Properties of hydrated TiO₂ and SiO₂ nanoclusters: dependence on size, temperature and water vapour pressure

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Nanoscale titania (TiO_2) and silica (SiO_2) are massively produced technologically important nanomaterials used in a wide range of technological applications where nano-titania is the active component (e.g. water splitting, pollution remediation, self-cleaning coatings). Generally, these applications entail contact with water and a degree of hydration of these nano-oxides. Although the hydration of nano-silica has been fairly well studied, the corresponding level of microscopic understanding for nano-titania is severely lacking. Here, using accurate electronic structure calculations we perform a detailed and comprehensive study of the hydration of titania nanoclusters. Firstly, using global optimisation, we establish the most energetically stable structures of a set of $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters with sizes ranging through $M = 4 - 16$ and with N/M ratios of ≥ 0.5 . Using this extensive dataset we investigate how the structures, energy gaps, and thermodynamic stabilities of these species depend on size, temperature and water vapour pressure. To provide a chemical context for our study we also provide this full set of data for the respective set of $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters which we use to compare and contrast the results for nano-titania. Our broad systematic study thus provides a comparative and foundational reference study for a thorough understanding how hydration affects the structure, energetics and properties of both nano- SiO_2 and nano- TiO_2 .

Introduction

Nanoparticles of titania (TiO_2) and silica (SiO_2) are two of the most massively produced nanomaterials in the world.¹ Nano- TiO_2 and nano- SiO_2 are both widely used as fillers to improve the properties of materials, whereby the former typically imparts enhanced (photo)electroactive properties and the latter increased structural resistance and visible light transmittance (e.g. proton conducting electrolytes,² photo-resistive rubbers,³ pollutant-degrading durable mortars⁴). This synergy has also led to a number of mixed-oxide titanosilicate nanomaterials with applications in (photo)catalysis,⁵ water remediation,⁶ and self-cleaning.⁷ In all the above applications, the nano- TiO_2 and nano- SiO_2 components typically, and often deliberately, come into contact with water-containing environments. Understanding and controlling such interactions is thus essential for optimising the performance of these systems. The aqueous chemistry of nano- SiO_2 and nano- TiO_2 is also important for understanding the bottom-up solution syntheses of nanoporous silicates⁸ and TiO_2 -based nanomaterials⁹ and the possible eco-toxicity of these species.¹⁰ Many studies have specifically focussed on the interaction of water with nano- TiO_2 due to the potential these systems have for fuel production through photo-dissociative water splitting.¹¹

A number of recent theoretical studies have used top-down bulk cut nanoparticles containing 10s - 1000s of atoms in order to investigate the electronic properties of nano- TiO_2 photocatalysts^{12,13,14,15} and their interactions with water.^{16,17,18,19,20,21} Although such calculations can provide important new insights, in most cases the nanoparticles used are still relatively small idealised model systems compared to experimental systems where larger and more complex nanoparticles are typically used. Detailed spectroscopic experiments probing the interaction of water with small oxide (i.e. ~ 10 -30 atoms) systems have tended to focus on hydroxylated silica (e.g. ^{29}Si nuclear magnetic resonance spectroscopy^{22,23,24} and mass spectroscopy²⁵). As such there are a number of theoretical studies proposing corresponding structures for small $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ species with $M=2$ -4^{26,27,28} and their oligomerisation reactions.^{27,29,30} Recently, cluster beam experiments by Weichman *et al.*³¹ reported infrared (IR) photodissociation spectra for gas phase $[(\text{TiO}_2)_M(\text{D}_2\text{O})_N]^+$ for $M=2$ -4 and $N=1$ -3. In their work, direct comparison of the experimental IR spectra with theoretically calculated IR spectra from low energy cluster isomers was used to assign structures to the experimental clusters. The assignments utilised cluster structures from a previously reported global optimisation search.³² The use of global optimisation provides a means to find stable structures of small nanoclusters which are generally unrelated to simple cuts from the respective bulk crystal. The global optimized structures show a huge range of variability with respect to size and chemical composition, yet, for small sizes they are more stable than crystal cuts of the same size.^{33,34} Herein,

following our previous theoretical work on anhydrous SiO_2 ,^{35,36,37} TiO_2 ,³³ and $\text{TiO}_2\text{-SiO}_2$ ³⁸ nanoclusters and hydroxylated SiO_2 ^{39,40,41} nanoclusters, we use global optimisation to provide detailed bottom-up insights into the structures and stabilities of $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters with sizes from $M = 4 - 16$ and N/M ratios of ≥ 0.5 (i.e. up to 72 atoms). We compare the obtained structures with the corresponding global minima $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters. Further, we calculate how the free energies of both $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ and $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters depend on size, degree of hydroxylation, temperature and water vapour pressure. In this way we provide an unprecedented detailed comparison between nano- TiO_2 and nano- SiO_2 in terms of how they interact with water, while bridging the gap between very small molecular species and bulk-like nanoparticles for these important hydrated nano-oxide systems.

Methodology

In this study we apply the Monte Carlo Basin Hopping (MCBH) algorithm⁴² for exploring the potential energy surface (PES) of hydrated $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters. This global optimisation methodology consists of repeated steps whereby in each step random structural distortions are applied to a cluster followed by optimisation of the cluster structure to a local energy minimum on the PES. The Metropolis criterion⁴³ is applied after each step to decide whether or not to accept the new minimum energy structure. This is a probabilistic criterion which depends on the simulation temperature and the energy difference between the present cluster structure and the previously accepted one. An accepted cluster is used as initial structure in the following step. In each step, we use interatomic potentials (IPs) for the structural optimisation. The IPs we use are empirical functions that provide a computationally efficient means to evaluate the relationship between structure and energy. Although the IP-MCBH approach is a very effective means to quickly assess many low energy minima on the PES, IPs generally provide only a reasonable estimate of energetic stability of any cluster structure. In order to refine the accuracy of our predictions we selected a set of low energy structures from each global optimisation run which were then fully optimised using density functional theory (DFT) based calculations (see details below). We have successfully applied this method in several previous studies, often finding new improved global minima candidates with respect to other reported cluster isomers.^{35,36,37,38,39,40}

Global optimization of $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ systems

The choice of the IP plays a decisive role in determining the accuracy of predicting the structure of low energy clusters. For titania-water systems, although there are a number of empirical IPs available in literature,^{44,45,46,47} such IPs are parameterized for bulk titania and were found to be inappropriate for finding low energy nanoclusters which have non-bulk-like structures and in which the coordination of Ti cations ranges from 4 to 6. Therefore, in order to have an IP suitable for global optimisation of $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters we constructed a new IP. Due to the structural similarities between globally optimized nanoclusters of bare silica and titania,³⁸ we based our IP on a well-established silica IP for hydroxylated silica systems (FFSiOH).⁴⁸ In particular, we have previously shown that FFSiOH is very effective in accurately predicting low energy structures and stabilities of hydroxylated silica nanoclusters.^{49,50}

