Christopher Ehlert | 07.03.2024

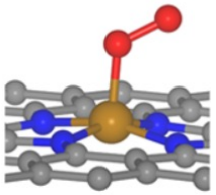
Recent Developments in ORR Catalysis

Introduction

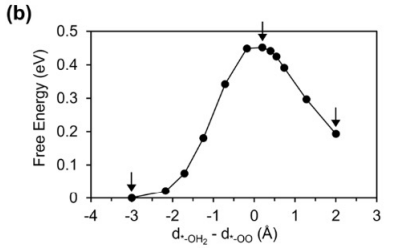
- Oxygen Reduction Reaction (**ORR**) is a key chemical process fuel cells and metal air batteries.
- Platinum-free catalysts will boost large-scale applications.
- Here: overview of the last developments (2023 and 2024).

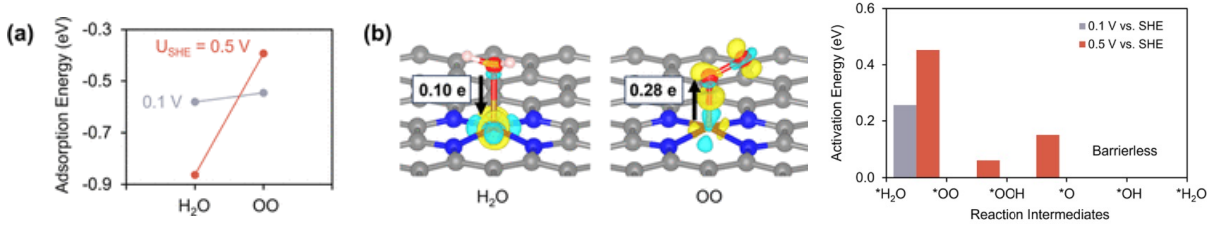
What Is the Rate-Limiting Step of Oxygen Reduction Reaction on Fe–N–C Catalysts? [1]

- Single iron atoms embedded in nitrogen-doped graphene (Fe–N–C).
- Constant potential AIMD (VASP, so-called "constant-potential hybrid solvation-dynamic model", or CP-HS-DM).



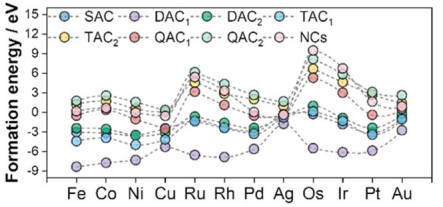
- Before O_2 can adsorb, the Fe-site is already occupied by a water molecule
- At TS, O_2 and H_2O are bound to Fe.
- This is a new perspective on the reaction mechanism. O_2 (H_2O) adsorption (desorption) occur at once, not in two steps.
- That step is supposed to be **the rate determining** step!
- The activation barrier for this step is potential dependent!
- **But:** no comments on spin states.



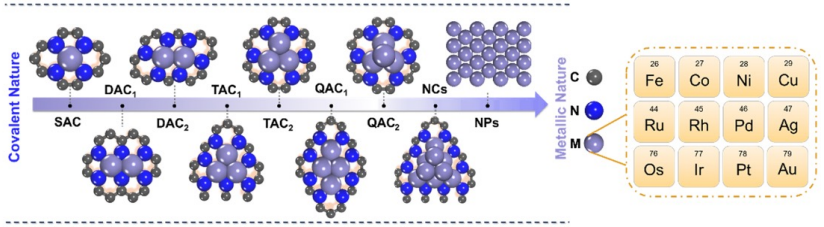


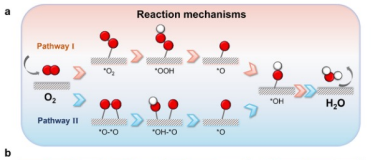
[1] Reprinted with permission from *J. Am. Chem. Soc.* **2023**, 145, 25352. © 2023 American Chemical Society.

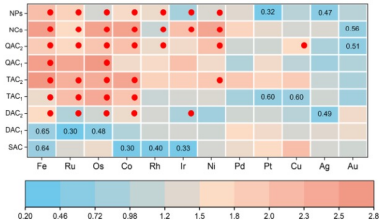
First-Principles Landscape of Single Atomic Catalysts to Metal Catalysts [2]



- PBE-D3 study (zero potential) on intermediate adsorption energies with different catalysts.
- **Formation energies**: DAC1 very stable.
- **Results: Adsorption energies** of reaction intermediates; Scaling relationships + Volcano plots.
- For some catalysts, a new pathway was proposed.
- High catalytic activities around SAC/DACS and Pt-NP.







[2] Reprinted with permission from *J. Phys. Chem. C* **2024**, 128, 1964. © 2024 American Chemical Society.

Enhanced Activity for the Oxygen Reduction Reaction in Microporous Water [3]

- Low solubility of O_2 in water limits achievable current densities.
- Idea: introduce a porous solid with *hydrophilic* external surface+ *hydrophobic* internal surface → **aqueous porous liquid** (zeolitic nanocrystals = silicalite-1-NCs).
- O_2 is physiosorbed on the (large) surface.
- Current densities are increased by a factor of 3.9 with silicate added.
- Reason: The diffusion coefficient of the zeolite is much larger than that of O_2 → **better mass transport.** Comparison with different particle size + particle types (hydrophilic internal surface does not work).

[3] Nat. Catal. **2023,** 6, 425.