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Understanding Iron-based catalysts with efficient Oxygen Reduction Activity from First Principle calculations

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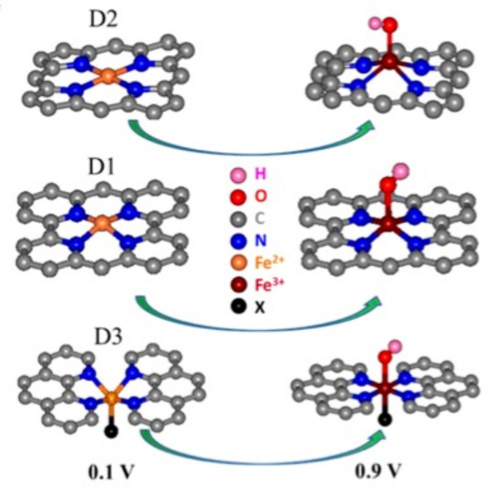

Figure 1: Different FeNC active sites D1, D2 and D3.

Catalysts based on Fe/N/C clusters can fulfill the oxygen-reduction reaction (ORR) without the use of expensive metals such platinum. We have performed spin polarized calculations on a various Fe/N/C fragments with the Vienna Ab initio Simulation Package (VASP) code. By using the DFT results, we have explained the Fe-N switching behavior of the Fe atom moving with respect to N_4 plane observed by synchrotron based *in situ* x-ray absorption spectroscopy (XAS) experiments on iron meso-tetraphenylporphine chloride (FeTPPCl) pyrolyzed at various temperatures and the polyaniline (PANI)−Fe−C catalyst. By examining the displacement of the Fe atom from the N_4-plane, we have identified three $Fe^{2+}-N_4$ like active sites with distinct Fe displacements: $Fe-N_4-C_{12}$ (D2), $Fe-N_4-C_{10}$ (D1), and $N_{axi}-Fe-N_4-C_8$ (D3), in which our computations reproduce the distinct Fe−N switching behaviors exhibited in experiments by FeTPP−300−C, FeTPP−800−C, and PANI−Fe−C respectively [1] (see Fig. 1).

Reference

[1] Q. Jia, N. Ramaswamy, H. Hafiz, U. Tylus, K. Strickland, G. Wu, B. Barbiellini, A. Bansil, E. F. Holby, P. Zelenay and S. Mukerjee, "Experimental Observation of Redox-Induced Fe–N Switching Behavior as a Determinant Role for Oxygen Reduction Activity," *ACS Nano* **9**, 12496–12505 (2015).