In order to provide relevant data to fit our new IP we first selected global minima candidates of anhydrous $(\text{TiO}_2)_M$ from our previous work³³ with sizes between $M = 4 - 14$. All the clusters were then manually hydrated by adding molecular water in a dissociative way for low degrees of hydration and via molecularly adsorbed water for highly hydrated clusters. For each cluster we then ran DFT-based *ab initio* molecular dynamics (AIMD) for 3 ps at 300 K employing the PBE functional⁵¹ with a light/tier-1 basis of numerical atom-centred basis functions employing the FHI-AIMS code.⁵² In this way we produced a large and varied training set of structures for fitting the parameters of our IP. By adapting the original FFSiOH parameters to reproduce the radial distribution functions of the AIMD runs we produced a new parameterisation which we refer to as FFTiOH. Using FFTiOH in the MCBH runs, we found that it was often difficult to optimise randomly distorted geometries when large core-shell separations occurred. To overcome this issue, we generated a simpler version of FFTiOH where core-shell polarizable ions were removed and the O-H interaction was fitted to a Buckingham potential to mimic as much as possible the original Morse potential. We refer to this simplified version as FFTiOH*. To overcome bias of using a single IP in the MCBH global optimisation procedure we also slightly modified the degree of O-O repulsion in FFTiOH* to generate FFTiOH*-mod. The use of FFTiOH*-mod generates slightly more open cluster structures allowing the MCBH searches to explore PES regions not accessible with only FFTiOH*. The full set of parameters for FFTiOH, FFTiOH* and FFTiOH*-mod are provided in the ESI.

We used the MCBH runs to globally optimise $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ clusters with $M = 4, 8, 12$ and 16 and for each M respectively $N = 1 - 4, 1 - 5, 1 - 6$ and $1 - 8$. A typical MCBH run employed either FFTiOH* or FFTiOH*-mod for 20000-100000 steps depending on the system size. Our MCBH algorithm uses the Atomic Simulation Environment (ASE)⁵³ for manipulating structures and the GULP⁵⁴ code for structural optimisations. During the MCBH procedure the temperature was dynamically adapted to maintain the ratio of accepted steps close to 65%. The MCBH procedure was

repeated a number of times for each distinct cluster $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ stoichiometry using both FFTiOH* and FFTiOH*-mod to better ensure a thorough search of the respective PES. Our MCBH searches were also further extended by data mining from hydrated silica nanoclusters from our previous works.^{39,40,41}

From each MCBH run a selection of isomers were optimised using progressively more accurate methods. Firstly, the 200-500 lowest energy cluster isomers optimised using FFTiOH* and FFTiOH*-mod during each MCBH run were first post-optimised optimized with FFTiOH. Afterwards, between 50 and 150 (depending on the system size) of the energetically lowest lying structures were fully optimized with DFT based calculations using the PBE functional and a tier1/light numeric atom-centred orbital basis set. Then, all cluster isomers within 0.5 eV of the energetically lowest PBE-optimised structure were further optimized using the PBE0⁵⁵ functional and a tier1/tight basis. These calculations were also used to extract the difference in energy between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in order to estimate the vertical electronic energy gap magnitudes. All DFT based calculations were performed with FHI-AIMS package.⁵² We note that the employed basis set approximately provide results of a similar or higher quality to those obtained with valence triple-zeta plus polarization Gaussian type orbitals.⁵⁶ Generally, the higher the hydration degree and/or the system size the higher the number of structures were optimized using DFT because of the correspondingly higher density of distinct cluster structures with respect to energy.

Energetics of hydration

As discussed above, both nano-TiO₂ and nano-SiO₂ are prone to incorporate water which we can formally write as

Where X is the cation (i.e. Si, Ti), M and N are the number of formal oxide units and the number of in-cluster incorporated water molecules, respectively. The first measure of stability of water incorporation can be assessed by calculating the energy change for each hydration step, which is known to be system size dependent. Using the lowest energy $(\text{XO}_2)_M(\text{H}_2\text{O})_N$ structures for each degree of hydration ($R_{N/M} = N/M$) for any single system size (M) we can calculate the energy change upon hydration with relative to the respective anhydrous bare $(\text{XO}_2)_M$ cluster via

$$\Delta E_{Hyd} = E_{(XO_2)_M(H_2O)_N} - E_{(XO_2)_M} - NE_{H_2O} \quad (\text{eq 2.2})$$

where $E_{(XO_2)_M(H_2O)_N}$ and $E_{(XO_2)_M}$ are the energies of hydrated and anhydrous nanoclusters respectively, and E_{H_2O} is the energy of the water molecule. ΔE_{Hyd} provides the energetic strength of the interactions between water and silica/titania for each nanocluster size, M, considered. A negative ΔE_{Hyd} indicates thermodynamic favorability of cluster hydration and *vice versa*.

For a more accurate assessment of the thermodynamics of hydration, free energies must be considered. Following a similar approach to that previously applied to the oxidation of small oxide clusters,⁵⁷ using standard statistical thermodynamics we can calculate the free energies of hydroxylation of our titania and silica nanoclusters entirely from the relevant partition function. The partition function for N non-interacting indistinguishable particles is defined as:

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!} \quad (\text{eq 2.3})$$

where $q(V, T)$ is the molecular partition function and N is the number of particles in the system.

$$q(V, T) = q_{trans}(V, T) q_{rot}(T) q_{vib}(T) q_{sym}(T) q_{elec}(T) q_{nuc} \quad (\text{eq 2.4})$$

From the partition function, we can calculate the free energy as:

$$\begin{aligned} G(T) &= -k_B T \ln(q(V, T)) + pV \simeq F(V, T)^{trans} + F(T)^{rot} + F(T)^{vib} + F(T)^{sym} + E^{DFT} \\ F(V, T)^{trans} &= -\frac{3}{2} k_B T \ln \left(\frac{2\pi m k_B T}{h^2} \right) - k_B T \ln(V) \\ F(T)^{rot} &= -k_B T \ln \left[8\pi^2 \left(\frac{2\pi k_B T}{h^2} \right)^{\frac{3}{2}} \right] + \frac{1}{2} k_B T \ln(I_x I_y I_z) \\ F(T)^{vib} &= \sum_i \frac{h\nu_i}{2} + \sum_i k_B T \ln \left[1 - \exp \left(-\frac{h\nu_i}{k_B T} \right) \right] \\ F(T)^{sym} &= k_B T \ln(\sigma) \end{aligned} \quad (\text{eq 2.5})$$

where m is the system total mass, $I_{x,y,z}$ are the system inertial moments along the x, y and z axes, ν_i are the harmonic vibrational frequencies and σ is the symmetry number. Frequency rotational contributions are calculated within the harmonic and rigid rotor approximations respectively. All systems are treated as ideal gases. Symmetry contributions should formally be considered in order to avoid over-counting the number of possible states. However, for the hydrated systems the

presence of hydroxyl groups usually breaks any symmetry and even for the highest symmetric anhydrous systems effect of symmetry has an almost negligible effect on the cluster free energies.

Considering nanoparticles to be in equilibrium with water vapour, the actual degree of hydration of a system will depend on the experimental temperature and water vapour pressure conditions. In a gas-phase hydration reaction, the free energy of the process is described as:

$$\Delta G_{hyd}(T, P) = G_{(XO_2)_M(H_2O)_N}(T) - G_{(XO_2)_M}(T) - N\mu_{H_2O}(T, P) \quad (\text{eq 2.6})$$

where $\mu_{H_2O}(T, P)$ is the water chemical potential in equilibrium with the clusters dependent on temperature T and water vapour partial pressure P . Both clusters free energies and the water chemical potential can be computed from *ab initio* data by means of statistical thermodynamics as shown in equation 2.5. The water vapour partial pressure dependency arises from $-k_B T \ln(V)$ term which can be written, according to the ideal gas law, as $-k_B T \ln(k_B T / P)$. The same term, in the cluster case can be omitted because the reference volume cancels out since we consider differences in free energy. All quantities were calculated using DFT based calculations using the PBE0 functional and using tier1/tight numerical basis set. Harmonic frequencies were calculated by the finite difference method using a displacement of 0.0025 Å for each degree of freedom.

