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On the Oxygen Reduction Reaction Mechanism Catalyzed by Pd Complexes on 2D Carbon. A Theoretical Study

Marco Bonechi ¹, Walter Giurlani ^{1,2} , Martina Vizza ¹, Matteo Savastano ¹ , Andrea Stefani ³, Antonio Bianchi ^{1,4} , Claudio Fontanesi ⁵  and Massimo Innocenti ^{1,2,4,6,*} 

¹ Department of Chemistry “Ugo Schiff”, University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy; marco.bonechi1@stud.unifi.it (M.B.); walter.giurlani@unifi.it (W.G.); martina.vizza@unifi.it (M.V.); matteo.savastano@unifi.it (M.S.); antonio.bianchi@unifi.it (A.B.)

² National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy

³ Department of Physics, Università Degli Studi di Modena e Reggio Emilia, Via Campi 213, 41125 Modena, Italy; andrea.stefani@unimore.it

⁴ Center for Colloid and Surface Science (CSGI), Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

⁵ Department of Engineering “Enzo Ferrari”, DIEF, Università Degli Studi di Modena e Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy; claudio.fontanesi@unimore.it

⁶ Institute of Chemistry of Organometallic Compounds (ICCOM), National Research Council (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

* Correspondence: minnocenti@unifi.it



Citation: Bonechi, M.; Giurlani, W.; Vizza, M.; Savastano, M.; Stefani, A.; Bianchi, A.; Fontanesi, C.; Innocenti, M. On the Oxygen Reduction Reaction Mechanism Catalyzed by Pd Complexes on 2D Carbon. A Theoretical Study. *Catalysts* **2021**, *11*, 764. <https://doi.org/10.3390/catal11070764>

Academic Editors: Jaroslaw Polanski, Piotr Bartczak and Tomasz Studyga

Received: 11 June 2021

Accepted: 23 June 2021

Published: 24 June 2021

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Abstract: Oxygen Reduction Reaction (ORR) is the bottle-neck strategic reaction ruling the fuel cell efficiency process. The slow kinetics of the reaction require highly effective electrocatalysts for proper boosting. In this field, composite catalysts formed by carbon nanotubes functionalized with palladium(II) complexes showed surprising catalytic activity comparable to those of a commercial Pt electrode, but the catalytic mechanisms of these materials still remain open to discussion. In this paper, we propose the combination of experimental and theoretical results to unfold the elementary reaction steps underlying the ORR catalysis.

Keywords: fuel cell; ORR; PM6; band-gap; 2D carbon catalyst; SACs

1. Introduction

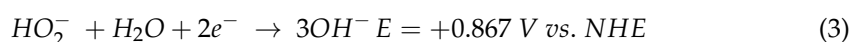
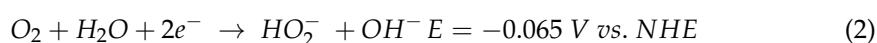
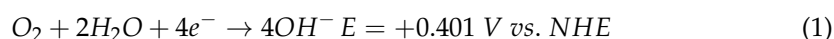
In recent years, issues concerning the energy sector have been at the focus of international discussions; the progressive depletion of fossil reserves and the increase in energy demand have led to the rise in fuel and electricity prices. Moreover, we are witnessing an increasing attention to pollution and environmental impact. New stricter standards for vehicle emissions are directing manufacturers to find new systems for energy production and storage. In this context, fuel cells are promising candidates for a sustainable future. The oxygen reduction reaction (ORR) is one of the most studied reactions in the field of energy. This reaction allows the release of chemical energy stored in the vector molecule H_2 in the form of electricity without producing any waste. For this reason, ORR is regarded as a highly strategic reaction. The oxygen reduction reaction can take place in two main ways: from a direct reduction to water (H_2O), with the exchange of 4 electrons per oxygen molecule or from an intermediate reduction to hydrogen peroxide (H_2O_2), with the exchange of two electrons. The slow kinetics of the reaction constitutes the theoretical and practical limit to its use in the energy sector. The use of a cathode catalyst is mandatory to achieving a satisfying ORR conversion rate; in fact, it is very difficult to electrochemically break the O_2 bond, which has an exceptionally strong bond energy. Many types of catalysts have been developed in order to improve kinetics and achieve better efficiencies. Semi-empirical quantum mechanical based methods offer the possibility to derive useful

