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Title: Investigation of Structure and Reactivity Relationship in M-N-C Type Catalysts using Density Functional Tight Binding

Author(s): Negre, Christian Francisco Andres  
Gonzales, Ivana

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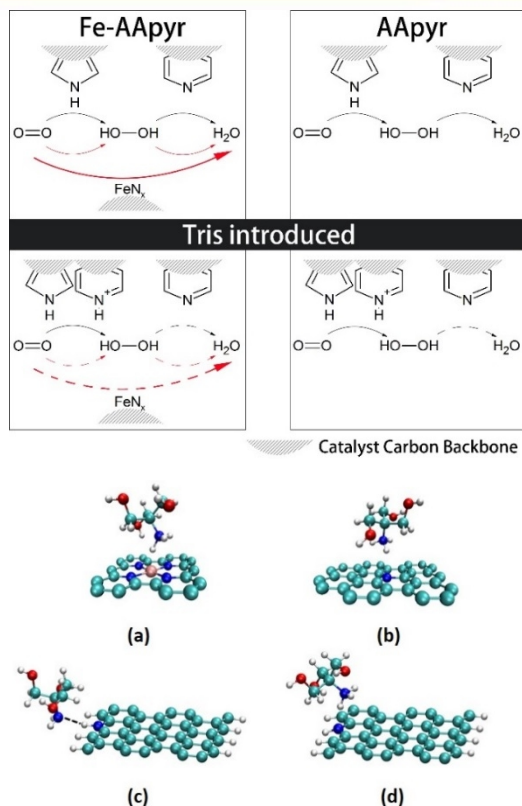
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# Investigation of Structure and Reactivity Relationship in M-N-C Type Catalysts using Density Functional Tight Binding

Christian F. A. Negre, T-1; Ivana (nee Matanovic) Gonzales, UNM, T-1



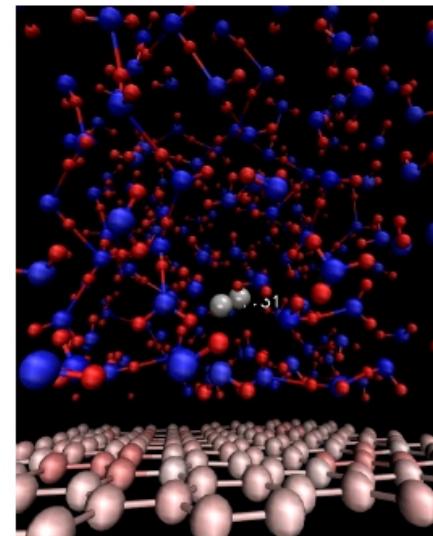
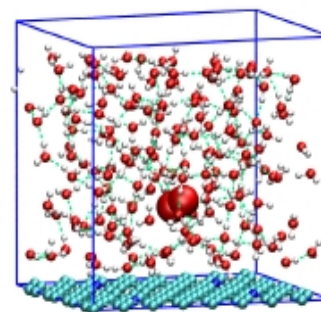
**Figure: Upper:** Schematic diagram of ORR mechanism before and after addition of Tris, established based on DFT calculations. **Lower:** DFT calculated geometries of TrisH with different active sites in Fe-N-C catalyst.

- Catalysts inhibition studies were performed to indisputably confirm the role of various metal, carbon, and nitrogen moieties in the individual steps of oxygen reduction reaction (ORR) on M-N-C catalysts. ORR activity was studied at University of New Mexico by rotating ring disk electrode method in the acidic electrolyte with the addition of Tris (tris(hydroxymethyl)-aminomethane) as inhibiting agent. To understand the interaction of Tris with different defects that exist in Fe-N-C materials and provide the support for the experimental data, we used density functional theory (DFT) and modeled the interaction of protonated Tris (TrisH) with Fe containing-centers ( $Fe-N_4$  and  $Fe-N_2C_2$ ), pyridinic nitrogen, graphitic nitrogen, and pyrrolic nitrogen both as in plane and edge defects.
- A DFT calculated adsorption energies of TrisH on different defects, show that *TrisH has the strongest interaction with pyridinic-N and  $Fe-N_x$  sites, followed by the graphitic-N and hydrogenated nitrogen defects (pyrrolic and hydrogenated pyridine)*. Therefore,  $Fe-N_x$  and pyridinic nitrogen are the most preferential sites for TrisH binding. Importantly, DFT calculations show that the proton from protonated Tris is being transferred to pyridinic nitrogen due to the lower pK value of the pyridinic nitrogen (6.5 for pyridinic nitrogen and 8.06 for Tris molecule). Protonation of *pyridine could be one of the reasons for oxygen reduction inhibition in N-C materials*. Furthermore, it was found that Tris can be more easily removed from protonated pyridinic nitrogen, pyrrolic nitrogen, and graphitic nitrogen, while  $Fe-N_x$  sites may be irreversibly blocked by Tris.
- The DFT calculations together with electrochemical observations for metal-free and metal-containing electrocatalysts confirmed the multiplex mechanism of oxygen reduction in which numerous species perform partial and full reduction of oxygen to peroxide or water, respectively.

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- ORR mechanism in metal-free catalysts was studied using Density Functional Tight Binding. Quantum dynamics simulations (QMD) of the fully solvated system containing oxygen and N-doped graphene (used to model graphitic nitrogen sites) were performed by applying extended Lagrangian QMD technique. This allowed us to perform Self-Consistent-free QMD simulations saving almost an order of magnitude in the calculations of the forces.
- The simulations showed that the oxygen molecule does not have to fully reach the surface in order to get reduced since the solvent is mediating the electron transfer by creating partially reduced species that eventually react with the  $O_2$  molecule. *These results confirm an outer-sphere electron transfer mechanisms of ORR over graphitic nitrogen sites.* Our results also verified that graphitic nitrogen increases the reduction potential of the surface since the  $sp^2$  hybridization of nitrogen in the graphitic sheet requires the transfer of the negative charge from the nitrogen to the surrounding atoms. This negative charge promotes the  $O_2$  reduction on graphitic nitrogen sites of N-C catalysts by an outer-sphere electron transfer mechanisms.



**Figure:** **Left:** One unit cell used to model a fully solvated system containing oxygen and N-doped graphene (red - O, white - H, light blue - C, blue - N) **Right:** A snapshot from the QMD simulation of the fully solvated system containing oxygen and N-doped graphene. Atoms are colored according to the calculated charge (red - positive, blue - negative).