Results and Discussion

In the following, we provide a comparison of structures and thermodynamic stability of known and newly found globally optimized hydrated titania and hydrated silica nanoclusters.

Hydrated nanocluster structures

Figure 1. Global optimized $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ and $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ clusters for $M = 4$ and 8 . Numbers in the cluster labels show M , the number of XO_2 units, and N , the number of water molecules incorporated in the cluster. $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ clusters are obtained from refs 37,39,40 except for the $(\text{SiO}_2)_8(\text{H}_2\text{O})_5$ nanocluster which was found in this study.

Figure 2. Global optimized $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ and $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ clusters for $M=12$. Numbers in the cluster labels show M , the number of XO_2 units, and N , the number of water molecules incorporated in the nanocluster. $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters with $N=3-6$ are obtained from ref 41 while systems with $N=1, 2$ were generated applying exactly the same methodology as in ref 41.

Figure 3. Global optimized $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ and $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ clusters for $M = 16$. Numbers in the cluster labels show M , the number of XO_2 units, and N , the number of water molecules incorporated in the cluster. $(\text{SiO}_2)_M(\text{H}_2\text{O})_N$ clusters are obtained from ref 37,39,40. Notice that our most stable $(\text{SiO}_2)_{16}(\text{H}_2\text{O})_8$ nanocluster is different from the global minima candidate reported in ref 39 since is found to be very slightly more stable (0.07 eV in total energy) with the method employed herein.

Both crystalline bulk SiO_2 and TiO_2 have very low solubility in water but both can dissociatively adsorb water on their surfaces. Amorphous phases and nanoclusters absorb dissociated water more readily due to the presence of reactive surface defects such as terminal non-bridging oxygens (NBOs) or strained rings of different sizes.^{58,59,60,61} Hydration of bare $(\text{SiO}_2)_M$ nanoparticles proceeds by saturating terminal oxygen defective sites first, as they are generally the most reactively unstable defects.⁶² Depending on system size, one (for the large particle sizes $M=12$ and 16) or two (for the small particle sizes $M=4$, $M=8$) water molecules are enough to fully saturate such surface defects on the silica nanoclusters. Further incorporation of water molecules leads to hydroxylation of silicon atoms until each silicon atom has one hydroxyl group forming cage-like nanoclusters. Beyond this level of hydration geminal silanol groups begin to be formed (i.e. two hydroxyl groups attached to a single silicon centre) which tends to open up the cage-like structure. The limit of this behaviour is the complete dissolution of each silicon atom to generate silicic acid $(\text{Si}(\text{OH})_4)$ monomers. We note that this tendency is size dependent whereby silica nanoclusters with larger sizes tend to form denser

non-cage-like cluster form cages and are more resistant to dissolution.³⁹ For these larger sizes and at high degrees of hydration, silica nanoclusters start to absorb water rather in a molecular fashion rather than form germinal silanols (e.g. for $(\text{SiO}_2)_{24}$ see ref. 39). Atomic coordinates of all clusters reported in Figs 1, 2 and 3 are reported in the Supporting Information.

Hydration of titania nanoclusters proceeds in a similar way to silica nanoclusters at low hydration degree and small nanocluster size. As for silica nanoclusters, depending on the system size, one or two incorporated water molecules are enough to hydroxylate the terminal oxygen defects on anhydrous titania nanoclusters. With further hydration, titania also generates cage-like structures, in some cases even identical to silica (e.g. for $M=4, N=2$ and $M=8, N=4$). For relatively higher degrees of hydration titania and silica nanocluster systems are no longer so similar. Unlike Si in silica, the Ti cations in titania readily assume a higher coordination than four (i.e. Ti can be 4-, 5- and 6-coordinated) and thus titania can more easily retain its $-\text{Ti-O}-$ bonding network with increasing hydration. Indeed, highly hydroxylated titania systems, especially those with $M=16$, become more compact with 6-coordinated Ti atoms in their centres. With respect to silica, titania nanoclusters can also more easily adsorb molecular water without breaking their bonded $-\text{Ti-O}-$ networks. This capacity is linked to the character of d orbitals in titanium centres which can participate in dative bonds with lone pairs of water molecules.

Despite of these differences some hydrated titania and silica nanocluster structures are found to be very similar. The structures of the $(\text{XO}_2)_4(\text{H}_2\text{O})_2$, $(\text{XO}_2)_4(\text{H}_2\text{O})_3$, $(\text{XO}_2)_8(\text{H}_2\text{O})_2$, $(\text{XO}_2)_8(\text{H}_2\text{O})_4$, species, for example, are essentially the same for both systems. Larger sized nanoclusters with different degrees of hydration also are found to have a similar structures, such as (e.g. $(\text{TiO}_2)_{12}(\text{H}_2\text{O})_4$ and $(\text{SiO}_2)_{12}(\text{H}_2\text{O})_5$, $(\text{TiO}_2)_{16}(\text{H}_2\text{O})_2$ and $(\text{SiO}_2)_{16}(\text{H}_2\text{O})$).

Hydration free energies

The hydration free energy (ΔG_{hyd}) indicates the thermodynamic tendency of an anhydrous nanocluster to be hydrated at specific temperature and pressure conditions (eq. 2.6). In Fig 5 we plot the ΔG_{hyd} of silica (solid lines) and titania (dashed lines) with respect to incorporated water ratio ($R_{N/M}$) at several temperatures (0, 300, 600, 900 K). All hydration energies are normalized by number of oxide units (i.e. M). In the 0 K case each term of eq. 2.6 is approximated by only DFT energies and to distinguish this quantity from free energies we indicate it as ΔE_{hyd} . In all other cases, ΔG_{hyd} is calculated under the assumption that the system is in equilibrium with water vapour at a partial pressure of 1 Pa.

Figure 4. Hydration energies free energies of silica (dashed lines) and titania (solid lines) nanoclusters for sizes for: a) $M=4$, b) $M=8$, c) $M=12$, d) $M=16$. Hydration free energies are reported at different temperatures while keeping the water partial pressure at 1 Pa which is sufficiently low to consider water as an ideal gas even at ambient conditions. Values of total energy, hydration energy at 0K and hydration free energy at 300 K for all systems reported in these graphs are reported in Table S1 of the Supporting Information.

