



Understanding the chemisorption-based activation mechanism of the oxygen reduction reaction on nitrogen-doped graphitic materials



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ABSTRACT

To optimize nitrogen-doped graphitic materials as metal-free catalysts for the oxygen reduction reaction mechanisms have to be better understood. Here, the role played by pyridinic nitrogen-dopants in the chemisorption-based activation of the target reaction is revealed. The study is centered on the monodentate chemisorption of molecular oxygen as the first step of the process. Several configurations of unclustrered nitrogen dopants in which there was always a nitrogen dopant in the edge of the material were tested using DFT. A clearly favorable chemisorbed state for molecular oxygen was found when the pyridinic nitrogen-dopant is hydrogenated and located at an armchair edge. The found chemisorbed state is further favored by additional available charge. By contrast, the chemisorbed state of oxygen is much less favorable when the hydrogenated pyridinic nitrogen-dopants are located at zigzag edges. Moreover, it was found that the charge involved in the hydrogenation of pyridinic nitrogen-dopants remains segregated, becoming available for reduction processes. Detailed reasons for the described facts are given, and an integrated model for the target activation mechanism is proposed including graphitic nitrogen-dopants effects.

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1. Introduction

Controlled oxidation of fuels in electrochemical cells is a promising energy conversion technology [1], whose future success depends on the development of an efficient catalyst for the oxygen reduction reaction (ORR). Platinum ORR catalysts have enabled the proof of concept but, mainly because of sluggish kinetics, cost and scarcity, low-platinum [2–5], non-platinum [6–9] and even metal-free [10–12] ORR catalysts are being investigated. Among these, nitrogen-doped graphitic materials exhibit activity towards the ORR [13–20]. However, the nature of the sites and the mechanisms explaining the observed activity are still under discussion. It has been suggested that the ORR on nitrogen-doped graphitic materials could take place without involving chemisorption [20]. However, without chemisorption, only hydrogen peroxide would be produced, which is an undesirable byproduct for fuel cell applications. Moreover, since the ORR is very sensitive to the surface structure and composition of the electrode, it is clear that

chemisorbed species are always involved in the process. Thus, ORR mechanisms based on chemisorption have to be better understood to optimize the performance of these catalysts. In all the proposed mechanisms [16,21] the first step in the reaction would give rise to a monodentate chemisorbed state of molecular oxygen, generally in the form of a superoxide. From that point, two possible scenarios arise. The first one considers the formation of adsorbed peroxide. Then, the reaction could yield hydrogen peroxide or evolve sequentially to water. In the other possible scenario, the adsorbed oxygen species would give rise to a bidentate configuration. From that, the oxygen-oxygen bond would be broken yielding finally water.

To determine the most probable mechanism, different facts and arguments can be considered. First, a significant production of hydrogen peroxide has been observed on nitrogen-doped graphitic materials [15,17,18]. Second, the stabilizing solvation shell formed during the monodentate chemisorption of molecular oxygen [22] originates a significant barrier in order to evolve to the bidentate configuration. Finally, high activation energies for the cleavage of the oxygen-oxygen bond have been computed on these materials [16]. Moreover, the measured ORR activity on the investigated materials has been mainly attributed to the effect of graphitic [20]

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and pyridinic nitrogen dopants [19]. So, determining the role played by those dopants on graphitic materials to favor the monodentate chemisorption of molecular oxygen was established as the research goal. The evolution mechanisms from the investigated state to water [23] and optimal design strategies based on the adsorption energies of the intermediates [24] have been already reported.

To explain the ORR on nitrogen-doped graphitic materials, mechanisms involving graphitic nitrogen-dopants in the basal plane have been investigated [20,23,25–28]. However, a single nitrogen dopant or specific configurations of dopants in cluster have been usually considered. Motivated by the experimental visualization of unclustered graphitic nitrogen-dopants perfectly integrated in the graphene lattice [29], and by the fact that such a kind of defect has been identified as the one presenting the lowest energy [30], we explored recently the role played by unclustered graphitic nitrogen-dopants to activate oxygen in the basal plane [22]. In spite of the fact that the monodentate chemisorption of molecular oxygen on the basal plane of graphitic materials is usually considered as an unfavorable process [20], it was found that unclustered graphitic-nitrogen dopants would promote it, provided that two specific conditions are fulfilled. It was realized that the monodentate activation of molecular oxygen on graphitic materials requires of locally destabilized carbon atoms and globally available charge. The calculations demonstrated that graphitic nitrogen-dopants would be capable of playing both roles. So, it was shown that the monodentate chemisorption of molecular oxygen can take place on carbon atoms neighboring a graphitic nitrogen-dopant if, for instance, an additional graphitic nitrogen-dopant provides the required available charge. Moreover, solvation effects were found to be important in the mechanism, suggesting guidelines in order to capture it.

