First-principles simulation of the intracage oxidation of nitrite to nitrate sodalite

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ABSTRACT

We study the oxidation of NO2– to NO3– by dioxygen in the cages of sodalite, by using the combined blue moon ensemble (BME) and Car Parrinello approaches. Our results indicate the active participation of the zeolite framework in the reaction via peroxy-like defects. Moreover, a molecular level explanation of the experimentally found first-order kinetics is given. A spin-unpolarized density functional approach has been adopted. However, our results suggest that interactions in the zeolite cage may reduce the O2 triplet-singlet energy gap, therefore, justifying the adopted approximation.

INTRODUCTION

We present a simulation on an oxidative reaction, $NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$, inside sodalite cages. This intracage reaction has been experimentally studied in the temperature range 900–1000 K [1–3]: the oxidizing agent is molecular oxygen, and the reaction, first-order with respect to NO_3^- is completed in 30 h. The reported experiments do not allow a microscopic analysis of the reaction mechanism.

We have studied the intracage oxidation by using the constrained molecular dynamics (blue moon ensemble, BME) method [4,5] together with the ab initio molecular dynamics approach [6]. These two combined techniques have been applied to both liquid phase reactions [7,8] and heterogeneous catalysis [9,10]. We have adopted perfect spin-pairing in our calculations, therefore, one of the reactants, molecular oxygen, is in the singlet excited state, which is about 100 kJ mol^{-1} above the triplet ground state in the gas phase.

MODEL AND COMPUTATIONAL METHOD

Both nitrite sodalite $Na_8[Al_6Si_6O_{24}](NO_2)_2$ and nitrate sodalite $Na_8[Al_6Si_6O_{24}](NO_3)_2$ have cubic cells [1,3,11]. Sodalites are porous aluminosilicates characterized by a bcc lattice of cubo-octahedral cavities (β -cages). Each cage contains one anion surrounded by four Na⁺ cations.

The reaction occurs in air at high temperature: molecular oxygen diffuses inside sodalite causing an expansion of the crystals and then oxidizing of the nitrate. As the dissociation energy of O_2 is 493.7 kJ mol⁻¹ [12], a homolytic event is improbable. Moreover, due to the ionic character of the caged species, a different path should be favored. We studied the reverse reaction, i.e., the $NO_3^- + \frac{1}{2}O_2 \rightarrow NO_2^-$ intracage reduction. This choice makes the BME easier to apply. It consists of performing a series of *constrained* simulations, in which a degree of freedom is kept constant and the constraint force is averaged over each simulation. The degree of freedom is constrained to different values from an initial to a final state. The integral of the constraint forces corresponds to minus the difference in free energy.

In the nitrate sodalite (Fig. 1) the constrained degree of freedom is one of the NO bonds of NO_3^- in one cage. We performed a series of simulations with different values of such distance, constrained by using the RATTLE algorithm [13], starting from the equilibrium value of such a distance. Moreover, we performed other 'unconstrained' simulations as well: the nitrite sodalite, the nitrate sodalite, and the nitrite sodalite with one oxygen molecule. All simulations were performed with the Car–Parrinello method at a constant temperature of 1000 K [14]. Norm-conserving pseudopotentials [15,16] were used, the Beck–Perdew functional



Fig. 1. Ball-and-stick snapshot of nitrate sodalite from a trajectory at 1000 K. Black spheres represent oxygens, white spheres represent nitrogens, dark gray spheres represent sodium, light gray silicon and aluminum atoms.

was chosen [17,18]. A plane waves cutoff of 60 Ry at the Γ point was used. Unconstrained systems were studied for about 4.5 ps, while constrained simulations were continued till convergence in the constraint force was reached, 3–5 ps depending on the value of the constraint.

The gas phase ground state of oxygen is a ${}^{3}\Sigma_{g}^{-}$ triplet and the first excited state is a singlet 94.3 kJ mol⁻¹ higher [19]. With the DFT used here, such a difference amounts to 156 kJ mol⁻¹ and to 241 kJ mol⁻¹ by using the Hartree–Fock approximation, with a triple-zeta + polarization basis set.

The dissociation energy of O_2 is 554 kJ mol⁻¹ for the triplet and 398 kJ mol⁻¹ for the singlet with the DFT approximation (the experimental value is 493.7 kJ mol⁻¹). The calculated gas phase ΔE for the reaction $2NO_2^- + O_2 = NO_3$ is -402.2 kJ mol⁻¹ using a spin-unpolarized functional and -246.2 kJ mol⁻¹ when a spin-polarized (triplet) functional is used. However, interactions may contribute to reduce the triplet–singlet gap. Test calculations have been carried out, and are discussed below.

