**Ammonia and Hydrazine Synthesis Mechanism at Intrinsic Nitrogen Vacancies on Mn3N2-(100) Surfaces**

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**Abstract**

Elucidating the mechanism of catalytic reactions is crucial to the design of new catalysts. In this computational study, we have used dispersion-corrected Density Functional Theory (DFT) theory to investigate various potential intermediates (NxHy) for the ammonia synthesis reaction on Mn3N2-(100) surfaces. We have used a simple Lewis structure representation algorithm in order to locate various possible NxHy intermediates. Two of the intermediates, HN=NH and N=NH were studied for their ammonia synthesis reaction mechanisms via a (i) Langmuir–Hinshelwood and subsequent Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2 and (ii) via various Eley–Rideal mechanisms at intrinsic nitrogen vacancies on η-Mn3N2. We present that the hydrogenation of dinitrogen results in significant activation of the inert triple bond and that this intermediate may have a significant role in the ammonia synthesis reaction on this material via the Langmuir-Hinshelwood reaction. We anticipate that these findings are significant for the development of new catalysts that can synthesize ammonia at moderate conditions.

keywords: DFT, ammonia synthesis, manganese nitride, intermediates, mechanism

**Introduction**

Industrial ammonia synthesis via the Haber-Bosch (H-B) process1-3 operates at a global annual production rate of ca. 174 million tonnes.4 It uses a Fe-K2O-Al2O3 catalyst that operates under high temperatures (>400ºC) and pressures (150-200 atm). It is, therefore, an energy-intensive process and improvement of the catalysis would be socio-economically beneficial. Some newer industrial plants use the Kellogg advanced ammonia process that uses a graphite-supported alkali/alkaline-earth promoted Ru catalyst, which operates at milder conditions but is expensive.5 We are currently seeking catalytic materials and/or processes that could potentially produce ammonia at lower temperatures (T = 200-300 ºC) in order to save energy.6 This would maximise production yield as it would shift the equilibrium of the nitrogen to ammonia synthesis reaction towards the products according to Le Chatelier's principle as ammonia synthesis is an exothermic reaction.

The use of atom vacancies in catalysts as catalytic centers has long been recognised. We have recently determined that ammonia synthesis can follow different reaction pathways on the very active cobalt molybdenum nitride (Co3Mo3N) catalyst7-12 when nitrogen vacancies are present.13 Such vacancies are present in large concentrations even at ambient temperatures (i.e. 1013 cm-2) and can efficiently activate N2.14 Other recent DFT studies determined that N-vacancies can participate in the mechanism for the electrochemical reduction of ammonia on Zr, Nb, Cr, V mononitrides 15, 16 and in the two-step solar-energy drove ammonia synthesis on metal-nitrides. 17, 18 It is, therefore, evident that the inclusion of nitrogen vacancies, either *intrinsic* or *extrinsic* in a mechanism of ammonia synthesis on metal nitrides may lead to the possibility of new lower energy mechanistic pathways. In this study we have studied the adsorption of various possible ammonia synthesis intermediates (i.e. NxHy) on the (100) surface of Mn3N2. Identification of the various intermediates is crucial for the validation of reaction mechanism from *in situ* and *operando* surface analytical techniques and also to reduce the number of possible reaction pathways that have to be modelled computationally.

There are three possible reaction mechanisms for ammonia synthesis on catalysts. The most accepted mechanism is the Langmuir-Hinshelwood (L-H) mechanism, which is the mechanism that takes place on the iron19, 20 and ruthenium12, 21, 22 catalyst. In addition to this general mechanism which is dissociative, other associative mechanism23 which follow Mars-van Krevelen (MvK) and Eley-Rideal (E-R) mechanisms have been recognised for ammonia synthesis on metal nitrides. 13, 14, 24

Initially we used Lewis representations to predict various possible surface intermediates for the ammonia synthesis reaction. Out of the 18 Lewis structures with stoichiometries NxHy (where x ≤ 2 and y ≤ 3) we found that there are eight stable intermediates for the ammonia synthesis reaction. Our detailed computational study determined that some of these adsorbates bind to the surface of Mn3N2-(100) and that the inert bond of dinitrogen becomes significantly activated due to hydrogenation reactions. We have then calculated various L-H and E-R mechanisms for ammonia synthesis at intrinsic nitrogen vacancies of the on Mn3N2-(100) surfaces.