information for understanding the reaction mechanism and evaluate different conformational structures, complexation energies, and species interaction energies [1]. The study of the energy levels of molecular orbitals allows the understanding of the phenomena of charge transfer and electrical reduction [2]. This kind of information allows one to evaluate the different reactivity of catalysts. Currently, platinum-based compounds show the best catalytic activity; however, the cost of this metal limits large-scale commercialization. For this reason, alternative catalysts are being experimented on, in which attempts are made to reduce the content of so-called Pt group metals (PGMs) or to replace them with a less precious metal [3–5]. Several substrates have been proposed as possible solid supports, among which are many carbon-based materials, including a new class of green catalysts made by pyrolysis of waste materials such as tires [6–9]. Carbon nanotubes (CNTs) have gathered a lot of attention in recent years due to their peculiar chemical and physical properties that make them suitable for catalytic processes [10]. They show a graphitic conductivity that can occur both in the plane of the π orbitals and inside the nanotube itself and do not show heating effects as a result of a current flow. Noncovalent functionalization approach offers the possibility to keep composite systems together, preserving the electrical properties of CNTs. CNTs-Pd(II) complexes have been used to prepare functionalized surfaces and working electrodes, which proved to be effective in catalyzing the ORR process [3,4,11]. Thus, in this paper, we aim to rationalize the catalytic role of such a class of composite catalysts. The latter showed surprising catalytic activity in ORR: MWCNTs/HL1-Pd(II), (Cat1), and MWCNTs/HL2-Pd(II) (Cat2) [11].

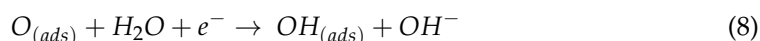
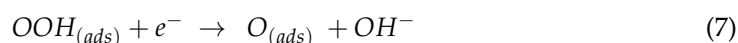
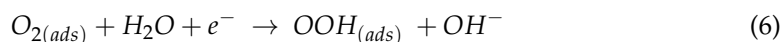
2. Oxygen Reduction Reaction: ORR

The two studied catalysts consist of carbon nanotubes functionalized with two different ligands, which are adsorbed on the nanotube surface by π - π stacking interactions. The two different ligands employed (HL1 and HL2) are organic molecules consisting of three main moieties: a pyrimidine group, which serves as the anchoring site, an aliphatic carbon spacer, and a terminal macrocycle. The latter acts as an organic ligand able to form a stable complex with the Pd(II) cation. HL1 has a shorter spacer group than HL2: $-(CH_2)_2-$ and $-(CH_2)_3-NH-(CH_2)_2-$, respectively. Experimentally, Cat1 and Cat2 were obtained through a supramolecular approach [12]. Moreover, adsorption of the catalyst, through the pyrimidine ligands on the graphitic surface, allows one to obtain active sites consisting of a single metal ion, implying a significant reduction of precious metal mass. Within the catalyst structure, the Pd(II) cation is coordinated by three nitrogen atoms from the macrocycle, and one hydroxide (OH^-) anion (provided from the bulk alkaline solution where the ORR process is carried out). The terminal macrocycle behaves as a tridentate ligand, leaving an active position in the first coordination sphere of Pd(II); in this way, the uptake of an oxygen molecule is assisted. Both systems have quite positive onset potential (vs. RHE) with a four electrons overall reduction process, eventually leading to the direct production of water (a significant reduction of hydrogen peroxide, a dangerous side-reaction byproduct, concentration is also observed experimentally [11]). Cat2 has the best catalytic activity, especially with regard to reduced production of hydrogen peroxide; we are led to believe that the longer spacer of HL2 produces a brush-like arrangement of the catalytic sites that promotes the capture of gaseous reactants from solution.

