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Intracage chemistry: nitrite to nitrate oxidation via molecular oxygen. A Car Parrinello study.

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1 Abstract

We present a theoretical study of the oxidation reaction of NO_2^- to NO_3^- by dioxygen in the cages of sodalite. The combined Blue Moon Ensemble and Car Parrinello Molecular Dynamics approaches were used.

Our results indicate the active participation of the zeolite framework in the reaction mechanism via the formation of 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 for the electron-electron interactions, notwithstanding the triplet state is the ground state for molecular oxygen. However our results suggest that interactions in the zeolite cage may reduce the O_2 triplet-singlet energy gap, therefore justifying the adopted approximation.

2 Introduction

The microscopic description of a chemical reaction in condensed phases is hindered by a series of difficulties that locate the problem at the edge of nowadays physical chemistry.

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Many are the issues that challenge researchers in the field: a proper thermal averaging and an accurate description of the quantum many body problem are only two facets of the challenge.

A naive description of the main steps of a reactive event can be sketched: two reactants approach each other in the reaction medium, and the result of such approach (collision) may or may not lead to the products, depending both on the molecular states and reciprocal orientation and the interactions with the medium. While liquid phase reactions are favourite in laboratories, solid matrices are also used as reaction media. Among solids, zeolites, with their arrays of molecular sized cages and channels, are used as *reaction pots* in many synthetic processes both in research laboratories and in large scale industrial plants.

With respect to liquids, reactions in matrices may be easier to study as diffusional and rotational motions of solvent molecules are missing in solids, and moreover, due to their crystalline order, zeolites may be viewed as *simple* environments where a chemical reaction can be investigated microscopically.

In this perspective we have afforded the study, via computer simulation, of an oxidative reaction, $NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^-$, inside the sodalite cages. Such intracage reaction has been experimentally studied by IR and *uv*-visible spectroscopies, powder X-rays diffraction and thermogravimetry in the temperature range 900-1000 K [1, 2, 3]. It has been proved that (*i*) the reaction occurs in air, (*ii*) the oxidizing agent is molecular oxygen, (*iii*) the reaction is first order with respect to NO_3^- and is completed in 30 hours. However, the reported experiments do not allow a detailed microscopic analysis of the reaction mechanism.

We have studied the intracage oxidation of nitrite sodalite to nitrate sodalite by using the Constrained Molecular Dynamics (Blue Moon Ensemble) method [4, 5] together

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with the Car Parrinello *ab initio* Molecular Dynamics approach [6]. The application of these two combined techniques has been proved useful when applied to both liquid phase reactions [7, 8] and heterogeneous catalysis [9, 10].

The choice of investigating such reaction stems from two main considerations. Most zeolites-based industrial reactions occur at high temperature in oxidizing conditions such as calcination processes. Therefore the nitrite to nitrate intracage oxidation may give useful indications of general relevance for zeolites technologies in these conditions. The second point is that sodalites with their relatively small number of atoms in the unitary cell can be theoretically studied at high accuracy with an easy computational effort.

We have chosen to adopt perfect pairing of spin in our calculations, therefore one of the reactants, the molecular oxygen, is in the singlet excited state. Such a state is about 100 KJmol⁻¹ above the triplet ground state in gas phase. However, in condensed phases, in particular in a highly ionic environment like the studied nitrite sodalite, such approximation may be less drastic with respect to gas phase. We anticipate here that actually interactions with ionic species can significantly reduce the O₂ triplet-singlet gap.

3 Model and Method

It has been found experimentally that 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, with lattice parameter larger in the case of the nitrate specimen [1, 3, 11]. Sodalites are porous aluminosilicates characterized by a bcc lattice of cubo-octahedral cavities, the β -cages of many zeolites. Each cage contains four Na⁺ ions and one anion, located just in the center of the cage and surrounded by the four cations. The unitary cell contains two of such cages.

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In natural sodalite the anion is Cl^- , however many sodalites have been synthesized with different cations and anions. It is known that anions with symmetry lower than spherical, like NO_2^- and NO_3^- , show orientational disorder inside the cavity, namely the crystallographic positions of the anions are not unique. This may be due to either different energy minima or rotational motion.