As we can see from Fig. 4, the hydration reaction is a more exothermic process on silica nanoclusters than on the correspondingly sized titania nanoclusters. As the system size (M) increases, the magnitude of the hydration energies decreases. At 0K, for both titania and silica systems irrespectively of the size, the hydration energy decreases indicating a higher stability of hydrated systems with respect to anhydrous ones. The energetic gain through hydration for both systems can be roughly divided into two regions. At first, the slopes are rather steep, and the energy drop per incorporated water molecule is rather constant, although of different magnitude, in both cases. For silica we find a decrease of -0.4 eV for each 0.1% increase of water content, and a decrease of -0.2 eV per 0.1% increase of water content for TiO_2 . Thus in all cases hydration of silica nanoclusters is more energetically favourable than for respectively sized titania nanoclusters. At a certain degree of

hydroxylation, depending on the size and system type, the magnitude of the energy change due to hydration begins to reduce and the hydration energies appear to saturate towards a constant value. In this saturation region, the difference in hydration energy between similar sized titania and silica systems stabilizes to a constant maximum value. This difference varies from 1 eV for system sizes of $M = 4$ to 0.6 eV for sizes $M = 16$. When including thermal contributions to the hydration free energy, the magnitude of the energy changes due to incremental hydration are reduced compared to the 0K case. Although, as in the 0K case, the ΔG_{hyd} data initially decreases with increasing water incorporation, when reaching hydration level marking the beginning of the 0K saturation regime, the energies pass through minimum point beyond where ΔG_{hyd} starts to increase again. Both these effects are enhanced with increasing temperature. Indeed, at 900K for most of titania systems the ΔG_{hyd} is nearly zero or positive showing that hydration is thermodynamically unfavourable. This is caused mostly by the vibrational contributions to the entropy and enthalpy of highly hydrated systems. The minimum in ΔG_{hyd} tends to move towards smaller values of $R_{N/M}$ as the system sizes increase. This indicates that as the system becomes larger, its tendency to be hydrated decreases, or in other words, it tends to be more hydrophobic. Moreover, it is interesting to notice that the silica and titania ΔG_{hyd} minima for small sizes (i.e. $M=4, 8$) corresponds to the same water incorporation ratio, $R_{N/M}$, but, for larger sizes (i.e. $M=12, M=16$), $R_{N/M}$ is shifted towards smaller values for titania nanoclusters relative to silica. This indicates that, already at the nanoscale, titania tends to be more hydrophobic than silica.

To best of our knowledge, the work of Dixon *et al.*³² is the only other study attempting to determine global minima of small hydrated titania nanoparticles. Here the authors reported several low lying structures for $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ systems with $M = 1 - 4$ and $N = 1 - 2$ and few with $M = 8$ and $N = 3, 4, 7$ and 8 . In this section we compare their reported structures for $M = 4$, and some of the predictions and trends they reported for their systems, with our findings. For systems with $M = 8$ and $N = 3$ and 4 we obtain the same set of global minima structures, hence we will limit our comparison to systems with $M = 4$. For systems with $M = 4$ and $N = 1$ and 2 we obtain the same lowest energy structures as those reported from Dixon *et al.* which further enhance the likelihood that such systems are global minima. For $M = 4$ and $N = 3$ and 4 we find isomers not reported in their work whose energetic stability is found to be essentially degenerate with their systems (i.e. differences of only 0.0076 eV for $N=3$ and in 0.029 eV for $N=4$ in total energy in favour of our structures). In Fig. 5 we report both structures found by our search as compared with those found in ref [32]. In our $M = 4$ and $N = 3$ nanoclusters, the water molecule is incorporated into the nanocluster in a dissociative way, opposed to structures reported in ref 32 where the water adsorbs in a molecular way via a $\text{Ti-O}(\text{H}_2)$ Lewis acid-base complex. Therefore, since the water dissociation is

energetically competitive with the molecular adsorption, the hydrolysis limit (i.e. maximum number of water molecules that can be dissociated upon hydration of titania nanocluster) is likely to be in equilibrium between two and three dissociated water molecules rather than simply two as predicted in ref [32].

Figure 5. Titania nanocluster structures reported from Dixon *et al.* in ref [32] (right side) as compared with geometries found in this study (left side). In parenthesis we report our calculated relative electronic energies in eV.

One factor that can affect the hydrolysis limit of titania nanoclusters is the presence of “unsaturated” Ti centres. Such species are either under coordinated Ti atoms with less than 4-fold coordination, and are mainly present in small nanoclusters (i.e. $M \leq 4$) and/or highly distorted tetra-coordinated Ti centres. In $M = 4, N = 3$ systems, the hydrolysis limit appears to be determined through a competition between factors that favour the fully dissociated form such as the cage strain and hydroxyls hydrogen bond and factors favouring the molecular adsorption of water such as the Ti-O(H₂) Lewis acid-base interaction. We note that other factors affecting the hydrolysis limit such as the hydroxylation of bridging oxygens, flexibility of Ti centres to adopt different coordinations (i.e. 4-, 5- and 6-coordinated) etc., appear as the system size increases.

Figure 6. $(\text{TiO}_2)_8(\text{H}_2\text{O})_5$ isomers found from our global optimization search. Number in parentheses show our calculated relative total energies in eV.

The contribution of such factors is not trivial to evaluate, however, $(\text{TiO}_2)_8(\text{H}_2\text{O})_5$ isomers found from our search, are small enough to qualitatively highlight their relevance. In Fig. 6 we show three different $(\text{TiO}_2)_8(\text{H}_2\text{O})_5$ isomers for which in the most energetically stable case (i.e. left-side of Fig. 6), the hydration occurs via fully dissociated water molecules. In this case the hydration reaction induces hydroxylation of bridging oxygens and a small degree of structural rearrangement in which three Ti centres increase their coordination from 4 to 5-fold. This structure is energetically favoured over nanoclusters which adsorb water molecularly (Fig. 6 middle isomer) or in which the Ti centres are all 4 coordinates and the cage-like cluster is opened (Fig. 6 right-hand isomer).

We further notice that the hydrolysis limit, in addition to being system size dependent, is also temperature and water vapour pressure dependent. Indeed, as the temperature increases, gas-phase titania nanoclusters with the inclusion of N waters displaying one molecularly adsorbed H_2O (i.e. $(\text{TiO}_2)_4(\text{H}_2\text{O})_4$ and $(\text{TiO}_2)_{16}(\text{H}_2\text{O})_8$) will present progressively more positive and therefore endothermic ΔG_{hyd} with respect the nanocluster with $N-1$ waters, as shown from hydration free energies in Fig. 4.

Aggregation of hydrated nanoclusters

Using the data in the previous section we can compare the energetics of nanocluster aggregation for silica and titania, and how it depends on temperature. For simplicity, we consider only the aggregation reactions of $(\text{XO}_2)_M(\text{H}_2\text{O})_N$ nanoclusters to form a twice larger nanoclusters with the same degree of hydration, i.e. reactions of the type:

Figure 7. Reaction energies for the aggregation of $(\text{XO}_2)_4(\text{H}_2\text{O})$ nanoclusters (left) and of $(\text{XO}_2)_4(\text{H}_2\text{O})_2$ nanoclusters (right) at temperatures of 0K, 300K and 600K. The corresponding reactions are shown above each plot. The energy of the initial aggregating species is set to zero in all cases for ease of comparison of the energy profiles.

