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Pyrite oxidation: Characteristics of $(FeS_2O)_{12}$ species, a possible reaction intermediate

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Abstract:
We evaluated by quantum calculations the properties of pyrite-oxygen species $(FeS_2O)_{12}$ that can appear in the first stages of the oxidation process of pyrite with dissolved oxygen. The calculations were made with the Amsterdam Density Functional software. The obtained results suggest that $(FeS_2O)_{12}$ can be formed only after the dissociation of the oxygen molecule into much more reactive species.

Keywords: pyrite, oxidation, reaction intermediates

1. INTRODUCTION

Pyrite (FeS_2) is the most important and abundant mineral sulfide. Through its reaction with dissolved oxygen, sulfuric acid results [1-3], which acidifies the aqueous environments with which it comes into contact. Besides the contamination with sulfuric acid, the waters also accumulate a series of chemical species of Mn, Co, Ni, Pb, Cd, Hg, Sb, As etc. Acidic waters that contain these species are called Acid Mine Drainage [3]. Therefore, knowledge of the reaction intermediates of the pyrite oxidation process with dissolved oxygen is important for water quality control.

Most of the time these reaction intermediates cannot be analyzed experimentally, therefore the study of their characteristics is carried out by means of theoretical calculations.

In this study, we investigated by quantum calculations the characteristics of the pyrite-oxygen species $(FeS_2O)_{12}$, a possible reaction intermediate that can appear in the first moments of the pyrite oxidation process with dissolved oxygen.

2. METHODS

The quantum calculations were performed with the Amsterdam Density Functional (ADF) software. The calculation parameters were:

- exchange-correlation functional was Local-density approximation (LDA);
- basis set was Double Z (DZ).
- the size of frozen core was Large;
- numerical quality was Normal.

3. RESULTS AND DISCUSSION

The properties of the following species were calculated:

- a pyrite cluster with the size of $(FeS_2)_{12}$;
- a pyrite-oxygen cluster having the size $(FeS_2O)_{12}$;
- the O_2 molecule (the distance between the oxygen atoms is 1.21 Å).

Figure 1 shows the charges of Fe, S and O atoms in $(FeS_2)_{12}$ and $(FeS_2O)_{12}$ clusters. Note the positive charge of the S atom (S=0.219) linked to the O atom. In the case of the other atoms in the two clusters, the results are as expected, that is, the Fe atoms have positive charges, and the S and O atoms have negative charges. Table 1 shows the energies calculated for the species: $(FeS_2)_{12}$, O_2 and $(FeS_2O)_{12}$

Table 1. Calculated energies for the species $(FeS_2)_{12}$, O_2 and $(FeS_2O)_{12}$.

Species	$(FeS_2)_{12}$	O_2	$(FeS_2O)_{12}$
Energy (kJ/mol)	-2839.1	-571.8	-3363.4

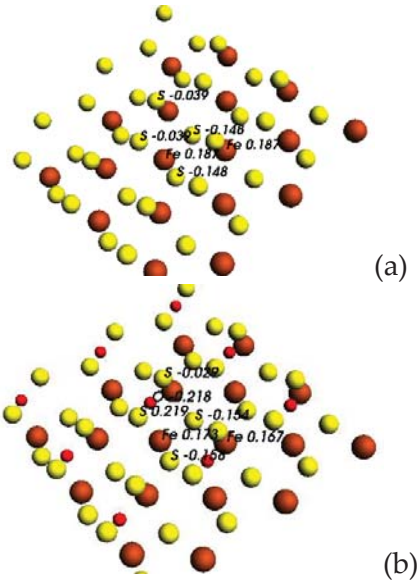

Figure 1. The charges on the Fe and S atoms on the $(FeS_2)_{12}$ cluster. (b) The charges on the Fe, S and O atoms on the $(FeS_2O)_{12}$ cluster.

The calculated reaction energy of the reaction $(FeS_2)_{12} + 6O_2 = (FeS_2O)_{12}$ is 2906.5 kJ/mol, which suggests that $(FeS_2O)_{12}$ (a possible reaction intermediate) can be formed only after the dissociation of the oxygen molecule into much more reactive species and not directly through the reaction of $(FeS_2)_{12}$ with molecular oxygen (O_2).

4. CONCLUSION

We evaluated by quantum calculations the properties of the pyrite-oxygen intermediate $(FeS_2O)_{12}$, which can appear in the first stages of the pyrite oxidation process with oxygen. The obtained results suggest that $(FeS_2O)_{12}$ can appear only after the dissociation of the oxygen molecule into much more reactive species.

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