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Euro Green Chemistry 2019-Transition Metal Nitride Catalysts for Electrochemical Reduction of Nitrogen to Ammonia at Ambient Conditions- Younes Abghoui- University of Iceland

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Introduction: Ammonia is one of the extremely produced chemicals in the globe, which is mainly used in production of fertilizer. Since many years ago, ammonia has been synthesized mainly through the Haber-Bosch process where gaseous nitrogen and hydrogen are passed through a Ru- or Fe-based catalyst at high pressure and high temperature to form NH_3. The essential hydrogen gas for this process is frequently provided by natural gas, which leads to increased production of a variety of greenhouse gases. Another gas is to produce hydrogen from water splitting, which is a cleaner but extremely energy intensive process. The Haber-Bosch process is in severe contrast to the function of the enzyme nitrogenase in bacteria in which ammonia is produced from solvated protons, electrons and atmospheric nitrogen at severe conditions. The active site of the enzyme is a MoFe7S9N group that catalyzes the electrochemical reaction:

N2 + 8H+ + 8e− □ $2NH_3 + H_2$ (2)

The basis of energy for this reaction is at least 16 adenosine triphosphate (ATP) molecules, which are used to enhance the chemical potential of the electrons and the protons. Therefore, it is easy that this natural process could be emulated in a human-made and commercial installation. As an alternative of a separate hydrogen production process, the protons could come from an acidic solution, while the electrons would be driven to the electrode surface by an applied electric potential. A variety of potential routes for ammonia synthesis at drastic conditions are currently being explored. Ionic liquids or salts also promote ammonia formation from low current efficiencies up to 72% at high temperatures .While having achieved low-pressure ammonia synthesis, the above mentioned research still bear from the requirement of relatively high temperatures, which leads to increased product decomposition. While having achieved low-pressure ammonia synthesis, the above mentioned studies still suffer from the requirement of relatively high temperatures, which caused to increased product decomposition. Another feedback is the use of complex and costly electrolytes that hinder commercialization. To the best of the authors' idea, the first clarification of ammonia synthesis at milder conditions were reported with homogeneous catalysts with tungsten and zirconium as the central atoms. However, for the purpose of distributed use of ammonia, simpler methods are needed, ideally using heterogeneous catalysis, which allows for too easy isolation of product.

Methodology: The low indicator results are considered for each crystal structure, the (100) results of the RS structure and the (110) facets of the ZB structure. Each nitride surface is modelled by 40 atoms in five layers, with each and every layer consisting of four metal atoms and four nitrogen atoms. The base two layers are fixed whereas the apex layers as well as the adsorbed species are allowed to get relax. Boundary circumstances are periodic in the x and y directions and surfaces are separated by 12 Å of vacuum in the z direction. The structural variation is considered converge when the forces in any direction on all manageable atoms are less than 0.01 eV/Å. The RPBE lattice constants are also included. The calibrations are conducted with density functional theory (DFT) using the RPBE exchanges correlation functional .A plane wave base set with an energy cutoff of 350 eV is used to notify the valence electrons with a PAW demonstration of the core electrons as implemented in the VASP code . Activation energies are measured as the highest point along the low energy path (MEP) calculated using the climbing image nudged elastic band method (CINEB).

Results and Discussion

Stability of the surface nitrogen vacancy

In the Mars-van Krevelen method considered in the present work, a surface nitrogen atom is deducted to form NH_3 after that results vacancy is replenished by a gaseous N_2 molecule. For this replacement to occur, the N-vacancy wants to be stable at the surface. If this is not in the case, the N-vacancy may move around to the bulk of the catalyst, that is, the reacted nitrogen on the surface is Replace with more nitrogen from the catalyst, rather than with gaseous N_2. This method will continue till all the nitrogen atoms of the metal nitride have reacted and formed NH_3, leaving only the unpolluted metal. The stability of the N-vacancy at the upper layer of the catalyst is measured by compare the difference in energy of a nitride slab with a single N-vacancy in the upper layer and to that of a single N-vacancy in the first below surface layer. The least energy configuration of each of these slabs is found and the energy difference (ΔEvac = (Evac,2) - (Evac,1)) used as an opinion of the thermodynamic stability of the vacancy at the surface of the nitride. Activation gap for vacancy migration (Ea,vac) are also evaluate and both ΔEvac and Evac are presented .

It is noticed that, for most of the nitrides, it is thermodynamically good for the vacancy to migrate to the bulk, with ΔEvac less than or close to zero. However, it is clear that many of the nitrides when the forces in any direction on all manageable atoms are less than 0.01 eV/Å. The RPBE lattice constants are also included. The calibrations are conducted with density functional theory (DFT) using the RPBE exchanges correlation functional. A plane wave base set with an energy cutoff of 350 eV is used to notify the valence electrons with a PAW demonstration of the core electrons as implemented in the VASP code. Activation energies are measured as the highest point along the low energy path (MEP) calculated using the climbing image nudged elastic band method (CINEB).