In Fig. 7 we plot the energies of aggregation of $(\text{XO}_2)_4(\text{H}_2\text{O})_N$ species with $N=1$ (left) and 2 (right) where in each case the (free) energy of the corresponding global minimum candidate nanocluster is used. The corresponding energy profiles thus track the energies of nanoclusters with a $R_{N/M}$ value of 0.25 and 0.5 respectively. For 25% hydration the aggregation reactions at 0K for both hydrated titania and silica systems are all highly exothermic (between 5.2-8.6 eV). Comparatively, however, the energies for hydrated silica aggregation are always significantly more exothermic (by between 2.1-3.5 eV) than the corresponding hydrated titania aggregation. The energy drop upon aggregation of 25% hydrated silica nanoclusters is found to be monotonically decreasing with increasing nanocluster size, with a slightly higher exothermicity for the aggregation of two $(\text{SiO}_2)_8(\text{H}_2\text{O})_2$ species as compared to that of two $(\text{SiO}_2)_4(\text{H}_2\text{O})$ species. However, for the 25% hydrated titania nanoclusters, the aggregation of two $(\text{TiO}_2)_8(\text{H}_2\text{O})_2$ is between 0.6-1.45 eV less exothermic than for the aggregation of two $(\text{TiO}_2)_4(\text{H}_2\text{O})$ species. With increasing temperature all energy profiles are still always exothermic but are shifted upwards in energy. These reaction energy profiles can be qualitatively rationalised by inspection of the comparative tendencies of silica and titania nanoclusters in the free energy of hydration plots in Fig. 4, and noting that at 25% hydration we are always in the highly exothermic pre-saturation regime.

In the case of nanoclusters with 50% hydration all aggregation reaction energy profiles are qualitatively similar in that the aggregation of two $(\text{XO}_2)_4(\text{H}_2\text{O})_2$ species is always more energetically favourable than the aggregation of two $(\text{XO}_2)_8(\text{H}_2\text{O})_4$ nanoclusters. Unlike in the 25% hydration case,

the energy decrease upon the initial aggregation of two $(\text{XO}_2)_4(\text{H}_2\text{O})_2$ nanoclusters at 0K is quite moderate and very similar in magnitude for both silica (2.3 eV) and titania (2.7 eV). Interestingly, in this case both silica and titania nanoclusters exhibit the same global minimum isomer (except for the orientation of hydroxyl groups) for both reactant and product.

For small systems such as those with $M=4$ that aggregate to form a larger nanocluster with $M=8$, the exothermicity of the reaction mainly arises by lowering the nanocluster ring and cage tension present in the reactant.

For the aggregation of slightly larger hydrated nanoparticles such as those having $M=8$, for poorly hydrated systems (i.e. $(\text{XO}_2)_8(\text{H}_2\text{O})_1$ and $(\text{XO}_2)_8(\text{H}_2\text{O})_2$) there is a strong aggregation energy. In such systems the products of their aggregation do not display unsaturated dangling oxygens contrary to their reactant. Such behaviour is particularly enhanced in the aggregation of silica nanoclusters given the destabilizing effect of dangling oxygens.

Electronic energy gaps

Figure 8. Electronic energy gaps of silica (a) and titania (b) nanocluster systems with respect to the incorporated water ratio, $R_{N/M}$.

In Fig. 8 we show the vertical electronic energy gaps of silica (Fig. 8a) and titania (Fig. 8b) systems with respect to $R_{N/M}$. We note that our discussion is only related to trends and not on absolute quantitative values of the electronic gaps for which DFT calculations are often unreliable. Generally, silica nanoclusters show a much higher variability in their gap magnitudes with respect to the degree of hydration than titania. Indeed, as example case, in $(\text{SiO}_2)_{12}$ systems, the magnitude of the gap ranges from 4 eV for the anhydrous case to around 9 eV at 33% hydration, while for the corresponding titania case the gap varies from a minimum of 5.3 eV at 8% hydration to a maximum of 6.2 eV at 33% hydration.

In silica nanoclusters the electronic energy gap is extremely sensitive to the type of oxygen defective sites. For instance, for bare nanoparticles with $M = 4, 8$ and 16 and $N = 0$, which have defective oxygen atoms in silanone species, we find that the energy gaps range between 6.5 and 7 eV, while for $(\text{SiO}_2)_{12}$ which has NBO defective sites the gap is only 4 eV. Generally, with increasing size these defects will be saturated with hydroxyl groups tending to heal the defects. Thus, as the hydration increases, the gap generally increases until a maximum value around 9 eV is reached at around 35% and 40% of hydration depending on the system size (50% for the $M = 4$ system). Further increase of hydration does not affect the gap magnitude with the only exception of $(\text{SiO}_2)_{12}(\text{H}_2\text{O})_6$ which shows a gap decrease of 3 eV at the highest hydration considered, probably due to the presence of geminal hydroxyl groups.

In titania systems there are only NBO defective sites, however there is much greater variety of titanium cation coordination (i.e. 4-, 5- and 6-coordinated Ti centres) and therefore the change in the gap magnitude with increasing hydration is less easy to rationalise than in the silica case. Overall, the titania gap magnitude evolution shows some similarities with silica systems: (i) there is a maximum value of the band gap as hydration increases and (ii) after the maximum the band gap remains rather constant (i.e. $M=4$ and 8). However, in some cases there is a slight decline (i.e. $M=12$ and 16) in the band gap.

Generally, the larger the gap magnitude the more electronically stable the system should be., Adsorption is known to help stabilise a large band-gap.⁶³ In both silica and titania nanoclusters we find that hydration contributes to maximise the gap magnitude and to stabilize the electronic state. In silica nanoclusters this effect is particularly pronounced showing that silica is more readily stabilized by hydration than titania. Conversely, our results also highlight the remarkable stability of the electronic state of titania nanoclusters with respect to hydration.

Ab initio thermodynamics of hydration

According to equation 2.6 ($\Delta G(T, P)$) it is possible to define the hydration reaction of clusters as function of both temperature (T) and partial pressure of water vapour (P). Since the most thermodynamically stable nanocluster at specific conditions of T and P is the one that minimizes the free energy of hydration, we can plot hydration phase diagrams where each region represents the most thermodynamically stable nanoclusters with specific amount of incorporated water within a certain T and P range. All necessary energy contributions can be derived from our DFT calculations within the framework of classical statistical thermodynamics through the canonical ensemble (NVT) partition function formulation as described above. Due to the assumed applicability of Boltzmann statistics and the harmonicity of molecular vibrations, we consider a T range between 100 and 1000 K for where the validity of the approach should be acceptable, in line with other studies.⁶⁴ Moreover, in our case we consider water as an ideal gas for a wide range of temperatures, although this assumption depends on the water partial pressure. Water vapour is in equilibrium with its condensed state at $\sim 3\text{ kPa}$ at 300K. In order to consider water as an ideal gas, however, we should consider a much lower partial pressure. In the phase diagrams reported in Fig. 9, the water partial pressure that we consider does not go above the $1 \times 10^5\text{ Pa}$ (e.g. $\sim 1\text{ atm}$). At this pressure we can consider water as an ideal gas from $\sim 450\text{--}500\text{ K}$ and higher. The saturation water pressure at 273K (0°C) is about 0.6 kPa. In order to treat water as ideal gas in these conditions we should consider either temperatures higher than 400K or pressures lower than 1Pa. Although considering water as an ideal gas at relatively low temperatures and high pressures is conceptually wrong, these conditions represent a small region of the phase diagrams reported in Fig. 9 and therefore do not affect most of the P versus T range considered.