The nitrite sodalite system was modeled by one cell (lattice parameter 8.923 Å). The nitrite sodalite $+ O_2$ system was simulated by using the cell parameter of nitrate sodalite (8.996 Å) [3].

RESULTS

The unconstrained simulation of nitrite sodalite, in agreement with experimental data, indicates that the NO₂⁻ anions in the β -cages present dynamical disorder, with the NO₂⁻ rotating inside the cavity [20].

The NO₃⁻ anions, in the unconstrained simulation, rotate as well. However, due to the larger size of NO₃⁻ with respect to NO₂⁻, the motion is more hindered. Experiments suggest orientational disorder for NO₃⁻ [1] as well.

The unconstrained simulation of nitrite sodalite + O_2 suggested a possible mechanism for the intracage oxidation. The O_2 molecule left its starting position (midway between adjacent NO_2^-), and diffused towards one of the two NO_2^- , forming a labile complex, $[NO_2 \cdots O_2]^-$ in equilibrium with the NO_2^- and O_2 species (Fig. 2). This simulation



Fig. 2. Ball-and-stick snapshot of nitrite sodalite $+ O_2$ from an unconstrained trajectory at 1000 K. Black spheres represent oxygens (large black spheres represent the oxygen atoms in O_2), white spheres represent nitrogens, dark gray spheres represent sodium, light gray silicon and aluminum atoms.

provides an indication about the structure of the 'final state' of the reverse reaction studied by BME.

The motion of the nitrate anions in the β -cages is a 'frictioned' rotational motion, as only two rotations of NO₃⁻ occurred in the simulation. This behavior is different from the one found in nitrite sodalite, where NO₂⁻ rotates on a time scale of about 100 fs. Therefore, our 'final' NO₂⁻ should behave in a similar fashion, rotating faster than the 'initial' NO₃⁻.

The calculated constraint forces are reported in Table 1. The calculated free energy (Fig. 3) shows that the nitrite sodalite $+ O_2$ system is less stable than nitrate sodalite, as in experiments. The activation free energy for the oxidative process was calculated to be 30 kJ mol⁻¹ and the reaction free energy to be about -75 kJ mol⁻¹.



Fig. 3. Free energy profile for the simulated reaction vs the constrained NO distance. Energy in kJ mol⁻¹, distances in Å. The free energy zero has been arbitrarily set at a value of the constraint of 4.0 Å. Chemical formulae in the panel represent the content of each β -cage at the beginning and at the end of the reaction. The free energy profile refers to a unitary cell (two β -cages).

In the first three simulations, constrained at 1.5, 1.75 and 2.0 Å respectively, the constrained NO_3^- behaved quite normally, as it slowly rotated like a nitrate anion. Now the oxygen atom should still be bonded to N. At a value of the constraint of 2.5 Å, the situation changed. There was a change in sign of the constraint force. This indicates that the forces exerted by the whole system have changed sign along the N–O distance, suggesting that the constrained oxygen and nitrogen were no longer chemically bonded. Now the NO_2^- fraction of the constrained nitrate rotates faster than a typical nitrate, and more similar to a 'free' NO_2^- in nitrite sodalite.

Now the constrained oxygen atom should be quite reactive, and as it is still far away from the other NO_3^- , it interacts with the zeolite framework. Indeed the constrained oxygen is now approximately midway between two β -cages and close to the oxygen atom forming the ring shared by two cavities. Actually the constrained oxygen 'links' to

Table 1

Calculated values of the constraint force f for each constrained distance r. Distances in Å, forces in a.u.

r	1.5	1.75	2.0	2.5	2.75	3.0	3.5	3.75	3.9	4.0
f	-0.0795	-0.0770	-0.0590	0.0142	0.0095	0.0064	0.0027	0.0035	0.011	0.017

the framework and forms various kinds of defects easily interchanging from one to another. Fig. 4 shows some characteristic structures (with the constraint at 2.5 A). The first one is a peroxy-defect (Fig. 4a), where the constrained O is linked to a framework oxygen. This structure then evolves, and the constrained oxygen 'enters' the sodalite framework. In Fig. 4b, a peroxy-bridge defect is shown, where a O_2 species is placed between an Al and a Si, each oxygen of the defect being linked to only one of the tetrahedral cations (Si or Al). Fig. 4c shows another defect, namely an O₂ species shared between two tetrahedral cations, with each oxygen linked to both Al and Si. We have monitored the total charge of the constrained $NO_3^$ anion in order to see whether the initial negative charge on the nitrate is conserved in the $NO_2^$ product: we found that the oxygen 'leaving' the nitrate is neutral, and the O₂ defect can be a real peroxy-species O_2^{-2} , considering an O^{2-} anion the framework oxygen.

