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Global optimisation of hydroxylated silica clusters: A cascade Monte Carlo Basin Hopping approach

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ABSTRACT

We report on a global optimisation study of hydroxylated silica nanoclusters $(SiO_2)_M{\cdot}(H_2O)_N$ with sizes M = 6, 8, 10 12, and for each size with a variable number of dissociatively chemisorbed water molecules (N = 1, 2, 3...). Due to the high structural complexity of these systems and the associated ruggedness of the underlying potential energy landscape, we employ a "cascade" global optimisation approach. Specifically, we use Monte Carlo Basin Hopping (MCBH) where for each step we employ two energy minimisations with: (i) a lightly parameterised but computationally efficient interatomic potential (IP) which does not distinguish between H-bonded conformational isomers, and then (ii) a more sophisticated IP which accounts for polarisation and H-bonding. Final energies from the MCBH search are then refined with optimisations using density functional theory. The reliability of our approach is first established via comparison with previously reported results for the $(SiO_2)_8{\cdot}(H_2O)_N$ case, and then applied to the M = 6, 10 and 12 systems. For all systems studied our results follow the trend in hydroxylation energy versus N, whereby the energy gain with hydroxylation is found to level off at a point where the average tetrahedral distortion of the SiO_4 centres is minimised. This optimal hydroxylation point is further found to follow an inverse power law with increasing cluster size (M) with an exponent close to −2/3, further confirming work in previous studies for other cluster sizes.

1. Introduction

Nanosized silica particles are widely used during the preparation of materials (e.g. cement-based materials [1], coatings [2], polymers [3]) to significantly enhance their physical and mechanical properties. In addition to their high intrinsic strength (e.g. the Si—O bond being 30% stronger than the C—C bond), the success of silica nanoparticles for such applications is also due to them having a relatively high proportion of reactive surface groups which can strongly interact with host materials. Silica is particularly prone to reaction with water, commonly resulting in a surface coverage of hydroxyl (Si—OH) groups [4]. The degree of hydroxylation is found to determine many of the properties of nanosilica. In solution, for example, the pH determines the solubility/hydroxylation of small silicate nanoparticles. Such species are central to the synthesis of technologically important nanoporous silicate materials such as zeolites [5] and occur in (bio)mineral nucleation, growth and dissolution processes [6]. The proportion of hydroxyls on small silica particles can also be deliberately increased by physico-chemical processing to produce enhanced properties for applications (e.g. epoxidation catalysis [7], mechanically robust anti-reflective films [8]). The surface hydroxyl density has further been reported to influence the biocompatibility and toxicity of silica nanoparticles [9,10].

From a computational perspective the reaction of water with silica surfaces has attracted much attention [11]. For atomic to nanosized hydroxylated silica systems studies have tended to either focus on the detailed thermodynamics of the condensation of small ring- or chain-like $(SiO_2)_M$ $N \leqslant 6$ oligomers in solution [12,13] using *ab initio* methods, or on larger scale (i.e. with 100 s or 1000 s of atoms) classical forcefield simulations of hydroxylated nanosilica [14–16]. Between these extremes, some recent studies have focused on attempting to find the most stable structures of

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hydroxylated silica nanoclusters in the approximate size range of 10–100 atoms [17–20]. This intermediate size regime is characterised by having non-trivial (i.e. not simply rings or chains) structures which are also not totally amorphous as typically assumed for larger nanoparticles. Hydroxylated silica nanoparticles with such sizes can thus be thought of as species which represent a structurally complex molecular-bulk crossover regime. Such species are likely to be particularly important in understanding nucleation of complex silica solids (e.g. zeolites). Although in such processes, many factors play an important role (e.g. pH, templates) [5] knowing the lowest energy hydroxylated nanosilica species in the absence of such factors provides a baseline to assess how and when they are important. Previous theoretical work in this size regime has specifically investigated hydroxylated silica clusters $(SiO_2)_M{\cdot}(H_2O)_N$ with sizes $M = 4, 8, 16, 24$, and each with a variable number of incorporated water molecules ($N = 1, 2, 3\ldots$) [17–20]. Due to their high structural complexity, global optimisation was employed in these studies to find low energy isomers for each stoichiometry. Specifically, a fairly simple set of interatomic potentials was used in conjunction with the Monte Carlo Basin Hopping (MCBH) [21] approach to first obtain initial cluster structures. Due to approximations in the IP set employed these non-refined structures provide only a poor account of OH···OH hydrogen bonding on the surfaces of the hydroxylated nanoclusters [19]. Optimisations using relatively computationally expensive density functional theory (DFT) calculations on a selection of IP-MCBH-generated structures were used to provide final clusters exhibiting hydrogen bonding.