Figure 9. P-T phase diagrams for silica (left side) and titania nanoparticles (right side). The temperature range goes from 100 to 1000 K and P (H_2O partial pressure) range from 1×10^{-10} to 1×10^5

Pa (from $\sim 1 \times 10^{-15}$ to ~ 1 atm). Blue and black dashed lines indicate the equilibrium vapour pressure with respectively ice and liquid water respectively. The colours of the P-T phase diagram regions are determined by hydration degree intervals in all the graphs. The cooler the colour (towards dark blue) the lower the hydration degree, the warmer the colour (towards dark red) the higher the hydration degree. From top to bottom graphs are arranged from that smallest sized nanoclusters $(\text{XO}_2)_4(\text{H}_2\text{O})_N$ to the largest sized nanoclusters $(\text{XO}_2)_{16}(\text{H}_2\text{O})_N$, where $\text{X}=\text{Si}, \text{Ti}$.

In Fig. 9 we plot P versus T phase diagrams for both titania and silica systems in thermodynamic equilibrium with water vapour. As discussed above, the pressure and temperature ranges have been chosen in order that water may be considered as an ideal gas in most of the conditions represented in the plots. Each region of each plot in fig. 9 represents the most thermodynamically stable hydrated cluster at the particular conditions of T and $P_{\text{H}_2\text{O}}$ according to equation 2.6. The regions are coloured consistently for each hydration degree in each plot (e.g. the 50% hydrated structures have same colour plots). The phase diagrams show that, silica and titania, which can have very different properties at macroscopic scale (amorphous silica can be hydrophilic and hydrophobic, while TiO_2 is always hydrophobic), have quite similar hydration behaviour at the nanoscale. This similarity is particularly pronounced at the smallest size considered, $M = 4$, and becomes less pronounced as the system size increases. For the systems with $M = 4$, most of the phase diagrams (see Fig. 9a and 9b) are dominated by the same tetrahedral isomer for both hydrated titania and silica (i.e. $M=4$; $N=2$ with 50% hydration degree.). However, the most stable structure at ambient temperature conditions for silica corresponds to the 75% hydrated system. At relatively higher $P_{\text{H}_2\text{O}}$ and lower T silica becomes 100% hydrated while titania barely reaches such a high degree of hydration. For $M = 8$, the silica phase diagram (Fig 9c) is dominated by two structures (i.e. for $N=3, 4$) while titania phase diagram (Fig 9d) shows four prominent structures (i.e. for $N=0, 2, 3, 4$). The $M = 8, N = 4$ isomer has the same structure again for both systems but for silica the P-T stability region is wider. At ambient conditions (i.e. $T=300$ K and 1k Pa water vapour partial pressure - the equilibrium vapour partial pressure with its condensed state at 300K is 4.2 kPa) this last structure is thermodynamically favourable for both systems. At temperatures below 900K silica is stabilised by losing one water molecule to form the $M = 8, N = 3$ structure. Titania for $M = 8$ shows a relatively higher variety of hydration degrees at high temperature, with structures going from $N = 3$ to $N = 2$ and finally to $N = 0$ as temperature increases. In the $M = 8$ phase diagrams we note that: (i) systems with $N=1$ do not appear in the P-T range considered in both titania and silica, and (ii) at very low temperatures and moderate to high pressures titania has a larger degree of hydration than silica. This second feature is not exclusive for $M=8$, but rather appears in all phase diagrams. A possible explanation is that TiO_2 is

able to adsorb water molecules more easily than SiO_2 (SiO_2 needs formation of hydroxyls, TiO_2 protonates bridging oxygens). It must be noted though that the such very low temperature regions tend to fall outside that within which water vapour can be strictly considered to be an ideal gas.

For $M = 12$, the silica phase diagram (Fig 9e) is mainly populated by two structures as in the case of $M = 8$ but with a the relatively lower hydration degrees of 42% and 33%, compared to the previous hydration degrees of 50% and 38% at $M = 8$. Less hydrated structures are found at higher temperatures ($> \sim 700\text{K}$). For titania systems of the same size (Fig 9f) the phase diagram is slightly more complex than silica and has more stable phases. Despite that, only 33% and 0% (i.e. $N=4$ and $N=0$ respectively) hydrated phases seems to play a dominant role. We note that $(\text{SiO}_2)_{12}(\text{H}_2\text{O})_5$ and $(\text{TiO}_2)_{12}(\text{H}_2\text{O})_4$ which occupy most of the area of their respective phase diagram and are close to the region representing ambient conditions contain the cube motif (i.e. as exemplified by the $M=8$, $N=4$ structures) incorporated in the cluster. This is an indicator of the stability of such a motif, not only as known for silica systems,^{22,23,25,40} but for titania systems as well. This suggests that such a structural motif could thus perhaps be used as a building block to synthesize more complex materials such as titanosilicates in a controlled way. For $M=16$, silica systems (Fig 9g) show one dominant phase at 31% hydration degree (i.e. $N = 5$). The maximum hydration degree reaches 50% for narrow regions in the phase diagram at low temperature as in the case of $M = 12$. As the temperature rises, the hydration decreases to 13%. This trend is similar to the case of titania systems (Fig 9h) but is shifted towards lower hydration degrees (i.e. from 25% to 0% hydration). Only the low temperature $M = 16$ titania phases (50% and 38% hydration) show similar stabilities with silica phases, albeit with a larger area of the respective phase diagram for the most hydroxylated case for titania.

Overall, the P-T phase diagrams for both systems highlight that the the tendency to be hydrated decreases with size. As the system size increases, the dominant colours in the phase diagrams gradually blueshift indicating a tendency towards lower degrees of hydration for both silica and titania. However, the shift towards less hydrated systems with size increase is less pronounced for silica than for titania systems indicating that silica nanoclusters are more hydrophilic. Indeed, at high temperature and low water vapour partial pressure silica becomes completely anhydrous at much higher temperatures than titania. Indeed, regions of the P-T diagrams with completely anhydrous silica are hardly present in the T and P range considered. We also note that at ambient temperature conditions, even with the presence of trace humidity, clusters tend to hydrate. Also, for all conditions of temperature and water vapour pressure considered in this work in which the hydration of nanoclusters is thermodynamically favoured, the adsorption of water molecules occurs exclusively in a dissociative way.

Vibrational frequencies

Figure 10. Simulated, infrared harmonic vibrational frequencies of silica (blue lines) and titania (black lines) systems for different numbers of incorporated water molecules (hydration degrees in parenthesis). a), b), c), d) represents IR spectra of system sizes $M = 4, 8, 12, 16$ respectively. Each plot is scaled with respect to the most intense peak. Intensities are in arbitrary units.

In Fig. 10 we plot the calculated infrared harmonic vibrational frequencies of all global optimized titania (black line) and silica (blue lines) nanoclusters. In all spectra the region of hydroxyl O-H stretching (ν_{OH}) around 3900 cm^{-1} is easily discernible. This peak is persistent with system size and hydration degree and is consistent in frequency in both titania and silica. As the hydration increases there are other stretching modes between 3000 and 3900 cm^{-1} due to involvement of OH groups in hydrogen bonds ($\nu_{\text{OH}\cdots\text{O}}$). As hydration increases, for a fixed system size M , the ν_{OH} intensity increases with the increasing number of OHs. As the system becomes larger (increasing M) the OH peaks weaken because the spectra are dominated by the more numerous cation-O vibrational modes. Differences between silica and titania cannot be easily appreciated by inspection of the hydroxyl stretching region but rather in the cation-O stretching/bending one. Indeed, between 600 to 1400 cm^{-1} in the spectra there are intense IR peaks mostly dominated by complicated coupling of cation-O

stretching and bending modes involving several centres ($\delta\nu$ -O-X-O). In silica systems this set of peaks is highly blue shifted (i.e. mostly with vibrational modes higher than 1000 cm^{-1}) with respect to titania ones (i.e. mostly with vibrational modes lower than 1000 cm^{-1}). Moreover, these $\delta\nu$ -O-X-O become slightly blue shifted in the case of silica systems as the hydration degree increases.