The reaction occurs in air at high temperature: molecular oxygen diffuses inside nitrite sodalite causing an expansion of the crystals and then giving rise to the oxidized nitrate sodalite (first order with respect to NO_3^-). The same sodalite in N_2 atmosphere does not react, and only the cell expansion is achieved. However the reaction mechanism is not known, indeed, it is quite difficult to devise a simple reaction path. Each NO_2^- is confined in the center of each cage and adjacent cages' centers are separated by more than 7 Å, a distance that corresponds to the separation between nearest NO_2^- 's as well. In order that NO_2^- becomes NO_3^- , the O_2 molecule has to dissociate in atoms and, formally, at the end of the reaction each O atom should be found in different cages to get the NO_3^- 's products. As the dissociation energy of O_2 is 493.7 KJmol⁻¹ [12] the simple homolytic event is extremely unlike. Moreover, due to the high ionic character of the species inside the cages, a different reaction path should be favoured with respect to the simple homolytic dissociation. These considerations led us to study the reverse reaction, *i.e.* the $NO_3^- \rightarrow \frac{1}{2} O_2 + NO_2^-$ intracage reduction. This choice makes the Blue Moon Ensemble (BME) technique easier to apply. Indeed such approach consists in performing a series of *constrained* Molecular Dynamics simulations, in which a degree of freedom is kept constant (a holonomic constraint) and the constraint force is averaged over each simulation. The degree of freedom is constrained to different values from an initial state to a final state. The integral of the constraint forces corresponds to minus the difference in free energy from the initial to the final state.



Figure 1: Ball-and-stick representation of nitrate sodalite. Black spheres represent oxygens, white spheres represent nitrogens, dark gray spheres represent sodium. The sodalite cages are represented by sticks. Only silicon and aluminum atoms are shown.

Examples of applications of BME have appeared in the literature, both using classical Lagrangean and the the Car Parrinello Lagrangean, such as in the study presented here. We selected the nitrate sodalite as the initial state for the reduction reaction (Figure 1) as it allows a straightforward definition of the reaction coordinate, *i.e.* the constrained degree of freedom, namely one of the NO bond lenghts of NO_3^- in one cage. We performed a series of *ab-initio* Molecular Dynamics simulations with different values of such a distance, constrained by using the RATTLE algorithm [13], starting from its equilibrium value. Moreover other "unconstrained" trajectories were calculated as well: we have simulated the nitrite sodalite, the nitrate sodalite, and the nitrite sodalite with one oxygen molecule in the simulation cell. All simulations were performed with at constant temperature of 1000 K [14] with the Car Parrinello method. Norm-conserving pseudopotentials were used to describe the valence electrons ionic

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core interactions [15, 16]; the Becke-Perdew gradient corrections to LDA was chosen for the electron-electron interactions [17, 18]. Wavefunctions were expanded in plane waves up to a kinetic energy cutoff of 60 Ry. The Γ point only was used in the Brillouin zone. Experimental lattice parameters were adopted and kept fixed for all simulations. The timestep for the integration of the equations of motion was 0.242 fs and a fictitious mass of 2000 a.u. for the electronic degrees of freedom in the Car Parrinello equations was used. Unconstrained systems were studied for about 4.5 ps, while constrained simulations were continued till convergence in the constraint force was reached, namely 3 to 5 ps depending on the value of the constraint. Ten constrained simulations were perfomed with different values of the constraint.

Notwithstanding the triplet state is the ground state for O_2 , we have used a spinunpolarized functional for a series of reasons, the first and more compelling one being due to the computational cost of using spin-polarized functionals in the case of systems with so many electrons (240 electrons per cell); another reason is that both nitrite and nitrate sodalite (reactant and product) are singlet states. In the gas phase the ground state of molecular oxygen is a ${}^{3}\Sigma_{g}^{-}$ triplet and the first excited state is a singlet 94.3 KJmol⁻¹ higher [19]. Such a difference amounts to 156 KJmol⁻¹ with the DFT approximation used here, and to 241 KJmol⁻¹ by using the Hartree-Fock approximation, with a triple-zeta + polarization basis set.