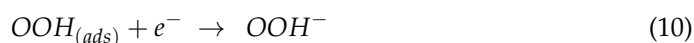
ORR in alkaline media is rationalized by a four steps $4e^-$ electron reduction mechanism, as originally proposed by Latimer [13–15]. In general, the overall reaction, (1), emerges as the combination of different elementary steps; see, for instance, Reactions (2) and (3). Disproportionation Reaction (4), as well as adsorption of the hydroxyl anion, play a role too [16].



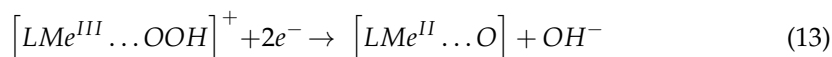
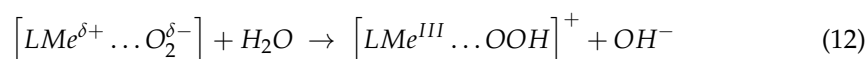
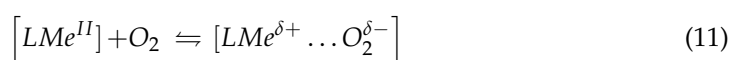
Thus, the kinetics of the oxygen reduction reaction depends on a quite complex reaction mechanism, involving a number of side-reaction intermediates as well as physical adsorption steps reactions from (5) to (9) (vide infra). As a final result, the ORR acts as the rate determining step in the water splitting [17–20].



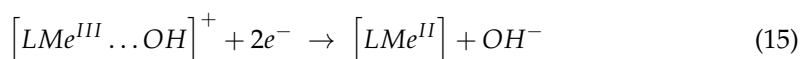
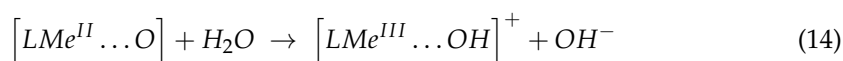
Equations (5)–(9) form the 4-electron reduction pathway, resulting in the production of four OH^- ions. Then, as an alternative to Reaction (7), OOH radical can be further reduced, eventually desorbing as a peroxide anion OOH^- Equation (10).



In the case of (10) as the end of the reaction chain, an overall two-electron reaction mechanism is obtained. The latter is claimed to be the effective pathway when using carbon based materials for the ORR, such as carbon nanotubes (MWCNTs) [21]. Indeed, in the case of single-atom catalysts (SACs), i.e., the class of compounds formed by carbon nanotubes functionalized with Pd(II) complexes, experimental evidence indicates that the main ORR reaction path involves the oxygen reduction mediated by Pd(II), eventually following a four-electron reaction mechanism. In this case, an associative mechanism involving direct contact between O_2 and the Pd(II) complex is assumed [3,4,11]. Thus, based on the already accepted ORR mechanism catalyzed by transition metal complexes in acidic media [22], we propose for the alkaline media a set of elementary reactions, from (11) to (13). Where: L represents the ligand and Me is the metal:



We propose the further set of elementary steps, which is consistent with the final ORR process:



In particular, Reaction (16) eventually gives due count to the formation of the peroxide anion, as it is reported in the literature [17,18,23].



3. Results and Discussion

The calculation of the electrochemical redox properties followed a heuristic approach. Systems of different complexity for Cat1 and Cat2 were considered; the ligand structure (HL1/HL2) had been optimized as a single molecule, then the complexed Pd(II) cation

and its counterion (OH^-) were subsequently introduced, followed by the C2D moiety and the oxygen molecule. HL1 and HL2 are structurally related compounds, as can be seen in Figures 1 and 2.

