Onset potentials for different reaction mechanisms of nitrogen activation to ammonia on transition metal nitride electro-catalysts

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ABSTRACT

Recent theoretical calculations with DFT suggest that transition metal nitrides (TMNs) are promising materials to catalyze N_2 electroreduction to ammonia at ambient conditions. To realize which mechanism is more favourable, we conduct DFT calculations to explore the catalytic activity of these materials in their most stable structures via conventional associative (AM) and dissociative (DM) mechanisms, and then compare the corresponding results with that of Mars-van Krevelen (MvK) mechanism we recently reported. The dissociation of N_2 on the clean surfaces is endothermic on most of these nitrides and the activation barriers large in all cases, which is inhibitive of a DM on these materials. The onset potential predicted for ammonia formation on these TMNs is always less negative via MvK than with AM, except a few cases, where both mechanisms have similar onset potentials. In those cases, the AM is less favourable than MvK since the adsorption of N_2 molecule is endothermic. Therefore, the MvK is almost always the favourable mechanism. We used the computational hydrogen electrode method and neglected any proton-electron transfer reaction barriers in this work but including those will be necessary to make a more definitive statement, which is the subject of future work.

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1. Introduction

The use of ammonia as an energy carrier and specially fertilizer has triggered numerous interests in developing alternative routes in pursuit of a more decentralized and environmentally friendly approach for ammonia synthesis. Without ammonia and thus deprived of inorganic fertilizer, almost half the worldís population would be at risk of starvation [1]. Human survival has thus been depending a great deal on the Haber–Bosch process [2], which is the most pivotal industrial installation for catalytic cleavage of N_2 and hydrogenating nitrogen to ammonia heterogeneously over promoted transition metal-based catalysts. Although Ru and Fe within the Haber-Bosch process show good activity for this catalytic conversion, the harsh operational conditions and sophisticated industrial setup of the Haber-Bosch process are all prohibitive to decentralization of ammonia synthesis. This complicates ammonia production in regions with relatively undeveloped infrastructure such as developing countries. Besides, the reliance of this process on natural gases for supplying its necessary hydrogen feedstock not only promotes severe CO_2 emission to the environment but it also makes the production of ammonia and accordingly food susceptible to natural gas price fluctuations and political conflicts in the oil-rich regions. Most importantly, a sustainable process needs to be developed for ammonia production to maintain food supply since at some point natural gas will be depleted.

A few reviews recently appeared in the literature that gather several potential routes for ammonia production [3–5]. In the last few decades, numerous efforts have been made towards manmade ammonia synthesis using photocatalytic [6] and electrochemical [7–12] methods. However, for many of these, it was difficult to regenerate the active nitrogen-fixing complex and only low current efficiencies of 0.1–8% at ambient conditions were obtained. To reach higher yields of ammonia, solid-state proton conductors have been investigated, and that contributed up to 78% conversion of cathodic supplied nitrogen to ammonia [13,14]. A recent study investigated cathodic synthesis of ammonia in a proton conducting double-chamber solid electrolyte cell where a ceramic proton conductor composed of $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$ (BZCY72) was used as electrolyte [15]. The catalyst used as the cathode was a Ni-BZCY72 cermet and a Pt film served as the anodic electrode. The highest production rate achieved was 0.5×10^{-9} mol s^{-1} cm^{-2}, but at -2.4 V and 620 °C. Very recently, Qing and co-authors reported anodic ammonia formation rate of around 2.0×10^{-10} mol s^{-1} cm^{-2} at +1.2 V and 220 °C [16]. They synthesized ammonia directly from N_2

and steam using a composite electrolyte based on $CsH_5(PO_4)_2/SiO_2$ and Pt/C-loaded carbon paper as both cathode and anode, but the current efficiency was only around 2%. Ionic liquids or molten salts were also found capable of promoting ammonia formation from low efficiencies to sometimes up to 72% but at relatively high temperatures [17–19]. Although low-pressure ammonia synthesis had been achieved, the aforementioned studies yet suffer from the necessity of relatively high temperatures, which leads to increased risk of product decomposition. The use of complex and expensive electrolytes is another downside that hinders commercialization.

There are also studies that investigated low-temperature ammonia synthesis at ambient pressure with the use of polymer electrolyte membranes (PEM) where the ammonia production can be separated from hydrogen feed gas and thus higher ammonia formation yields is achieved. The highest rate of ammonia formation reported in this fashion is 1.13×10^{-8} mol s^{-1} cm^{-2} with a current efficiency of ~90% obtained at 80 °C where $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ (x = 0–0.3) was used as the cathode and wet hydrogen as a feed gas [20]. Replacing the H_2 feed gas with water, Kordali and co-authors synthesized ammonia electro catalytically from N_2 and H_2O at room temperature using Ru cathode in a solid poly-mer electrolyte cell [21]. Only a low rate of ammonia formation (3.4×10^{-12} mol s^{-1} cm^{-2}) with a low efficiency of around 0.28% was achieved at a relatively high potential (~ −1.3 V vs. SHE) mainly due to competing hydrogen evolution reaction (HER) at the cathode. Using directly air and water as feed gases, the highest rate of ammonia synthesis reported thus far is 1.14×10^{-9} mol s^{-1} cm^{-2}, achieved using a mixed NH_4^+/H^+ Nafion membrane [22]. How-ever, again a low efficiency of around 1% is observed at a relatively high overpotential of −1.6 V. What is obvious here is that while solid-state electrolytes or PEMs offer promise as an electrochemi-cal route to ammonia synthesis, they are still in the early stage of development when compared with production rates nearing that of commercial viability (4.3–8.7×10^{-7} mol s^{-1} cm^{-2}) [23].