The dissociation energy of O_2 is 554 KJmol⁻¹ for the triplet and 398 KJmol⁻¹ for the singlet dioxygen with the DFT approximation (the experimental value is 493.7 KJmol⁻¹). The calculated gas phase ΔE for the reaction $2NO_2^- + O_2 = 2NO_3$ is -402.2 KJmol⁻¹ using a spin-unpolarized functional, rising to -246.2 KJmol⁻¹ when a spinpolarized (triplet) functional is used.

However, interactions may contribute to reduce the triplet-singlet energy gap e.g. by

removing the degeneracy of the highest singly occupied molecular orbitals of ground state oxygen. Test calculations have been carried out in order to substantiate the above statement, and are discussed below.

The nitrite sodalite system was modelled by one cell (lattice parameter 8.923 Å), so that the chemical formula $Na_8[Al_6Si_6O_{24}](NO_2)_2$ corresponds to the atoms in the simulation cell. This choice was adopted also for nitrate sodalite (constrained and unconstrained). The unconstrained nitrite sodalite + O_2 system was simulated by using the cell parameter of nitrate sodalite (lattice parameter 8.996 Å) [3], locating in the starting configuration the O_2 molecule midway between two NO_2^- in the simulation cell.

4 Results

The unconstrained simulation of nitrite sodalite indicates that NO_2^- anions in the β cages present dynamical disorder, in agreement with experimental data. In particular the simulation showed that the NO_2^- is rotating inside the cavity and this rotational motion is also present at room temperature [20].

The NO₃⁻ anions, in the unconstrained simulation, show rotational motion as well. However, due to the larger size of NO₃⁻ anions with respect to NO₂⁻, the rotational motion results more hindered. Unfortunately, while for nitrite sodalite all atomic positions have been experimentally resolved, the structure of nitrate sodalite was not completely refined yet, so that no direct comparison with experimental data is possible. However, in this case too, experimental data suggest orientational disorder for the NO₃⁻ anions inside the β -cages [1].

Interestingly, the unconstrained simulation of nitrite sodalite + O_2 suggested a possible mechanism for the intracage oxidation. The O_2 molecule left soon its starting position (midway between adjacent NO_2^- 's), and diffused towards one of the two NO_2^- ,

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Figure 2: Ball-and-stick snapshot of nitrite sodalite $+ O_2$ from an unconstrained trajectory at 1000 K. Black spheres represent oxygens, white spheres represent nitrogens, dark gray spheres represent sodium. The sodalite cages are represented by sticks. Only silicon and aluminum atoms are shown.

forming a labile complex, namely $[NO_2 \cdots O_2]^-$ in equilibrium with the NO_2^- and O_2 species (Figure 2). Such a complex, however, never evolved to the reaction product, *i.e.* one NO_3^- in each cavity, because O_2 never dissociated in the sampled phase space (4.5 ps). But this does not imply that in the simulation conditions the reaction could not occur. The reaction event was not observed during the elapsed time of our simulation due to its low probability: enormously long simulations are needed in order to observe a rare event like a reactive step. However, this simulation is relevant, because it provides information about the structure of the "final state" of the reverse reaction studied by BME. Before examining the constrained simulations, it is worth noticing that the anions in the unconstrained simulations never diffuse from the center of the respective cages. In other words, anions never approach closely to each other. The motion of the

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nitrate anions in the β -cages can be qualitatively described as a "frictioned" rotational motion, as we observed only two complete rotations of NO₃⁻ in the elapsed simulation time. This behavior is different from the one observed in nitrite sodalite, where NO₂⁻ anions rotate around their cage centers on a time scale of about 100 fs. As we are studying the reverse reaction, our "final" NO₂⁻ should behave in a similar fashion, namely it has to rotate faster than the "initial" NO₃⁻.