Figures 3 and 4 show potential energy surfaces relevant to the combination of the different moieties (i.e., reaction path), which concur to form the complete Cat1 and Cat2 catalyst. The energy pattern found in Figures 3 and 4 gives due count to the spontaneous (down-hill in energy) stabilizing interaction between the Pd(II) complexes and the C2D moiety (which simulates the CNT). Remarkably, the HL2/C2D energy stabilization is larger than that corresponding to the HL1/C2D one. Moreover, Cat2 shows the highest oxygen interaction energy. With the energy values obtained, we can state that the oxygen molecule does not replace the hydroxyl anion (as previously assumed) but is coordinated by Pd(II) in the apical position. This information is especially interesting in terms of catalyst design. While the presence of an ancillary fast-exchangeable ligand (Cl^-) was essential for Sonogashira cross-coupling [12,24], as the process requires simultaneous coordination of two different reagents on Pd(II), this is not mandatory for ORR, as O_2 is able to form an apical bond on the d^8 metal center anyway. This could pave the way to direct usage of Pd(II) square planar complexes with tetradentate ligands. Interaction energies for Cat1 and Cat2 are listed in Table 1.

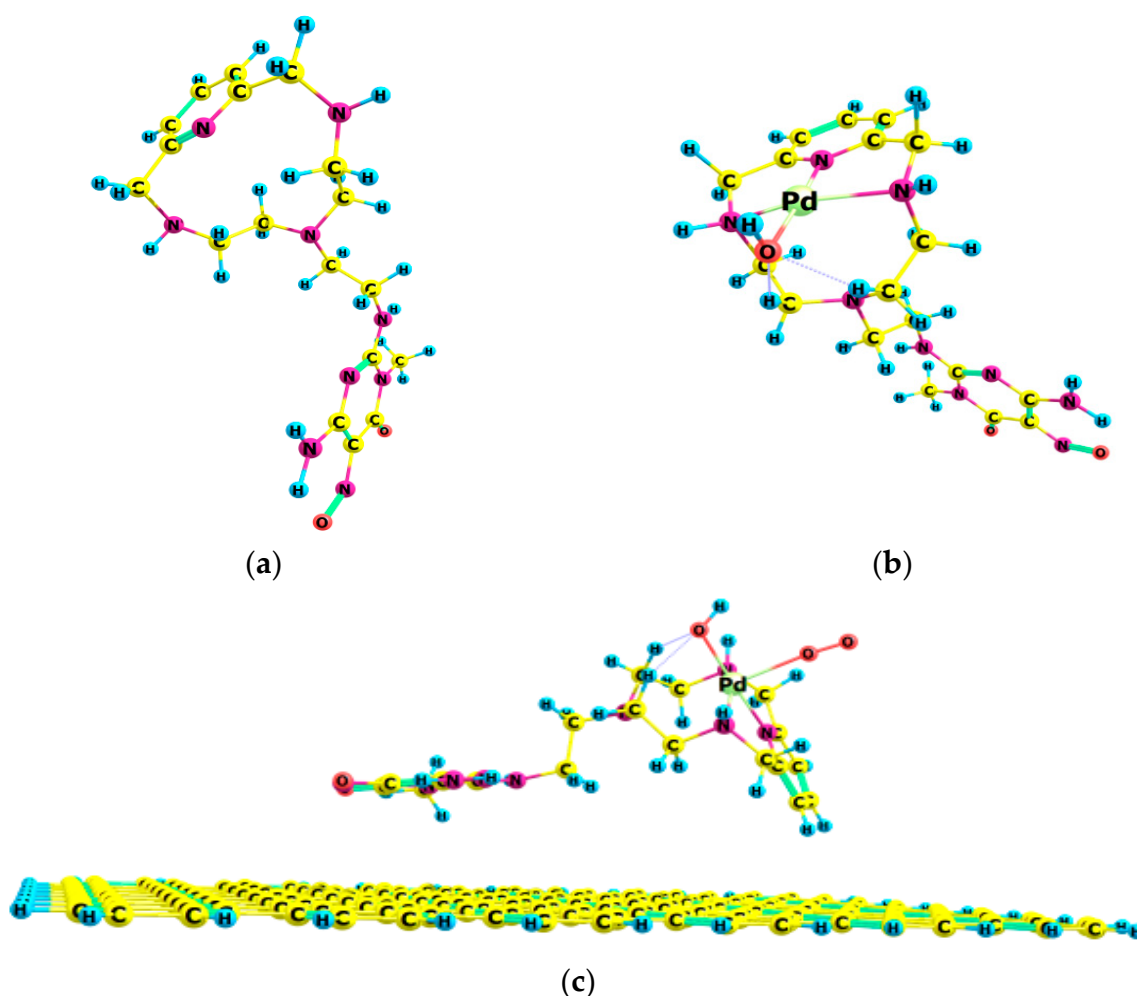


Figure 1. Molecular structures for the ORR catalyst: (a) HL1 (b); HL1-Pd(II)-OH⁻ complex; (c) Cat1 final adduct C2D-HL1-Pd(II)-OH⁻ with O₂ interaction.

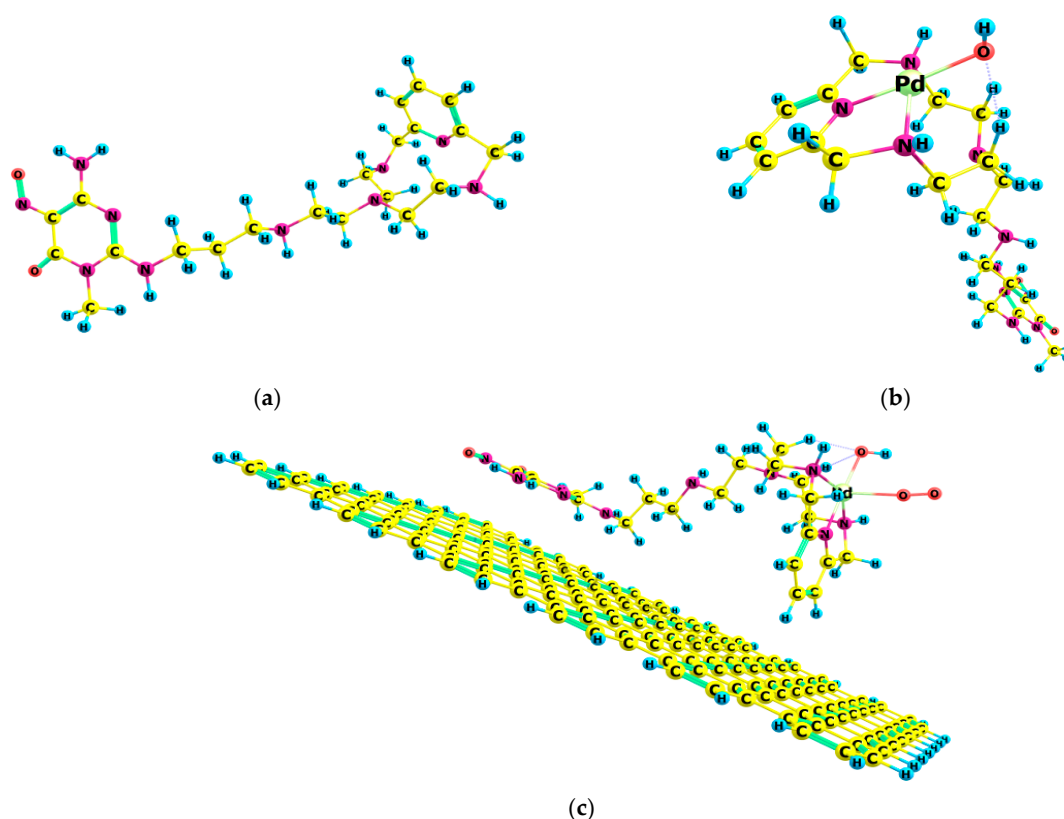


Figure 2. Molecular structures for the ORR catalyst: (a) HL2; (b) HL2-Pd(II)-OH⁻ complex; (c) Cat2 final adduct C2D-HL2-Pd(II)-OH⁻ with O₂ interaction.

