimized with the cc-pvdz basis set.

No significant structural differences are observed between geometries optimized using the two different basis sets. The relative energies between energy minima structures and low-lying isomers vary by less than 0.2 eV. For higher-energy structures (>0.2 eV above the energy minima) the relative energies vary by up to 0.55 eV but none of these geometries become competitive for the global energy minimum. Therefore, we estimate that any of the low-lying isomers within 0.2 eV could potentially be the global energy minima. Hence, all structures lying within 0.2 eV of the energy minima predicted using the B3P86/SDD level of theory are discussed below.

Binding energies, ionization energies, electron affinities and HOMO-LUMO gaps were calculated for all re-optimized minima geometries, and are listed in Table S1 (Supplementary Information). Between the SDD and cc-pvdz calculations, the overall trends in the data remain the same across both basis sets, with the overall differences in values rarely larger than 15% with respect to the SDD calculations. In general, use of cc-pvdz over-estimates total molecular binding energies and under-estimates all other parameters relative to SDD. Hence, the overall effect of switching to an all-electron basis set for titanium and oxygen is minimal upon both the predicted cluster geometries and energetic properties.