Average Coordination Number (ACN)

Figure 11. Average Coordination Number (ACN) as a function of N incorporated water molecules for Si and Ti cations. Respective bulk coordination numbers (for quartz and rutile respectively) are also indicated by dashed lines. The CAN number is defined by taking all nearest neighbours within a $2.1\text{ \AA}$ cut-off in the case of SiO_2 nanoclusters and within a $2.5\text{ \AA}$ cut-off in the case of TiO_2 nanoclusters.

In Fig. 11 we report the cations Average Coordination Number (ACN) in nanoclusters with different sizes (M) as a function of incorporated water molecules (N). Distance cut-off values to count a neighbour as a coordinating atom has been chosen according to a cation-O distance distribution in all clusters. All atoms within $2.1\text{ \AA}$ from Si cations and within $2.5\text{ \AA}$ from Ti cations are counted inside their respective coordination shell. In Fig S1 of the Supporting Information we report the Si-O and Ti-

O distance distributions used to justify the choice cut-off distance adopted in this work. In all cases Si atoms tends to display at most a 4-coordinated anion environment rapidly reaching the bulk value as the number of included water molecules increases. In the case of TiO_2 , $M = 4$ and $M = 8$ systems Ti cations tend to display similar coordination environments and after a small increase with the addition of the first one or two water molecules their ACN does not change. This behaviour is mainly due to the large structural strains possessed by these small systems, which is mitigated by the nanoclusters opening up after a dissociative water adsorption rather than allowing for increased Ti coordination. Larger systems, such as $M=12$ and 16 , are found to be more structurally flexible allowing for higher coordination of Ti cation centres without opening up their structures. Here the CAN of Ti centres tends towards the bulk value as the number of included water molecules increase. However, as shown from Fig. 4 and Fig. 8, the hydration reaction free energy for highly hydrated systems (close to $R_{N/M} \sim 50\%$) tends to be unfavourable, therefore such species will not form under realistic equilibrium conditions.

Conclusions

In this work we have investigated the hydration of titania and silica nanoclusters and their associated relative structural and energetic properties of the by means of accurate *ab initio* modelling. All nanocluster structures were generated by employing an IP-based global optimization search which yielded several new global minima candidate isomers for $(\text{TiO}_2)_M(\text{H}_2\text{O})_N$ with $M=4, 8, 12, 16$, each for a range of N values. In order to improve the efficiency reliability of these searches a newly parameterised IP for hydrated titania nanosystems was also developed. For the nanocluster size regime considered the hydration energy at 0K is found to be exothermic over a wide range of hydration both for nano- SiO_2 and nano- TiO_2 with characteristic dependencies on nanocluster size and degree of hydration. We have also calculated hydration free energies which are found to thus showing how the 0K exothermicity of hydration decreases with increasing temperature. In particular, some of the highly hydrated titania systems are found to be thermodynamically unstable as the temperature increases. By *ab initio* atomistic thermodynamics we also provide phase diagrams showing the stability dependence on both temperature and water vapour pressure for hydrated silica and titania nanoclusters. Our study shows that under ambient conditions, silica and titania nanoclusters would be hydrated even with trace amounts of water vapour. In addition to the thermodynamic properties we also calculate how the structural and electronic properties of all these considered nanoclusters depend on the degree of hydration and nanocluster size. Overall, our study provides a wide range of detailed new insights into the interaction of water with titania and silica

nanoclusters and how their behaviour compare with one another. We hope that our comprehensive and systematic work will inspire experimental studies, especially from the cluster beam community, in order to further our understanding of nanoscale hydration of these important systems.

Conflict of interests

There are no conflicts of interest to declare

Acknowledgements

This research was supported by the Spanish MINECO / AEI-FEDER grant: CTQ2015-64618-R and, in part, by Generalitat de Catalunya grants: 2014SGR13 and XRQTC. We acknowledge the Red Española de Supercomputación for provision of computing time. AC acknowledges PhD funding from the ITN-EJD in Theoretical Chemistry and Computational Modelling with EU H2020 Marie Curie Skłodowska-Curie grant agreement No.642294.

Supporting information

In Supporting Information, we report Ti-O and Si-O distance distributions over the whole set of reported global minima candidate nanoclusters. For these nanoclusters we also include, atomic coordinates, total energy, hydration energy at 0K and hydration free energy at 300K. Atomic coordinates will be also uploaded to the open access Nomad repository (<https://nomad-repository.eu/>).