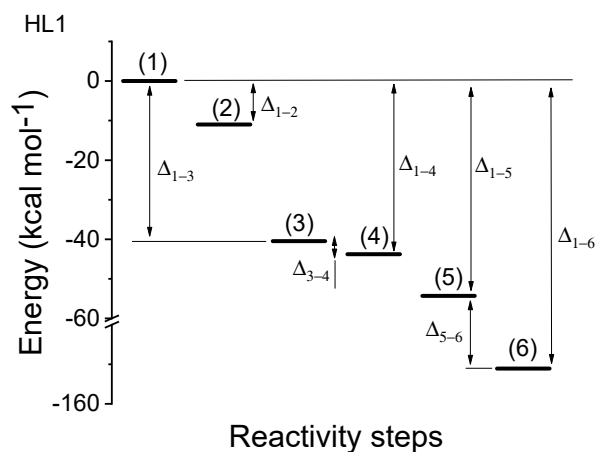


Figure 3. Potential energy surface (PES) for the elementary reactions yielding the composite catalyst: 1 to 5 (Cat1). Energy difference 6 corresponds to the catalyst/oxygen interaction, in the case of the HL1 supramolecular catalyst, UHF PM6 level of theory (compare Table 1 and Results and Discussion section for the details). SCF energy of (1) $Energy_{C2D} + Energy_{HL1} + Energy_{Pd(II)} + Energy_{OH^-} + Energy_{O_2}$, (2) $Energy_{C2D-HL2} + Energy_{Pd(II)} + Energy_{OH^-} + Energy_{O_2}$, (3) $Energy_{C2D} + Energy_{HL2-Pd(II)-OH^-} + Energy_{O_2}$, (4) $Energy_{C2D} + Energy_{HL2-Pd(II)-OH^- - O_2}$, (5) $Energy_{C2D-HL2-Pd(II)-OH^-} + Energy_{O_2}$, (6) $Energy_{C2D-HL2-Pd(II)-OH^- - O_2}$. The energy level (1) represents the sum of the energies of the non-interacting species, while (6) represents the energy of the complete catalyst supermolecule. The energy of the O₂ molecule was calculated in the electronic triplet state. The energy levels of the six steps have been normalized to the energy of state (1), which corresponds to a 748.42 kcal mol⁻¹ absolute value.

