

# Evidence for specific arrangements of surface sites of silica that promote peptides formation

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Interaction of molecules with surfaces plays a significant role in many fields such as heterogeneous catalysis and biomedical applications e.g. drug delivery field [1, 2]. Among the huge variety of molecular events involved in the interaction with surfaces, the catalytic formation of C-N bonds (amides and peptides) by condensation of unactivated reagents is garnering interest, owing to its high importance in fine chemistry. This reactivity may also explain the formation of (bio)macromolecules such as oligopeptides from amino acids in prebiotic conditions [3, 4], a phenomenon that constituted a crucial step in the development of complexity at the origins of life.

In this contribution, the mechanism of the catalytic formation of polyglycine (Gly<sub>n</sub>) on the surface of amorphous silica is elucidated at the molecular level by the means of IR spectroscopy and mass spectrometry. Our results suggest a high selectivity of specific silica surface sites that catalyze the polymerization of Gly to long linear oligomers: only one sub-family of Si-OH surface groups (nearly-free silanols located around 5 Å apart) are active toward peptides formation. More precisely, we focus on strained silica rings (3 or 4-membered), pre-reacted with formic acid. The reaction proceeds through two steps: (i) silica ring opening by reaction with formic acid to form a Si-O-C(=O)- surface ester with a subsequent hydrolysis of surface species by the adsorption of water vapor and (ii) reaction of the silanols pairs formed in this way with Gly adsorbed through chemical vapor deposition (CVD), to form the poly-Gly chains. Parallel experiments carried out on amorphous silica untreated with formic acid result in less abundant and shorter oligomers. Furthermore, the results show the reorganization of the poly-Gly on the surface when contacted with water vapor to form organized self-assembled structures containing both helical and β-sheet-like structural motifs comparable to the secondary structure of proteins. We also observe that the polypeptides formed by condensation of Gly on the silica are linked to the surface by covalent bonds resulting in their strong resistance to desorption when washing with liquid water. In summary, these findings can shed light on the complexity of the interactions between mineral surfaces and biomolecules and their interplay in the amide bond formation.

<sup>†</sup> Prof. Martra who designed and supervised this work, recently passed away.

## References

- [1] Védrine, J. C. (2019). Metal oxides in heterogeneous oxidation catalysis: State of the art and challenges for a more sustainable world. *ChemSusChem*, 12(3), 577-588.
- [2] Adibnia, V., Mirbagheri, M., Salimi, S., De Crescenzo, G., & Banquy, X. (2020). Nonspecific interactions in biomedical applications. *Current Opinion in Colloid & Interface Science*, 47, 70-83.
- [3] S. Cazaux, M. Minissale, F. Dulieu, S.Hocu, Dust as interstellar catalyst, *A&A*, 585 (2016) A55
- [4] J.-F. Lambert, Adsorption and polymerization of amino acids on mineral surfaces: a review, *Orig. Life Evol. Biosph.* 38 (2008), 211-242.