



## Model Aluminosilicate sites on nanowires stabilize singlet O<sub>2</sub> state

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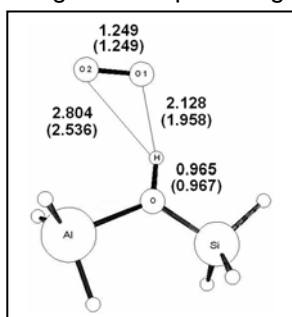
**Abstract** – The behavior of O<sub>2</sub> molecule in models of acid aluminosilicate sites on nanowires was investigated using reliable QM ab-initio calculations. Models of aluminosilicate active sites interacting with oxygen in their singlet and triplet electronic states were considered for two kinds of O<sub>2</sub> arrangements. Geometry optimizations were performed on both non-corrected and corrected BSSE potential energy surfaces, realizing that heavy atom – hydrogen interactions are sensitive to BSSE corrections during these processes. Energies were further evaluated at higher level of theory to test the tendencies. Singlet oxygen appears more attractive to those active aluminosilicate sites on nanowires than those calculated with triplet oxygen, indicating a source of oxidative efficiency for designed nanostructures containing such molecular residues. Some elegant features of oxygen interactions with such sites were further analyzed by means of the atoms in molecules (AIM) theory.

Inorganic systems designed as catalysts on demand are part of the strategy of material sciences long ago. [1] On the other hand, catalysts in well designed nano environments are very promising for most of the current necessities of human society. At present, theory and computations continue to play an important role in developing our understanding of O<sub>2</sub> and complexes of oxygen with other molecules, particularly with respect to phenomena that involve singlet oxygen. [2]

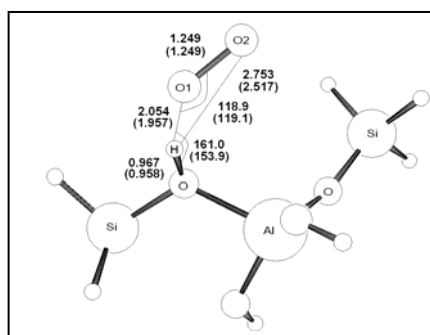
The behavior of singlet and triplet O<sub>2</sub> molecule on polar environment was investigated by theoretical ab initio MP2 methods. The energy gap between triplet and singlet decreases around 10 kJ mol<sup>-1</sup> due to a stronger interaction of singlets with the zeolite framework. According to our present work, aluminosilicates reduce the triplet-singlet oxygen energy gap, showing that this system is a suitable medium for the oxidation reactions because the expected increase of singlet oxygen population.

The interaction of O<sub>2</sub> with silicate and aluminosilicate clusters lead to the formation of van der Waals molecular adsorption complexes. The formation of this kind of complex is dominated by an interaction that occurs between the O atom of the non polar molecule (O<sub>2</sub>) and the terminal hydroxyl of the Brønsted acid site of the aluminosilicate. The weakest interaction is the corresponding to the oxygen molecule with the terminal silica hydroxyl groups. Singlet oxygen molecule interaction is energetically more favorable with respect to isolated molecules than the triplet oxygen molecule one. It is shown that the use of CP-corrected PES is necessary in order to obtain a good description of these very weak bonds. In such cases, BSSE have important consequences in determining the stabilization energies. A higher basis set improves the values of the interaction energies and reduce the BSSE. Overall results are in rather good agreement with the experiment.

Consistent with AIM theory, three kinds of interactions: O-H...O, O...O, Al...O and Si-H...O appeared in the aluminosilicate-O<sub>2</sub> studied complexes. The O-H...O appears as the most important. The larger stabilization energy of singlet complexes with respect to the triplet can be associated with the larger electron density sharing in the bcp relating with the O-H...O interaction.



**Figure 1:** Geometrical data for the optimized stationary points of complexes with  $^1\Sigma_g^+$  O<sub>2</sub> in CP corrected and CP uncorrected (in parenthesis) at MP2/6-311g (d, p) level. Distances in Å



**Figure 2:** Geometrical data for the optimized stationary points of complexes with  $^1\Sigma_g^+$  O<sub>2</sub> in CP corrected and CP uncorrected (in parenthesis) at MP2/6-311g (d, p) level. Distances in Å

[1] S. Mann, G. A. Ozin, Nature 382 (1996), 313-318.

[2] O. K. Varghese, M. Paulose, T. J. LaTempa, C. A. Grimes Nano Letters 9 (2009), 731-737.