References

- ¹ F. Piccinno, F. Gottschalk, S. Seeger, B. Nowack, J. Nanopart. Res. 14, 1109 (2012).
- ² H. Gao H, K. Lian, ACS Appl. Mater. Interfaces. 6, 464 (2014).
- ³ H. Yang, Q. Gao, Y. Xie, Q. Chen, C. Ouyang, Y. Xu, X. Ji, J. Appl. Polym. Sci., 132, 42806 (2015).
- ⁴ L. Senff, D. M. Tobaldi, S. Lucas, D. Hotza, V. M. Ferreira, J. A. Labrincha, Composites Part B-Engineering, 44, 40 (2013).
- ⁵ We. Dong, Y. Sun, C. W. Lee, W. Hua, X. Lu, Y. Shi, S. Zhang, J. Chen, and D. Zhao, *J. Am. Chem. Soc.*, 129, 13894 (2007).
- ⁶ P. Wilhelm, D. Stephan, J. Photochem. Photobio. A: Chem., 185 19 (2007).
- ⁷ K. Qi, X. Chen, Y. Liu, J. Xin, C. Mak, and W. Daoud, *J. Mater. Chem.*, 17, 3504(2007).
- ⁸ C. S. Cundya, P. A. Cox, Microporous and Mesoporous Materials, 82 1 (2005).
- ⁹ M. Cargnello, T. R. Gordon, C. B. Murray, Chem. Rev., 114 9319 (2014).
- ¹⁰ L. K. Adams, D. Y. Lyon, P. J. J. Alvarez, Water Res. 40, 3527 (2006).
- ¹¹ Y. Ma, X. Wang, Y. Jia, X. Chen, H. Han, C. Li, Chem. Rev. 114, 9987 (2014).
- ¹² K. C. Ko, S. T. Bromley, J. Y. Lee, F. Illas, J. Phys. Chem. Lett. 8, 5593 (2017).
- ¹³ F. Nunzi, S. Agrawal, A. Selloni, F. De Angelis, J. Chem. Theory Comput., 11, 635 (2015).
- ¹⁴ G. Fazio, L. Ferrighi, C. Di Valentin, J. Phys. Chem. C, 119, 20735 (2015).
- ¹⁵ O. Lamiel-Garcia, K. C. Ko, J. Y. Lee, S. T. Bromley, F. Illas, J. Chem. Theor. Comput. 13, 1785 (2017).
- ¹⁶ A. Iacomino, G. Cantele, D. Ninno, I. Marri, S. Ossicini, Phys. Rev. B 78, 075405 (2008).
- ¹⁷ E. Berardo, M. A. Zwijnenburg, J. Phys. Chem. C, 119, 13384 (2015).
- ¹⁸ E. G. Brandt, L. Agosta, A. P. Lyubartsev, Nanoscale, 8, 13385 (2016).
- ¹⁹ K. Shirai, G. Fazio, T. Sugimoto, D. Selli, L. Ferraro, K. Watanabe, M. Haruta, B. Ohtani, H. Kurata, C. Di Valentin, Y. Matsumoto, J. Am. Chem. Soc., 140, 1415 (2018).
- ²⁰ D. Cho, K. C. Ko, O. Lamiel-Garcia, K. C. Ko, S. T. Bromley, J. Y. Lee, F. Illas, J. Chem. Theor. Comput. 12, 3751 (2016).
- ²¹ D. Selli, G. Fazio, C. Di Valentin, Catalysts, 7, 357 (2017).
- ²² N. Pienack, W. Bensch, Angew. Chem. Int. Ed., 50, 2014 (2011).
- ²³ C. T. G. Knight, R. J. Balec and S. D. Kinrade, Angew. Chem. Int. Ed., , 46, 8148 (2007).
- ²⁴ M. Haouas and F. Taulelle, J. Phys. Chem. B, 110, 3007 (2006).
- ²⁵ S. A. Pelster, W. Schrader and F. Schüth, J. Am. Chem. Soc., 128, 4130 (2006).
- ²⁶ M. J. Mora-Fonz, C. R. A. Catlow and D. W. Lewis, J. Phys. Chem. C, 2007, 111, 18155.
- ²⁷ T. T. Trinh, A. P. Jansen, R. A. van Santen and E. J. Meijer, J. Phys. Chem. C, 2009, 113, 2647.
- ²⁸ C. E. White, J. L. Provis, G. J. Kearley, D. P. Riley, J. S. J. van Deventer, Dalton Trans., 2011, 40, 1348.
- ²⁹ C. L. Schaffer, K. T. Thomson, J. Phys. Chem. C, 2008, 112, 12653.
- ³⁰ T. T. Trinh, X. Rozanska, F. Delbecq, P. Sautet, Phys. Chem. Chem. Phys., 2012, 14, 3369.
- ³¹ M. L. Weichman, S. Debnath, J. T. Kelly, S. Gewinner, W. Schoellkopf, D. M. Neumark, K. R. Asmis, Top. Catal. 61, 92 (2018).
- ³² M. Chen, T. P. Straatsma, D. A. Dixon, J. Phys. Chem. A, 119, 11406 (2015).
- ³³ O. Lamiel-Garcia, A. Cuko, M. Calatayud, F. Illas, S. T. Bromley, Nanoscale 9, 1049 (2017).
- ³⁴ C. R. A. Catlow, S. T. Bromley, S. Hamad, M. Mora-Fonz, A. A. Sokol, S. M. Woodley, Phys. Chem. Chem. Phys., 12, 786 (2010)
- ³⁵ E. Flikkema, S. T. Bromley, J. Phys. Chem. B, 108, 9638 (2004).
- ³⁶ S. T. Bromley, E. Flikkema, Phys. Rev. Lett., 95, 185505 (2005).
- ³⁷ E. Flikkema, K. E. Jelfs, S. T. Bromley, Chem. Phys. Lett., 554, 117 (2012).
- ³⁸ A. Cuko, M. Calatayud, S. T. Bromley, Nanoscale 10, 832 (2018).
- ³⁹ K. E. Jelfs, E. Flikkema, S. T. Bromley, Phys. Chem. Chem. Phys., 15, 20438 (2013).
- ⁴⁰ K. Jelfs, E. Flikkema, S. T. Bromley, Chem. Commun., 48, 46 (2012).
- ⁴¹ A. Cuko, A. Macia, M. Calatayud, S. T. Bromley, Comput. Theor. Chem. 1102, 38 (2017)
- ⁴² D. J. Wales and J. P. K. Doye, J. Phys. Chem., 1997, 101, 5111 (1997).
- ⁴³ N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, E. Chem. Phys. 21, 1087 (1953).
- ⁴⁴ S. Y. Kim, N. Kumar, P. Persson, J. Sofo, A. C. T. Van Duin, and J. D. Kubicki, Langmuir, 29, 7838 (2013).
- ⁴⁵ G. Ricchiardi, A. de Man, and J. Sauer, Phys. Chem. Chem. Phys., 2, 2195 (2000).
- ⁴⁶ A. V. Bandura and J. D. Kubicki, J. Phys. Chem. B, 107, 11072 (2003).
- ⁴⁷ E. Dushanov, K. Kholmurodov, and K. Yasuoka, Nat. Sci., 4, 313 (2012).

-
- ⁴⁸ A. Pedone, G. Malavasi, M. C. Menziani, U. Segre, F. Musso, M. Corno, P. Ugliengo, *Chem. Mater.*, **20**, 2522 (2008).
- ⁴⁹ A. Macià Escatllar, P. Ugliengo, S. T. Bromley, *J. Chem. Phys.*, **146**, 224704 (2017).
- ⁵⁰ A. Macià Escatllar, P. Ugliengo, S. T. Bromley, *Inorganics*, **5**, 41 (2017).
- ⁵¹ J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996).
- ⁵² V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Phys. Commun.*, **180**, 2175 (2009).
- ⁵³ S. R. Bahn, K. W. Jacobsen, *Comput. Sci. Eng.* **4** 56 (2002).
- ⁵⁴ J.D. Gale, *J. Chem. Soc., Faraday Trans.*, **93**, 629 (1997).
- ⁵⁵ C. Adamo and V. Barone, *J. Chem. Phys.*, **110**, 6158 (1999).
- ⁵⁶ O. Lamiel-Garcia, K. C. Ko, J. Y. Lee, S. T. Bromley and F. Illas, *J. Chem. Theory Comput.*, **2017**, **13**, 1785-1793.
- ⁵⁷ S. Bhattacharya, S. V. Levchenko, L. M. Ghiringhelli, M. Scheffler, *Phys. Rev. Lett.* **111**, 135501 (2013)
- ⁵⁸ V. G. Avakyan, V. F. Sidorkin, E. F. Belogolova, S. L. Guselnikov, L. E. Gusel'nikov, *Organometallics*, **25**, 6007 (2006).
- ⁵⁹ M. A. Zwijnenburg, A. A. Sokol, C. Sousa, S. T. Bromley, *J. Chem. Phys.*, **131**, 34705 (2009).
- ⁶⁰ S. Hamad, S. T. Bromley, *Chem. Comm.*, **0**, 4156 (2008).
- ⁶¹ M. A. Zwijnenburg, F. Illas, S. T. Bromley, *J. Chem. Phys.*, **137**, 154313 (2012).
- ⁶² S. Hamad, S. T. Bromley, *Chem. Commun.* 4156 (2008).
- ⁶³ M. Calatayud, A. Markovits and C. Minot *Catal. Today* **89/3** 269-278 (2004).
- ⁶⁴ S. Bhattacharya, S. V. Levchenko, L. M. Ghiringhelli, M. Scheffler, *New J. Phys.*, **16**, 123016 (2014).