Exploring Amino Acid Peptide Bond Formation/Break in Presence of Clay Surface: An *Ab Initio* Study

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The fundamental understanding of biomolecule-clay interaction and peptide bond formation or break is of great relevance to the biotechnology industry.[1-4] To this end, we use density functional theory (DFT) to examine the relationship between the two simple alanine amino acids and the most common type of clay mineral, montmorillonite (MMT).[5] Five model systems were investigated in order to gain a better knowledge of peptide bond formation/break catalyzed by inorganic substrate: (1) no substrate as a reference point, (2) a clay surface without defects, (3) a clay surface with a missing oxygen atom, (4) a clay surface with a missing silicon atom, (5) an iron-doped clay surface. To trace the system's total energy as a function of the reaction coordinate, the transition state (TS) search approach is ultimately used for each of the model systems. In accordance with the findings, only the fifth system has positive binding energy while the other models all have negative binding energies. The lowest binding energy occurs in the fourth system, and the binding energies of the oxygen-defective and pristine models are nearly equal. Furthermore, studies from heating and molecular dynamics (MD) demonstrate that the original system's (#1) peptide bond breaks at 500 K. The results of this work pave the way for the specifically tailored design of clay-based materials in the realms of biotechnology and prebiotic chemistry.

References

(1) Moro D, Ulian G, Valdrè G. Amino acids-clay interaction at the nano-atomic scale: the L-alanine-chlorite system. Applied Clay Science. 2019 May 1;172:28-39.

(2) Aquino AJ, Tunega D, Gerzabek MH, Lischka H. Modeling catalytic effects of clay mineral surfaces on peptide bond formation. The Journal of Physical Chemistry B. 2004 Jul 15;108(28):10120-30.

(3) Zhu C, Wang Q, Huang X, Yun J, Hu Q, Yang G. Adsorption of amino acids at clay surfaces and implication for biochemical reactions: Role and impact of surface charges. Colloids and Surfaces B: Biointerfaces. 2019 Nov 1;183:110458.

(4) Contreras-Torres FF, Basiuk VA. Imidazo [1, 2-a] pyrazine-3, 6-diones derived from α-amino acids: a theoretical mechanistic study of their formation via pyrolysis and silica-catalyzed process. The Journal of Physical Chemistry A. 2006 Jun 15;110(23):7431-40.

(5) Ghazanfari S, Han Y, Xia W, Kilin DS. First-Principles Study on Optoelectronic Properties of Fe-Doped Montmorillonite Clay. The Journal of Physical Chemistry Letters. 2022 May 6;13:4257-62.