Regarding the ORR on the target materials, mechanisms involving pyridinic nitrogen-dopants at the edges have been also investigated [19,31]. In fact, ORR activity on carbon atoms adjacent to pyridinic nitrogen-dopants has been recently demonstrated [19]. However, the microstructure and mechanisms have not been yet identified. We will provide computational evidence that the hydrogenation of unclustered pyridinic nitrogen-dopants could act as a switch activating molecular

oxygen on these materials. The hydrogenation [32] of pyridinic nitrogen-dopants in graphitic materials has been associated to high ORR activity in alkaline media. Although in some calculations for graphitic materials that can be active for ORR, nitrogen dopants are hydrogenated [33], to our knowledge, no relevant role has been previously explicitly attributed to hydrogenated pyridinic nitrogen-dopants in explaining the activation of the ORR on the investigated materials. We will show that hydrogenated pyridinic nitrogen-dopants at armchair edges of graphitic materials can give rise to a clearly favorable monodentate chemisorbed state of molecular oxygen on their laterally adjacent carbon atoms. The found chemisorbed state would be further favored by additional available charge. By contrast, hydrogenated pyridinic nitrogen-dopants at zigzag edges would not be capable of so favorably activating oxygen on their adjacent carbon atoms. We will also show that the charge involved in the hydrogenation of pyridinic nitrogen-dopants remains segregated, becoming available for reduction processes. Moreover, detailed explanations for the described facts will be given and, considering also the role played by graphitic-nitrogen dopants, an integrated model for the target activation mechanism will be proposed.

2. Computational methods

Mechanisms of the ORR on molecular and periodic models of nitrogen-doped graphitic materials have been previously investigated performing DFT calculations under the GGA approximation and using the PBE [34] functional [20,23,27,30]. Thus, in this research, the monodentate chemisorption of molecular oxygen on nitrogen-doped graphitic materials was investigated using mainly different molecular models of nitrogen-doped graphene and performing DFT calculations under the GGA approximation and using the PBE functional and numerical basis sets of double-numerical plus polarization quality [35] as implemented in the Dmol³ code [36]. Moreover, each one of the found fundamental effects was verified using also periodic models of armchair and zigzag nitrogen-doped graphene nanoribbons, and molecular models of armchair and zigzag nitrogen-doped single-walled carbon nanotubes. All the calculations were performed under neutral charge conditions. All the electrons were explicitly

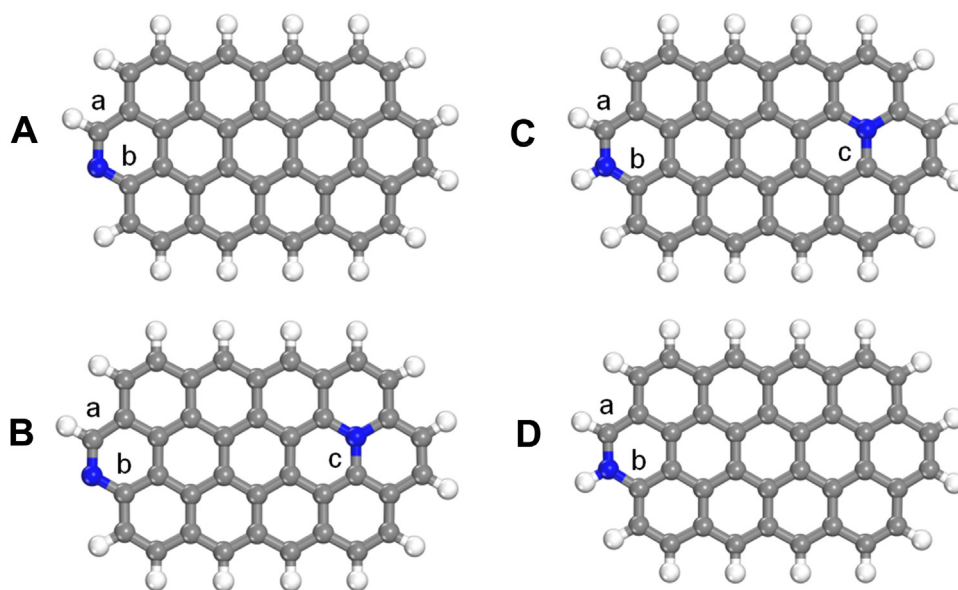


Fig. 1. Different unclustered nitrogen dopants configurations with a pyridinic nitrogen-dopant located at an armchair edge: (A) A single nitrogen dopant in a pyridinic form. (B) A pyridinic nitrogen-dopant in addition to a distant graphitic one. (C) A hydrogenated pyridinic nitrogen-dopant in addition to a distant graphitic one. (D) A single nitrogen dopant in a hydrogenated pyridinic form.

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