The above examples clearly indicate that (electro-) catalytic ammonia synthesis is a particularly feasible method due to the potential of utilizing renewable energy sources and mild operating conditions. But finding (electro-) catalysts that are selective enough towards nitrogen electroreduction reaction (NER) and have a low overpotential is challenging. First-principle calculations have been used to provide more insight about the mechanisms of the reaction and to explore new class of materials with higher activity and selec-tivity towards NER. Using DFT calculations, a few pure transition metals [24] and transition metal nano-clusters [25] were reported capable of ammonia formation. But for majority of the pure tran-sition metals usually large overpotentials are needed to activate nitrogen to ammonia as well as the surfaces of these materials are covered with H adatoms [24]. Thus, there is lack of available sites for adsorption of nitrogen, which inhibits reduction to ammonia. That mainly causes hydrogen evolution reaction (HER) on most of these surfaces instead of ammonia formation. On the early transi-tion metals, however, it is more likely to cover the surface with nitrogen than hydrogen, but those metals are known to readily form oxides and it remains to be seen if they can be used for N_2 activation. Conversely, transition metal nano-clusters were found capable of enhancing the ammonia activity compared to HER. How-ever, the presence of water in the electrochemical environment will reduce the efficiency of these catalysts by blocking its active site due to preferential adsorption of oxygen rather than nitro-gen [26]. A DFT study on cobalt molybdenum nitride enlightens that nitrogen vacancies can contribute to weakening of the strong triple bond of N_2 molecule and thus activate it to ammonia via a Mars-van Krevelen [27] (MvK) mechanism at low temperatures. There, a molybdenum triangular cluster can be a possible activa-tion site for nitrogen along with the surface cavity where N_2 is activated by the inner tetrahedral atom of a cobalt cluster [28,29].

Recently, transition metal nitrides (TMNs) were found promising for ammonia formation electrochemically [30–33] and chemically [28,34] via a MvK mechanism and also as redox materials for solar-driven ammonia synthesis [34,35]. The possibility of experimental growth of the thin films of these transition metal nitrides was already shown by i.e. cathodic arc techniques [36], sputter deposi-tion [37], plasma sputter-type negative ion source [38], and HiPIMS techniques [39]. Theoretical investigations show that earlier TMNs are more stable in the (100) facets of the rocksalt (RS) structure [31]. These are ScN, TiN, VN, CrN, MnN, YN, ZrN, NbN, MoN, HfN, TaN, among which the nitrides of Sc, Ti, Y, Hf, and Ta were found more selective toward HER rather than NER. On the other hand, the later TMNs are more stable in the (110) facets of the zincblende (ZB) structures [31]. These are FeN, CoN, NiN, RuN, RhN, PdN, OsN, and IrN. The surfaces of WN, ReN, PtN, CuN, AgN, and AuN showed significant distortion of the surface atoms during relaxation and thus were considered unstable and eliminated from further analy-sis in this study. In this paper we also include results of the most promising TMNs (ZrN, NbN, CrN and VN) in their ZB(110) structure.

The purpose of the current work is to determine the most prob-able reaction mechanism, from the overpotential perspective, for nitrogen activation to ammonia at ambient conditions when TMN surfaces are used to catalyze NER. Thus, we consider the most sta-ble structures and texture orientations of these materials, the (100) facets of the RS as well as the (110) facets of the ZB and exclude those found to be more selective for HER. The NER on these materials could proceed through either one or a combination of the following mechanisms: the MvK mechanism that we already investigated and reported before [31,32], the conventional AM and DM. To compare these two latter mechanisms with the MvK mechanism (where a surface N-atom is reduced to ammonia and the N-vacancy created during the process needs to be regenerated later by N_2 molecule from the solution), we consider conventional AM and DM as pro-cesses taking place on the clean surfaces without using a N-atom in the first layer of the surface. We calculate the free energy of the intermediates along the reaction path and construct free energy diagrams (FEDs) to estimate the overpotentials required to form ammonia. In the end, we compare the activity of these TMNs for ammonia formation obtained via these conventional AM and DM with that reported via MvK mechanism. By doing this analysis, we can predict which pathway represents higher likelihood of ammo-nia formation on the surfaces of these TMNs at ambient conditions.

2. Methodology

2.1. DFT calculations

DFT with the RPBE [40] exchange correlation functional was used to carry out all the calculations. A plane wave basis set with an energy cutoff of 350 eV was utilized to represent the valence electrons with a PAW [41] representation of the core electrons as implemented in the VASP code [42,43]. The self-consistent electron density was determined by the use of iterative diagonal-ization of the Kohn–Sham Hamiltonian, with the occupation of the Kohn–Sham states being smeared according to a Fermi–Dirac dis-tribution with a smearing parameter of kBT = 0.1 eV. A $4 \times 4 \times 1$ Monkhorst–Pack K-point sampling was used for all the surfaces. We modeled a five-layer nitride slab with four metal atoms and four nitrogen atoms in each layer. The bottom two layers were frozen and the uppermost layers as well as the adsorbed species were allowed to relax. To test convergence with respect to system size, we have carried out some test calculations for i) larger slabs in x and y directions to mimic lower concentration of defects, and ii) increased the number of layers in the slab. Fig. S1 in the supplemen-tary information compares the energy difference of the N-vacancy