**1. Computational Methods**

In order to model the bulk and surfaces of *η*-Mn3N2 we have used the coordinates as determined by powder neutron diffraction (ND) at ambient temperature.25 The bulk unit cell of *η*-Mn3N2 is an fcc arrangement of Mn with N occupying the octahedral sites. This unit cell is face-centred tetragonal with the following lattice parameters, a = 4.2046 Å, b = 4.2046 Å, c = 12.1311 Å, α = β = γ = 90°.25 The (100) surface was modelled via a slab of a thickness of 6.3Å measured between the centers of two surface Mn atoms. The slab model had a 20 Å vacuum gap from which the various adsorbates were let to interact with the surface. All DFT calculations were periodic Γ-point centered with a 3x5x1 Monkhorst-Pack grid26 spin-polarised obtained with the use of the VASP 5.4.1 code.27, 28 Exchange and correlation effects were considered within the generalized gradient approximation (GGA) using the revised Perdew-Burke-Ernzerhof (revPBE) exchange-correlation (XC) functional,29 with the projector augmented-wave (PAW) method30, 31 used to represent core states. These were 1s to 3p for Mn and 1s for N and H. The cut-off energy for the energy of the planewaves was 600 eV. Geometry optimizations were performed with a residual force threshold on each atom of 0.01 eV Å-1 using the conjugate-gradient algorithm. The electronic relaxation convergence criterion was set to 10-4 eV. The initial charge density was obtained by superposition of atomic charges.Initial adsorption configurations where such that the distance between the adsorbate and the nearest surface site was roughly that of the adsorbate-cluster distance. The various adsorption sites were every symmetry unique surface site determined in Figure 3, which resulted in 5 sites for the (100) surface. The adsorption energy was taken as the total energy difference between the fully relaxed bound state of the surface-adsorbate complex from that of the fully relaxed surface slab and the isolated molecules given by:

ΔΕads, D3 = Eslab-adsorbate - Eslab - Eadsorbate (1).

Dispersion corrections were included via the zero-damping DFT-D3 correction method of Grimme as implemented in VASP, 32 in which the following dispersion energy correction is added to the Kohn-Sham energies,

, (2)

where and denote the averaged (isotropic) 6th and 8th order dispersion coefficients for atom pair ij and is the internuclear distance between atoms i and j, respectively, and are the functional-dependent scaling factors.

**2 Results and Discussion**

The identification of surface intermediates in heterogeneous catalytic reactions relies mostly on chemical intuition and quantum chemical calculations. Therefore, elucidating reaction mechanisms on catalysts can be challenging given that these studies rely on methods that are not always experimentally verifiable and as sometimes entirely based on chemical intuition.

**2.1 Locating potential adsorbates via Lewis representations**

We have used Lewis representations to find possible structures of the intermediates of the ammonia synthesis reaction. An adsorbate that participates in the surface chemical reaction was constructed having a particular stoichiometry (e.g. NH, N=NH, HN=NH) by Lewis representations and then tested how well it interacts with the surface of Mn3N2-(100) surfaces. The structures that were generated using Lewis representations are depicted in Figure 1 and are based on the following algorithm: (i) assume that these adsorbates are not charged, (ii) nitrogen follows the octet-rule (i.e. the rule of eight33) (iii) nitrogen is bound to the manganese atoms of the substrate and not nitrogen of the metal nitride cluster (i.e. this excludes the formation of azido compounds that we observed to form on tantalum nitrides34) and that each substrate-N bond is due to equal sharing of one electron from nitrogen and one electron from the manganese atom. Additionally, For the 3D design of the adsorbates we have taken into account four design criteria for the nitrogen atoms (i) that when they bond to four chemical groups (e.g. 4 single bonds) they are tetrahedrally coordinated, (ii) that when they are bond to three electron groups (e.g. a double bond, a single bond and a lone electron pair) they are trigonally coordinated, (iii) that when they bond to two electron groups (e.g. a single bond and a triple bond) then they have linear configurations and (iv) that the dinitrogen configuration can be either *end-on*, *side-on* or *tilt end-on* based on the binding dinitrogen on another metal nitride.14 This approach significantly reduced the configurational space of the 3D structures that could be constructed using Lewis representations. From this algorithm generated 18 possible structures depicted in Figure 1 for NxHy adsorbates, where x ≤ 2 and y ≤ 3, that were designed to be bound to be bound to the Mn3N2-(100) surface and optimised using various starting structures. The resulting converged structures for these adsorbates are depicted in Figure 2. These structures are also given as supporting information in Figure S1. We found that cluster adsorbate calculations are generally difficult to converge and many different starting geometries were necessary in order to generate the results presented in Figure 2, which may be a result of the cluster being unable easily accommodate the additional charge from the adsorbate bond, while in the periodic calculations the empty d-states are extended, and therefore, charge transfer occurs more easily, giving more rapid convergence. In some cluster-adsorbates, we had to add a charge in order to find a stable structure for the adsorbate (i.e. **D**, **F**, **H** and **I**). However, these calculations are computationally inexpensive and need only a few hours to converge on a dual-core machine. Therefore, we could screen a large number of different starting geometries to sample thoroughly the configurational space of NxHy adsorbates, where x ≤ 2 and y ≤ 3. Study of the adsorption of adsorbates that have not previously been identified for the ammonia synthesis reaction on the (100) surface of Mn3N2 is performed in the following sections.



