The active centers of oxygen adsorption on thiolate-protected gold clusters in various solvents

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Thiolate-protected gold clusters have attracted considerable interest due to their unique structure and properties. They have been used widely in many fields: catalysis, biomedicine, electronics and other fields. Precisely defined atomic composition is characteristic for thiolate-protected gold clusters, this allows to establish the relationship between structure and properties. It should be mentioned that the mechanism of molecular oxygen interaction with clusters has been unclear yet and how this affects different processes: formation, reconstruction, catalytic processes.

The aim of the work is to simulate the interaction of O₂ with Au₂₀(SCH₃)₁₆ and its fragments and compare this process in gas phase, water and toluene. The DFT/PBE and SBKJC basis set were used in PRIRODA and Gaussian programs.

The interaction of oxygen with the gold atom is very weak in Au₂₀(SCH₃)₁₆ O₂ complexes without pre-activation. Two methods of pre-activation were considered: the photophysical activation way with using singlet oxygen and the removing ligand of the gold cluster. The reactions of singlet oxygen and Au₂₀(SCH₃)₁₆, and its fragments (CH₃S(AuSCH₃), CH₃S(AuSCH₃)₃, (AuSCH₃)₈ ) cluster are favorable. The O₂ adsorption energies on apart staple motifs are higher than on the cluster. This indicates that the separate fragments can really participate in oxygen activation. The molecular oxygen adsorption energies on different staple motifs are reduced by 11-12 kcal/mole, when modeling this process in water or toluene. This indicates that the homogeneous oxidation reaction is less favorable than the heterogeneous one.

The high dissociation barriers indicate that the oxygen on the cluster remains in molecular form. The electron-donor groups with respect to sulfur (some groups containing nitrogen) in the ligand increase the energies of O₂ interaction with the cluster in contrast to the electron-acceptor ones (a phenyl ring or carboxyl, hydroxyl groups).

At the thermal activation only with the certain amount of removed thiolate ligands, the oxygen adsorption becomes favorable. The de-thiolation with three ligands from various staple motifs makes possible the molecular oxygen adsorption. According to results, the O₂ adsorption energies at the thermal activation decreases in the order CH₃S(AuSCH₃)₃ > (AuSCH₃)₈ > CH₃S(AuSCH₃)₂. This confirms that a negative charge doesn't play a significant role in the oxygen adsorption.

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References:

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