Recently, the energetics and geometries of defect centers in zeolites in oxidative conditions have been reported [21]. Such investigation proves that peroxy-like defects in aluminosilicate structures may have a formation energy in the range 40-150 kJ mol⁻¹. Moreover, their presence is supported by several experimental studies [22–25].

In the other constrained simulations (constraint, respectively, at 2.75, 3.0, 3.5, 3.75, 3.9 Å) the formation of this kind of defect is observed in



The finding that the final state of the inverse reduction reaction is similar to the one found in the unconstrained simulation of nitrite sodalite + O_2 strongly supports the idea that the $[NO_2 \cdots O_2]^-$ complex is the first step in the direct reaction (after the O_2 diffusion inside the cavities). Such a complex may activate the molecular oxygen and actually when the O_2 was complexed to the NO_2^- , its bond length increased and its oscillation became wider, showing a weaker O–O bond (see Fig. 5). Once the O–O bond is weakened one of the oxygen atoms of O_2 can interact with the frame-



Fig. 4. Three ball-and-stick representations of peroxy-like defects. The geometries are taken from the trajectory with the NO constraint fixed at 2.5 Å. Black spheres represent oxygen atoms, gray spheres silicon (large) and aluminum (small).



Fig. 5. Normalized distribution $d(\mathbf{r})$ of the dioxygen O–O distance r (in Å) in the unconstrained simulation of nitrite sodalite + O₂ at 1000 K.

work forming the defects described above. Then, the reactive oxygen gets into the adjacent cage where there is still a NO_2^- , reacting to form a second NO_3^- . This proposed mechanism fits the first-order kinetics with respect to NO_3^- described in the literature: the formation of the first NO_3^- is the slow step, namely the transformation of the $[NO_2 \cdots O_2]^-$ complex in a NO_3^- and an oxygen atom linked to the frame should be the rate determining step.

The results presented so far were obtained by using spin-unpolarized DFT, implying that the O₂ is in the excited singlet state. Were the gas phase energy gap transferable to condensed phases, the presented results could be biased by the adopted approximation. However, in a highly ionic system, isolated system data may not be pertinent. We have calculated the triplet-singlet energy difference for the isolated $[NO_2 \cdots O_2]^-$ complex, by using the same scheme as for bulk calculations, for a series of geometries taken from the zeolite trajectories. The differences in energy for such a system reduce to 1–10 kJ mol⁻¹, always favoring the triplet state. For a few configurations of the bulk nitrite sodalite $+ O_2$, we have calculated the same energy gap: the triplet-singlet ΔE 's reduce to a few kJ mol⁻¹, however, this time favoring the singlet state. Such results indicate a stabilization of singlet oxygen in the nitrite sodalite system.

CONCLUSIONS

We have studied the intracage oxidation $NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$ in sodalite by means of the blue moon ensemble and Car Parrinello MD combined methods. The reaction was simulated by following the inverse reduction process. Such an approach has allowed us an easier application of the BME sampling and could be of general scope.

We have found a free energy for the oxidation at 1000 K of the order of -75 kJ mol^{-1} and an activation free energy of about 30 kJ mol⁻¹. A mechanism for this chemical reaction that may explain at microscopic level the experimentally found first-order kinetics with respect to NO₃⁻ was proposed. Furthermore, our simulations predict that the sodalite framework is directly involved in the reaction via the formation of defect centers after reacting with the dioxygen.

Beyond the relevance in this particular study, the peroxy-like defects can be reaction intermediates in other zeolites-based oxidations in industrial applications. On the basis of our results, it can be supposed that more effective oxidizing media can be obtained by modifying zeolites and mesoporous aluminosilicates in order to allow an easier formation of peroxy-like structures. In this respect, the presented data may suggest a possible activation of the inert triplet state of dioxygen in the cavities of nitrite sodalite to the more reactive singlet O_2 [26].

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