The role of oxygen and water on molybdenum nanoclusters for electro catalytic ammonia production

The presence of water often gives rise to oxygen adsorption on catalyst surfaces through decomposition of water and the adsorbed oxygen or hydroxide species often occupy important surfaces sites, resulting in a decrease or a total hindrance of other chemical reactions taking place at that site. In this study, we present theoretical investigations of the influence of oxygen adsorption and reduction on pure and nitrogen covered molybdenum nanocluster electro catalysts for electrochemical reduction of N2 to NH3 with the purpose of understanding oxygen and water poisoning of the catalyst. Density functional theory calculations are used in combination with the computational hydrogen electrode approach to calculate the free energy profile for electrochemical protonation of O and N2 species on cuboctahedral Mo13 nanoclusters. The calculations show that the molybdenum nanocluster will preferentially bind oxygen over nitrogen and hydrogen at neutral bias, but under electrochemical reaction conditions needed for nitrogen reduction, oxygen adsorption is severely weakened and the adsorption energy is comparable to hydrogen and nitrogen adsorption. The potentials required to reduce oxygen off the surface are -0.72 V or lower for all oxygen coverages studied, and it is thus possible to (re)activate (partially) oxidized nanoclusters for electrochemical ammonia production, e.g., using a dry proton conductor or an aqueous electrolyte. At lower oxygen coverages, nitrogen molecules can adsorb to the surface and electrochemical ammonia production via the associative mechanism is possible at potentials as low as -0.45 V to -0.7 V. © 2014 Howalt and Vegge.

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