The initial configuration for the constrained set of simulations was taken from an equilibrated structure of the unconstrained nitrate sodalite. This configuration was slightly modified by increasing the separation of one oxygen atom from the nitrogen in one of the two NO_3^- 's in the cell. In particular, such a distance, from its equilibrium value 1.29 Å, was fixed to 1.5 Å. After equilibration, a trajectory was integrated till the average constraint force did not converge. The final point of this trajectory was used as starting point for a second trajectory with the same NO bond now constrained at 1.75 Å. Such a procedure has been followed for the other constrained simulations. We stopped the BME sampling at a value of the constraint of 4.0 Å, when the reaction was found to occur.

The average constraint forces calculated along the path are reported in table 1. The integral of the constraint forces (with changed sign) is plotted vs the constrained NO distance in Figure 3. Firstly, it should be stressed that the calculated free energy shows unambiguously that the nitrite sodalite + O₂ system is less stable than nitrate sodalite, as shown by experiments. Such a finding make us confident in our computational approach and it is an *a posteriori* validation of the general idea of studying the inverse reaction whenever such a choice is easier to be implemented by means of the BME sampling, with respect to the more conventional approach of following the direct reaction.

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Figure 3: Free energy profile for the simulated reaction vs the constrained NO distance. Energy in KJmol⁻¹, distances in Å. The free energy zero has been arbitrarily set at a value of the constraint of 4.0 Å. Chemical formula 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).

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

Moreover it was possible to calculate from the free energy curve an activation free energy for the oxidative process of the order of 30 KJmol^{-1} and a reaction free energy of about -75 KJmol⁻¹.



Figure 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 oxygens, white spheres represent nitrogens, dark gray spheres represent sodium. The sodalite cages are represented by sticks. Only silicon and aluminum atoms are shown.

In the first three simulations, with the NO bond constrained at 1.5, 1.75 and 2.0 Å respectively, the constrained NO_3^- behaved quite normally, slowly rotating like a nitrate anion, in line with the other unconstrained anion in the adjacent cavity: at this point the oxygen atom should be still bound to the nitrogen atom. At a value of the constraint of 2.5 Å, the situation changed. First of all, the constraint force changed the sign. This indicates that the forces exerted by the whole system on the constraint have changed sign along the N-O distance, suggesting that the constrained oxygen and nitrogen were no more chemically bonded. In fact, the NO_2^- fraction of the constrained nitrate anion showed a rotational motion faster than that typical of nitrate and more similar to that found for "free" NO_2^- in nitrite sodalite, showing that its motion was quite independent on that of the constrained oxygen.

At this point the constrained oxygen atom should become quite reactive, and as it was still far away from the NO_3^- in the adjacent cage, it could interact strongly with other species, *i.e.* the zeolite framework. Now indeed, the constrained oxygen stays approximately midway between two β -cages, close to the oxygen atom forming the ring shared by two cavities. Actually the constrained oxygen "links" to the framework and forms various kinds of structural defects easily interchanging from one to another. Figure 4 shows some characteristic structures found at this step of the simulation (with the constraint at 2.5 Å). The first defect that we have monitored was a peroxy-defect (Figure 4(a)) where the constrained O is linked to a framework oxygen. This structure then evolves and the constrained oxygen "enters" the sodalite framework. In Figure 4(b), a peroxy-bridge defect is shown, where one O₂ species is placed between an Al and a Si of the frame, each oxygen of the defect being linked to only one of the tetrahedral cations (Si or Al). Figure 4(c) shows another defect, namely an O₂ species that is now shared between two tetrahedral cations, and each oxygen in the defect is linked to both the Al and Si cations.

Care must be taken in naming such defects as *peroxy*. The O_2 species is formed by an oxygen coming from the NO_3^- and one belonging to the framework. During the simulations the total charge of the constrained NO_3^- anion was constantly monitored in order to verify whether the initial negative unitary charge on the nitrate is conserved in the NO_2^- product: this is the case, namely the oxygen that "leaves" the nitrate is neutral, so that the O_2 defect could be considered a real peroxy-species O_2^{-2} formally considering the oxygen coming from the framework to be a closed shell anion O^{2-} .

