

Catalytic aspects of metallophthalocyanines adsorbed on gold-electrode.

Theoretical exploration of the binding nature role

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The need of deeper insights regarding the inner working of catalysts represents a current challenge in the search of new ways to tune their activities towards new chemical transformations. Within this field, metallophthalocyanines-based (MPc) electrocatalysis has gained tremendous attention due to their versatility, low cost, great stability and excellent turn-over properties. In this concern, here we present a quantum chemical study of the formation of supramolecular complexes based on the adsorption of MPcs on gold substrates, and the effect of the substrate on their electrocatalytic properties. For this purpose, we used iron- (FePc), cobalt- (CoPc) and copper-phthalocyanines (CuPc). To model the gold surface we used two gold clusters of different sizes, given by Au₂₆ and Au₅₈ accounting for gold electrode Au(111) surface. Thus, both electronic and binding strength features of the adsorption process between the complexes were analyzed in detail in order to gain a deeper description of the nature of the MPc-Au(111) formation, by using Density Functional Theory (DFT) calculations, at the PBE and TPSS levels including the dispersive contribution according to the Grimme approach (D3). Our results show that dispersion forces rule the MPc-gold interaction, with binding strengths ranging between 61 and 153 kcal mol⁻¹, in agreement to the reported experimental data. To provide a detailed picture of our findings we used the non-covalent interactions index (NCIs) analysis, which offers additional chemical insights regarding the forces that control their interaction strength. Finally, our calculations revealed that among the three MPcs, CuPc required less energy for its oxidation. However, the removal of the electron involves a tremendous

decrease of the MPC-gold surface interaction strength thus suggesting its desorption, which would prevent the required reversibility of the redox reaction, explaining its low performance observed experimentally. © 2016 the Owner Societies.