In this work we report on a MCBH global optimization approach to hydroxylated silica nanosystems employing a cascade local optimization method. First, our method is shown to be reliable by applying it to the previously studied $(SiO_2)_8{\cdot}(H_2O)_N$ system [18,19]. We then, generate global minima candidates for the as yet unreported systems: $(SiO_2)_M{\cdot}(H_2O)_N$, $M = 6$, 10, 12, each for a range of N values. In previous work it was shown that the hydroxylation reaction energy for silica clusters decreases by addition of water molecules until it levels off around an optimal number N. This optimal number was found to be cluster size dependent to follow an inverse power law of the form $2M^{-2/3}$. Using our new global minima candidates for $(SiO_2)_M{\cdot}(H_2O)_N$, M = 6, 10, 12 we also further probe the generality of this relation.

2. Methodology

In this work we apply the MCBH global optimization technique to find low energy global minima candidates for the cluster set $(SiO_2)_M{\cdot}(H_2O)_N$, $M = 6, 8, 10, 12$ for a range of N. The general idea behind this technique is based on repeated steps consisting of random structural distortion and a subsequent local optimization. The metropolis criterion [22] is applied in order to accept or refuse the local optimized structure according to a cost in passing from the initial (before the random distortion) and the final state, and a fictitious temperature. Usually the cost is the energy difference between the two states but in principle it is possible to generate other cost criteria based on system properties. Using cyclic repetitions of this procedure it is possible to explore the potential energy surface (PES) of the system. At each step, the structure is typically locally optimized with either by an *ab initio* method or a classical IP. In the first case, the applicability is limited to relatively small systems due to the high computational expense. This expense not only originates from local optimizations of the system but also from the higher number of steps required to properly sample the PES. Indeed, in principle, the number of energy minima is exponentially proportional to the number of atoms. A typical approach to make MCBH calculations more computationally amenable is to use IPs for efficient optimisation. Nevertheless, IPs alone, often, cannot be relied upon for an accurate description of a system's properties. Therefore, after an IP-based MCBH run, a certain number of resulting low energy structures can be re-optimized with more accurate methods (e.g. DFT). For some systems, quite accurate IPs have been developed for which parameters have been fitted to experimental and/or *ab initio* data. In principle, the better the IP, the lower the number of structures that require significant further optimization with a more accurate method. However, we note that to have an IP with higher accuracy, it is typically required to have correspondingly more complex functional forms with a higher number of terms. In turn, during a MCBH run, the direct use of such IPs can lead to practical problems in relaxing structures far from the equilibrium geometry (after a random distortion). Here we present a MCBH procedure in which for each step, a cascade structure optimization is performed with two different IPs. The general idea is to first use a robust and efficient IP to pre-optimize a distorted structure and then use the more accurate IP for fully relaxing this pre-optimized structure. The Metropolis criterion is then applied after the second optimization. Herein our cascade-MCBH approach interfaces with the GULP code [23] which offers the possibility of using a wide range of IP types. However, we have implemented this procedure in a general way using the Atomic Simulation Environment [24] (ASE), which has the ability to call a range of codes to perform the optimisations.

In the literature, IPs for bare silica (SiO_2) bulk systems, such as TTAM [25] and BKS [26], have been successfully used. Hassanali and Singer (HS) [27] introduced a IP parameterization for the silica-water interface by adding new three-body terms to the BKS IP in order to describe Si—O—H and H-bonds. All these IPs are based on the Buckingham mathematical form as shown in Eq. (1)

$$V_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A_{ij}\exp\left(-\frac{r_{ij}}{B_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where i, j ∈ {Si, O}, r_{ij} is the interionic separation, $q_{i,j}$ are the ionic charges and A, B and C are fitted parameters. With respect to nanosilica, Flikkema and Bromley (FB) re-parameterised a Buckingham IP specifically for treating bare silica nanoclusters [28]. Recently, Pedone et al. [29] have parameterized a new and more complex Buckingham IP with polarisable ions for hydroxylated silica. This IP also incorporates intra- and inter-bond Morse potentials and a three-body term for hydrogen bonds was shown to provide accurate structures and vibrational frequencies with respect to experimental and DFT-calculated data on hydroxylated silica surfaces. Recently, a systematic study has showed that this IP is also accurate for the treatment of hydroxylated nanoparticles [30].

In previous global optimization studies the FB IP and a simplified version of the HS IP (HS_{simp}) has been used for finding low energy clusters where the HS three-body terms were omitted for simplicity and computational efficiency [17,18]. By omitting these terms, the correct description of hydroxyl groups (OH) is lost, therefore, the clusters do not have any H-bond contribution to their stability (see Fig. 1). In this way, isomers stabilized by hydrogen bond contributions are not easily found only using HS_{simp} in a MCBH run. Such concerns are especially relevant to relatively large clusters and/or systems with a high hydroxylation degree where H-bonding can influence the energetic ordering and structure of low lying minima (each H-bond contributes of about 20 kJ/mol). Thus, for silica nanoparticles with increasing size and/or with moderate to high hydroxylation, a good description of OH groups and their H-bonding becomes essential in order to avoid missing possible low energy clusters.

In this work we consider hydroxylated silica clusters $(SiO_2)_M{\cdot}(H_2O)_N$ systems with $M = 6$, 8 10 and 12 each one with different hydroxylation ratio $N{:}M$ ($R_{N/M}$) up to ~65%. As a pre-optimization