Evaluation of the energetics of nitrogen adsorption on decorated iron oxides for the artificial photosynthesis of ammonia

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Ammonia is emerging as one of the most cost-effective solutions for hydrogen storage and transportation. However, its conventional production is both carbon and energy-intensive, accounting for approximately 2% of global carbon emissions and energy consumption. To address this issue, alternative synthetic routes, including photocatalysis, have been proposed. Photocatalysts for ammonia synthesis are typically carried out in metal oxides (such as titanium or iron oxides), and often enhanced with metallic nanoclusters to improve their efficiency [1].

This study investigates the energetics of nitrogen adsorption on different metallic nanoclusters using *in silico* methods. Specifically, an ONIOM approach using different levels of functional density models were employed to study the interactions of N_2 and NH_x (x = 0 to 3) with selected surfaces of these nanoclusters. The method, implemented in the Gaussian 16 package, was used for these calculations in combination with CPMD, used to pre-evaluate the energetics of the lattices using a lighter calculation method based on projector-augmented waves.

Preliminary results indicate that nitrogen adsorption energies on various metal surfaces are significantly lower, compared to a pure magnetite iron oxide (222), the core photocatalyst on which the metals are anchored. This suggests a higher affinity and potential for enhanced catalytic activity when these clusters are used. Notably, the adsorption of N_2 on Mo (110) and Fe (110) surfaces exhibited the lowest adsorption energies, at −0.21 eV and −0.15 eV, respectively. Conversely, adsorption on Ru (110) showed a slightly positive adsorption energy (E_{ads} = 0.02 eV), making it the least favourable cluster studied.

These preliminary results show the potential of metallic doping in iron oxide nanoclusters for efficient N_2 adsorption, suggesting a route to design more sustainable and energy-efficient ammonia synthesis. Detailed analyses and complete results will be presented at the conference, providing a clearer picture of the catalysts for green ammonia production.

References

[1] Run Shi, Yunxuan Zhao, Geoffrey I. N. Waterhouse, Shuai Zhang, and Tierui Zhang ACS Catalysis 2019 9 (11), 9739-9750. DOI: 10.1021/acscatal.9b03246