Recently, some work appeared, where the energetic and geometries of defect centers in zeolites in oxidative conditions were reported [21]. In particular, we quote that the sodalite four-ring system, like the one where we found the peroxy-defects, was studied.

The investigation proved that peroxy-like defects in aluminosilicate structures may have formation energy in the range 40-150 KJmol⁻¹. Moreover, their presence is supported by several experimental studies [22, 23, 24, 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 defects has been observed in the whole simulation times, and defects transform each other in a very short time (~100 fs). However for such values of the constraint, the reacting O atom was still bound to the framework. The reactive event occurred only when the constraint was set to an NO distance of 4.0 Å. After few fs, the oxygen previously trapped in the framework defects, left the four ring region and diffused in the adjacent cage colliding with the second NO₃⁻. Such collision first led to the transient species $[NO_2 \cdots O_2]^-$, that appeared in the unconstrained nitrite sodalite + O₂ simulation. Then, such species reached rapid equilibrium with the separated NO₂⁻ and O₂ compounds.

Now the intracage oxidation mechanism can be analyzed. First of all, 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 Figure 5).

Once the O-O bond is weakened one of the oxygen atoms of O_2 molecule can interact with the framework forming the series of defects described above. Such a defect further evolves and the reactive oxygen moves to the adjacent cage where there is still a $NO_2^$ anion. At this point the atomic oxygen reacts and form a second NO_3^- . This proposed mechanism seems to fit to the first order kinetic with respect to NO_3^- , as described



Figure 5: Normalized distribution d(r) of the dioxygen O-O distance r (in Å) in the unconstrained simulation of nitrite-sodalite + O_2 at 1000 K.

in the literature: the formation of the first NO_3^- appears to be the slow step, the trasformation of the labile $[NO_2 \cdots O_2]^-$ complex in a NO_3^- and one O atom linked to the frame should be the rate determining step.

The results presented so far were obtained by using a spin-unpolarized DFT, implying that the O_2 is in the excited singlet state, which is experimentally 94.3 KJmol⁻¹ above the triplet ground state (156 KJmol⁻¹ within our computational scheme). Were this gas phase energy gap directly transferable to condensed phase systems, the presented results could be biased by the adopted approximation. However, in a highly ionic system like nitrite sodalite, isolated system data may not be pertinent. We have calculated the triplet-singlet energy difference for the isolated $[NO_2 \cdots O_2]^-$ complex,



Figure 6: Relative energy of the Triplet state (continous line) vs the Singlet state (dotted line) for the nitrite sodalite $+ O_2$ systems at room Temperature.

by using the same computational scheme for the bulk calculations, for a series of geometries taken from the zeolite trajectories. The differences in energy for such a system reduce to 1-10 KJmol⁻¹, always favouring the triplet state. Moreover, we have performed some calculations on the nitrite sodalite + O_2 system by using the spin polarized DFT. In Figure 6 the relative energies for the Singlet and Triplet states at room temperature are reported. The triplet-singlet ΔE 's reduce to few KJmol⁻¹, but now favouring the singlet state.

Such results indicate that the adopted approximation is a good one for the study of the presented intracage oxidation, and suggest a possible stabilization of singlet oxygen in the nitrite-sodalite system.

5 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 Molecular Dynamics combined methods. The reaction was simulated by following the inverse reduction process. Such an approach has allowed an easier application of the BME sampling and could be of general interest.

We have found a free energy for the oxidation at 1000 K of the order of -75 KJmol⁻¹ and an activation free energy of about 30 KJmol⁻¹. A plausible mechanism for this chemical reaction was given, that may explain at microscopic level the phenomenological first order kinetics with respect to NO_3^- found experimentally.

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 present results, it can be argued 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 mechanism of the inert triplet state of dioxygen in the cavities of nitrite sodalite to the more reactive singlet O_2 [26].

In conclusion a microscopic description of a relatively complex chemical reaction "in laboratory conditions" was given. Despite such a description is presented in naive terms, it makes clear, were it necessary, the potentiality of the adopted methods.

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