



Theoretical study of the interaction between O₂ and cation exchanged Chabazite MCHA (M = H⁺, Na⁺ or Cu⁺)

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Abstract – O₂ adsorption in cation exchanged Chabazite has been studied using periodic and cluster approaches by means of density functional theory. The O₂-HCHA and O₂-NaCHA adsorption complexes present O₂ bent coordination. The adsorption energies are between -15 and -19 kJ mol⁻¹. On the other hand, the O₂ coordination to CuCHA is through a square planar coordination around the metal center. This structure favors the Cu-O₂ charge transfer. The O₂ highest singlet in energy is significantly more stabilized in MCHA than the triplet state by 14 to 24 kJ mol⁻¹.

The study of O₂ adsorption, in its triplet and singlet state, inside cation exchanged zeolites is an interesting first step to comprehend the oxidation mechanism of olefins inner zeolites. B3LYP periodic and cluster calculations have been carried out to understand the nature and energetics of O₂ adsorption in proton, sodium and copper exchanged zeolites. The Grimme's correction has been used to include the dispersion contribution to the B3LYP density functional values. [1] Two cation locations have been considered: one with the cation at the six-membered ring (MCHA(I)) and the other with the cation at the 8-membered ring (MCHA(IV)). The calculated adsorption energies (-14 to -18 kJ mol⁻¹) are in the same range to the experimental reported heat of adsorption (15-18 kJ mol⁻¹) [2], suggesting that the Grimme's correction does not only reproduce the main trends but predicts quite reasonably the dispersion contribution in this sensitive case. An ONIOM M12T:48T cluster model was taken into account. It included the channel ring where the adsorption takes place. The O₂ coordination to CuCHA is through a η²-sideon mode with a square planar coordination around the metal center. This different coordination is associated with a higher adsorption energy, -26.8 kJ mol⁻¹ for Site(I) and -68.1 kJ mol⁻¹ at Site(IV), which is due to the charge transfer from copper dπ in-plane orbital to the in plane π* O₂ orbital. The adsorption of singlet states of O₂ in HCHA and NaCHA is of the same nature than the triplet ones. Nevertheless, triplet-singlet state energy gap decreases between 15 and 25 kJ mol⁻¹. It is due to a stronger interaction of the later with the zeolite framework. The adsorption of singlet O₂ in Cu exchanged zeolites leads to a higher electron transfer from Cu to O₂ than that calculated for the triplet species. It stabilizes both singlet states with respect to triplet one. In all cases, singlet oxygen appears more attractive to active zeolite models than those calculated with triplet oxygen, indicating a source of oxidative efficiency for designed structures.

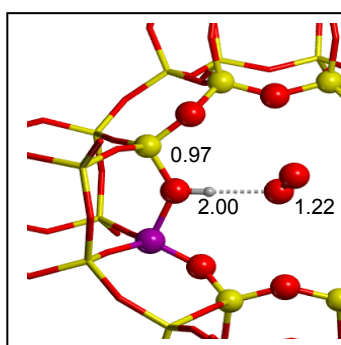


Figure 1: Local view of the B3LYP periodic ³O₂-HCHA(IV) adsorbed structures. Distances in Å

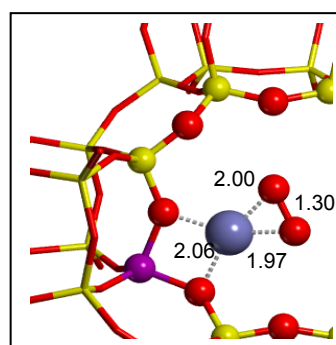


Figure 2: Local view of the B3LYP periodic ³O₂-CuCHA(IV) adsorbed structures. Distances in Å

References

- [1] S. Grimme Journal of Computational Chemistry 25 (2004), 1463-1473.
[2] S. Savitz, A. L. Myers, R. J. Gorte Microporous and Mesoporous Materials 37 (2000), 33-40.