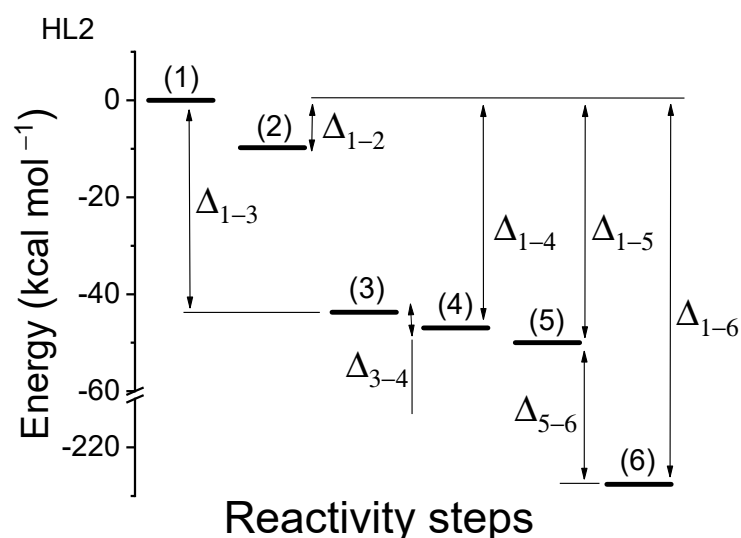


Figure 4. Potential energy surface (PES) for the elementary reactions yielding the composite catalyst: 1 to 5 (Cat2). Energy difference 6 corresponds to the catalyst/oxygen interaction, in the case of the HL2 supramolecular catalyst, UHF PM6 level of theory (compare Table 1 and Results and Discussion section for the details). SCF energy of (1) $Energy_{C2D} + Energy_{HL2} + Energy_{Pd(II)} + Energy_{OH^-} + Energy_{O_2}$, (2) $Energy_{C2D-HL2} + Energy_{Pd(II)} + Energy_{OH^-} + Energy_{O_2}$, (3) $Energy_{C2D} + Energy_{HL2-Pd(II)-OH^-} + Energy_{O_2}$, (4) $Energy_{C2D} + Energy_{HL2-Pd(II)-OH^- - O_2}$, (5) $Energy_{C2D-HL2-Pd(II)-OH^-} + Energy_{O_2}$, (6) $Energy_{C2D-HL2-Pd(II)-OH^- - O_2}$. The energy level (1) represents the sum of the energies of the non-interacting species, while (6) represents the energy of the complete catalyst supermolecule. The energy of the O_2 molecule was calculated in the electronic triplet state. The energy levels of the six steps have been normalized to the energy of state (1), which corresponds to a $744.78 \text{ kcal mol}^{-1}$ absolute value.

Table 1. Interaction energies of reactivity steps of Cat1 and Cat2 supramolecular catalysts.

Inter-Molecular Interaction [†]		Cat1 kcal mol ⁻¹	Cat2 kcal mol ⁻¹
Ligand adsorption on C2D Δ1-2	Δ1-2	-10.99	-9.77
Ligand Pd(II) OH ⁻ complexation	Δ1-3	-40.46	-43.71
Adduct adsorption on C2D	Δ1-4	-43.77	-46.97
Ligand O ₂ absorption	Δ3-4	-3.31	-3.26
Adduct stability	Δ1-5	-54.29	-49.98
Adduct O ₂ absorption	Δ5-6	-96.79	-177.64
Adduct O ₂ stability	Δ1-6	-151.09	-227.62

[†] Compare the Results and Discussion section and Figures 3 and 4 for the relevant details.

A very large variation in MO energies is found as a function of the molecular architecture. The presence of a graphitic-like plane simulating the surface of MWCNT drastically changes the MO energy hierarchy, giving due count to the experimental efficiency found for the more complex molecular structure. Full details concerning MO energy diagrams are shown in Supporting Information.

The energy ordering and shape of virtual orbitals for the HL1 moiety, Cat1, suggest that an electron “hopping” mechanism could explain the catalytic effect observed. Electrons can hop from the surface of the nanotube to the palladium complex to which the oxygen molecule is adsorbed, as can be seen in Figure 5.

expensive Pt electrode: Cat1 shows an onset potential of +0.91 V vs. RHE, whereas Cat2 shows a value of +0.95 V. The greatest differences between the two systems are observed with regard to the direct production of H₂O: the ORR process, Cat2 working electrode, is a four electrons process, whereas Cat1 promotes greater production of hydrogen peroxide. Among 2e⁻ reduced species, Cat2 – O₂ is the most stable as it has molecular orbital energies of less than approximately 1 eV. The reduced species have a molecular geometry very similar to that of the original species, so the reduction does not involve any significant changes in the structure of the ligands, which may explain the high stability in successive reduction cycles observed experimentally. All in all, the energy of LUMO ordering Cat1 vs. Cat2 gives due reason to the experimental outcome, where the most effective catalytic capability is shown by Cat2.

