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Peptide bond formation of alanine on silica and alumina surfaces as a catalyst.

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Abstract

Polymerization of amino acids has been important for the origin of life because the peptides may have been the first self-replicating systems. The amino acid concentrations in the oceans may have been too diluted in the early phases of the Earth. The formation of the biopolymers could have been due to the catalytic action of various minerals (such as silica or alumina). Our work is based on the comparison between alumina and silica minerals with and without prior activation of their silanol groups for the formation of peptide bonds using alanina like amino acid which it is the simplest quiral amino acid.

1. Introduction

Prebiotic chemistry studies the formation of complex organic molecules from simpler organic and inorganic molecules through chemical reactions in the Earth´s early history (1).
Inspite of the Earth´s conditions during the first phase of organic synthesis (synthesis of biomonomers), it is important in order to verify the origin of life to know what the conditions were like in the second phase, when the first biological polymers were formed (2).
The polymerization of amino acids by peptide bond formations that could occur during chemical evolution is one of the most important reactions because amino acids are biological building blocks, which are essential for the formation of proteins and fundamental for the first living systems (1).
Amino acid concentrations in the ocean could be too diluted and this made the reactions of polymerization extremely difficult. These reactions should occur in aqueous solutions at moderate temperatures (0-70 ^{o}C) from sufficient concentrations of biochemical monomers and a catalyst. The pH should be near neutrality and cyclic changes of temperature are necessary along with conditions of alternating humidity and dryness, allowing the evaporation of water and facilitating the condensation of biochemical monomers (2).
Recent experiments suggest that some amino acids are very strongly adsorbed by some mineral surfaces and it is believed that this adsorption could have facilitated peptide formation by increasing the effective concentration of the amino acids and due to catalytic sites on the surface. Minerals such as silicates, oxides and sulfides have been frequently present in various environments since the Early Ages. A few studies have examined the effects of mineral surfaces in the formation of peptide chains from aqueous solutions of amino acids (3).
In our experiments, we have been studying the formation of peptide bonds of alanina (ala) using silica or alumina as a catalyst. We study if this bond occurs and if the bonds are cyclic or linear; experimental parameters such as temperature or adsorption time were also considered to search for the most optimal conditions for the peptide bond formations.
Clay-catalyzed peptide bond formation is a complex process which includes amino acid dimerization, cyclic anhydride formation and peptide chain elongation. These three reactions depend on the conditions of the reactions. It is believed that one possible activation of amino acids is due to a condensation reaction of Si-OH groups with the amino acid carboxyl group forming esters (-Si-O-CO-) (4). To improve the catalytic action in the case of the mineral, silica, a strong oxidizing solution called Piranha (H_2SO_4 + H_2O_2) was added in order to activate the mineral and the results were compared with and without the Piranha. The study of alumina was conducted without prior activation.
All of the experiments were studied using the surface analysis techniques, X-Ray Photoemission Spectroscopy (XPS) and infrared Spectroscopy (IR), which are useful and innovative tools in prebiotic chemistry field. Both techniques allow us to study the bonds formation between amino acids, their cyclic or

linear distribution and peptide chain elongation, also which are the most optimal experimental conditions for the amino acids polymerization.

2. Experimental section

A comparative analysis was performed from the following three experiments:

1) Silica.
2) Silica activated by a strong oxidizing solution (piranha solution).
3) Alumina.

The experiments were performed at different temperatures (R.T, 80^{o}C and 100^{o}C) and different adsorption times (1, 3, 6, 8, 10, 13 and 15 days). Alanina was used for all the experiments.
A comparison study was performed between both catalysts (silica and alumina). Also the most optimal conditions of temperature and time for the formation of peptide were studied.
The surface analyses were done by XPS and IR spectroscopies. Both surface science techniques gave important information about peptide bonds, lengths of formed peptides chains and its distribution (cyclic or linear).

3. Results and Analysis

XPS and IR spectra of alanine on silica, silica activated and alumina, show important differences due to the use of different catalysts and due to the activation of silica using a strong oxidizing solution, Piranha. Furthermore, experiments were performed at different temperatures and at different adsorption times showing that, both, are critical parameters in this type of polymerization reaction.

4. Summary and Conclusions

Our study has focused on a detailed investigation on the polymerization of alanine using different minerals as catalysts. Experimental parameters such as adsorption time and temperature were studied to search the optimal reaction conditions. This innovative study was performed using powerfull and complementary surface techniques (XPS and IR).
This study focused on the context of prebiotic chemistry shows the relevance of different surfaces catalyst, temperature reaction or adsorption time as critical parameter for the formation of peptides bonds. The aim of this study is to search for a new findings on the formation of peptide chains and to find a relationship between the minerals that have existed on the Earth since the primitive ages and proteins which are essential molecules in the formation of living beings.

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