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Spectroscopic study of amino acids adsorption on pyrite surface: From vacuum to solution conditions.

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Abstract

We characterized the adsorption of cystine molecules among other amino acids on pyrite surface via X-ray photoelectron spectroscopy. A novel comparative analysis revealed remarkable differences with respect to molecular adsorption and surface chemistry induced by environmental conditions. Pyrite is a highly reactive surface and contains two crucial types of surface functional groups that drive molecular chemistry on the surface depending on the surrounding conditions. Therefore, the systems explored in this study hold interesting implications for supporting catalyzed prebiotic chemistry reactions.

1. Introduction

Understanding the interaction between biomolecules, such as amino acids, peptides or proteins, and minerals surfaces is of importance in the fields of surface chemistry, catalysis and prebiotic chemistry. Minerals can be very promising surfaces for studying biomolecule-surface processes; among such minerals is pyrite. Pyrite (FeS_2) is one of the most important and abundant sulfide minerals on earth. Additionally, due to its catalytic activity, pyrite surface plays an important role in heterogeneous catalysis [1]. Furthermore, the study of pyrite's physical properties and reactivity is also crucial to the ‘‘iron–sulfur world’’ [2]. Wächtershäuser proposed that the first reactions that led to the formation of amino acids did not occur in a bulk solution in the oceans (prebiotic soup theory) but on the surface of minerals (such as pyrite) because such surfaces have the potential to facilitate prebiotic polymerization. In fact, minerals may adsorb and concentrate these biomolecules and catalyze reactions. Mineral surfaces could potentially have allowed for almost any type of general catalysis, with low specificity and efficiency. Therefore, the role of mineral surfaces could be relevant to the origin of life [3].

Recent experiments suggest that amino acids are very strongly adsorbed on mineral surfaces and that this adsorption could have facilitated peptide formation by increasing the effective concentration of amino acids and by providing catalytic sites on the surface [4]. In this context, we studied the adsorption of the amino acid cystine on pyrite by evaluating the interaction between the two under different environmental conditions. Therefore, we focused our study on investigating the possible role played by mineral surface reactivity. We report the results of a spectroscopic study, specifically X-ray photoemission spectroscopy (XPS) data, obtained for L-cystine adsorption on a natural pyrite surface and discuss spectroscopic evidence of different molecular adsorption mechanisms on the surface of pyrite constrained by oxidizing or reducing conditions.

2. Results

The adsorption of organic compounds on pyrite has been studied here under different selected and well-controlled conditions. This strategy is designed to be able to evaluate how diverse environments favour or inhibit molecular adsorption on the surface. The interaction of some functional groups may drive molecular interaction with the iron and sulphur chemical groups from pyrite surface.

A comparative study of molecular adsorption in the presence and in the absence of oxidant conditions demonstrated that, in contrast to the behavior observed for metal surfaces, molecular adsorption on pyrite surface is favored under UHV conditions rather than in solution (Figure 1). Furthermore, longer exposure times in solution inhibit molecular adsorption on the surface. Our spectroscopic study revealed the presence of surface oxidation species and a low nitrogen signal as evidence of the oxidation process on pyrite, which inhibited molecular adsorption under solution conditions. Anoxic conditions facilitate molecular adsorption and the formation of a diversity of chemical species, whereas cystine adsorbs on the pyrite surface only in its anionic form when adsorbed from solution. Surface vacancies on pyrite could affect the chemical form in which cystine is adsorbed, determining the molecular chemistry on the surface.

3. Figures

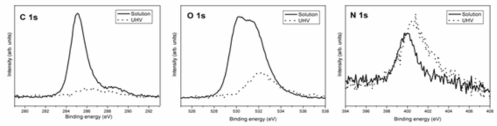

Figure 1: A comparison XPS photoemission spectra of C 1s, O 1s and N 1s core level peaks of L-cystine adsorbed from solution (-) and under UHV(…) conditions on the pyrite surface.

4. Summary and Conclusions

We have performed the first spectroscopic characterization of cystine adsorption on a pyrite surface. XPS analysis is employed to efficiently explore the molecular adsorption, to understand surface chemistry, and finally to describe critical influence of the presence of oxygen in cystine-pyrite systems. Successful interaction of cystine on a pyrite surface confirms the high reactivity of this surface, which could operate as a batch-reactor for prebiotic molecules. These studies could therefore shed light into prebiotic chemistry reactions.

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