4. Computational Details/Methods

Due to the sizable molecular structures here considered, all the theoretical results here reported concern species in all possible oxidation states, and spin multiplicity is performed in the framework of semi-empirical quantum mechanical based methods: PM6 Hamiltonian. In the calculations, the structure of the CNTs was approximated by a perfectly flat, two-dimensional 6 × 7 (aromatic rings) 2D carbon structure (C2D), in order to reduce the system complexity to a feasible degree. All calculations were performed using C1 symmetry and unrestricted wave function using the Gaussian 16 program [26]. The Chemcraft program [27] is used for visualization purposes, for both molecular structures and molecular orbitals display. Molecular geometries are obtained by full optimization carried out at UHF PM6 levels of the theory. To account for solute–solvent interaction, geometry optimization is carried out using Barone and Cossi's polarizable conductor model (CPCM) [28,29].

5. Conclusions

In this paper, we modelled theoretically the catalytic activity of two composite catalysts. These were obtained by suitably functionalized carbon nanotubes, using Pd(II) complexes. Indeed, functionalized carbon nanotubes (in this paper approximated by an ideally flat 2D-carbon sheet), proved to be an effective alternative to classical Pt-based catalysts [11].

In particular, the essential features of the ORR process are accounted for by considering them as a sequence of four elementary steps, which we showed to correspond to a down-hill in energy PES: compare Table 1 and Figures 3 and 4. Our theoretical results also show that VdW forces (physical interaction) are responsible for the stability of the intermolecular Pd complex@2D-carbon “supramolecular system” (π - π stacking): -13.8 and -6.3 kcal mol⁻¹, for HL1 and HL2, respectively.

The total supramolecular stabilization energies are -151 and -228 kcal mol⁻¹ for Cat1 and Cat2, respectively. What is more, the ordering of LUMOs energies suggests that an electron “hopping” mechanism is consistent with the observed catalytic effect: the electron uptake involves, *in primis*, the C2D structure followed by a transfer on a virtual orbital localized on the Pd(II) complex.

The reaction mechanism here proposed, and the relevant theoretical results obtained by using the PM6 semiempirical Hamiltonian, give due count to the experimental evidence of a more efficient ORR process based on the use of the HL2 complex molecular architectures. Remarkably, the oxygen/Pd(II)-complex stabilization energies are -96.79 and -177.64 kcal mol⁻¹ for Cat1 and Cat2, respectively.

Moreover, a few insightful pieces of information emerged from the data. First, an ancillary ligand on the Pd(II) center is not mandatory for ORR, as O₂ can still bind to the metal ion via an axial bond; this simplifies ligand design. Second, the energy of unoccupied molecular orbitals involving the metal center and/or its aromatic ligand, with respect to the anchoring group-centered LUMO, might play a significant role. While this is not a

direct simplification of the preparation of such a system, it surely offers space to make informed design choices.

Thus, the mechanism here proposed, in terms of single elementary steps, sheds light on the role played by single-atom catalysts (SACs) in the ORR overall process.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11070764/s1>: Further details are reported concerning molecular orbital energies. Table S1: Molecular orbitals energies of HL1 catalyst. Table S2: Molecular orbitals energies of HL2 catalyst. Figure S1: Molecular Orbital energies diagram for HL1 catalyst. Figure S2: Molecular Orbital energies diagram for HL1 catalyst.

Author Contributions: Conceptualization, C.F.; software M.B. and C.F.; writing—original draft preparation, M.B., M.S., and C.F.; writing—review and editing, W.G., M.S., M.V. and A.S.; supervision, A.B. and M.I.; funding acquisition, M.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the PRIN (“Progetti di Ricerca di Rilevante Interesse Nazionale”), which made possible the project “Novel Multilayered and Micro-Machined Electrode Nano-Architectures for Electrocatalytic Applications (Fuel Cells and Electrolyzers)”, grant number 2017YH9MRK.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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