Figure 1. Lewis structures of various possible intermediates NxHy (x = 1, 2 and y = 1, 2, 3) on a three-fold hollow of the substrate. The symbol "S" refers to a substrate atom which for the model system under investigation is a "Mn" atom.

**2.2 Adsorption of HN=NH and N=NH on Mn3N2 surface**

Table 3. Adsorption energy, percent activation and selected structural parameters for optimised structures of HN=NH and N=NH on Mn3N2-(100) surface calculated with Ecut = 600 eV , a 3x5x1 gamma-point MP grid and the revPBE functional. Fractional coordinates of the various structures are given as supporting information Figure S2.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Property** | **site 1** | **site 2** | **site 3** | **site 4** | **site 5** | **site 1** | **site 2** | **site 3** | **site 4** | **site 5** | **Units** |
|  | **HN=NH** | | | | | **N=NH** | | | | |  |
| **ΔEads,D3** | -155 | -133 | -134 | -103 | -184 | -150 | -135 | -138 | -178 | -181 | kJ/mol |
| **r(N-N)** | 1.336 | 1.323 | 1.323 | 1.394 | 1.424 | 1.283 | 1.277 | 1.279 | 1.375 | 1.374 | Å |
| a**(Mn-N-N)a** | 114.6 | 108.3 | 108.3 | 130.7 | 113.8 | 114.7 | 109.1 | 109.1 | 114.5 | 114.6 | ° |
| **r(N-H)b** | 1.027 | 1.028 | 1.026 | 1.031 | 1.028 | 1.030 | 1.033 | 1.032 | 1.030 | 1.033 | Å |
| **r(Mn-N)c** | 1.974 | 2.006 | 2.006 | 2.142 | 2.074 | 1.896 | 1.941 | 1.934 | 2.009 | 2.032 | Å |
| **N2 activationc** | 18 | 17 | 17 | 22 | 24 | 14 | 13 | 14 | 21 | 21 | % |
| a Angle taken as average of two angles | | | | |  |  |  |  |  |  |  |
| b Bond length taken as average of two bonds when two N-H groups present | | | | | | | | |  |  |  |
| c Bond length taken as average of two bonds | | | | |  |  |  |  |  |  |  |
| d Percent activation is defined as [r(N2H2,ads)-r(N2,g)]\*200/[r(N2,g) + r(N2H2,ads)] | | | | | | | | | |  |  |

The adsorption of N2, HN=NH and N=NH was studied on the surface of Mn3N2 using periodic DFT-D3 calculations. The results for HN=NH and N=NH are presented in Table 3. We have calculated the adsorption properties at five symmetry unique sites of the (100) surface of Mn3N2, which are depicted in Figure 3. The adsorption of N2 was found to be molecular at these five sites and very weak (-12 kJ mol-1 to 38 kJ mol-1). In particular, only at the nitrogen-vacancy (**site 5**) was it adsorbed close to the surface in a side-on configuration, residing in the four-fold hollow and simultaneously bound to four Mn atoms (ΔEads,D3 = 38 kJ mol-1). We anticipate that the N2 adsorbed at **site 5** can undergo further hydrogenation reactions as presented in scheme 1 in order to form the new intermediates of the ammonia synthesis reaction, N=NH and HN=NH. Dinitrogen activation at this site was calculated to be 12% which is comparable to the 11% activation of N2 on Co3Mo3N-(111) surface, where, however, it was adsorbed in an end-on configuration.14 These calculated intermediates should, therefore, be considered in attempts to elucidate the mechanism of ammonia and hydrazine synthesis. Particular attention should also be given to mechanisms in which the intrinsic nitrogen vacancies of this material actively participated in surface reactions, similar to the mechanisms of ammonia synthesis on cobalt molybdenum nitride.13

We next present the results for the adsorption of HN=NH and N=NH which are schematically depicted in Scheme 1 on the (100) surface of Mn3N2 at the five symmetry unique sites. Scheme 1 also depicts the hypothetical hydrogenation mechanism via L-H which for the ammonia synthesis reaction mechanism.



Scheme 1. Simplified schematic presenting the adsorption of N2 to nitrogen vacancies on the surface of Mn3N2 and their successive hydrogenation.

For the adsorption of N=NH, the average bond length of the Mn-NH was found to be consistently 8% longer than the Mn-N bond length, which is consistent with the fact that the additional hydrogen reduces the partial negative charge on the nitrogen making the Mn-N weaker. The percentage activation of the N-N bond was found to be consistently larger (17 to 24 %) for HN=NH than for N=NH which was (13 to 21%), which indicates that hydrogenation reactions such as the one presented in Scheme 1 can cause further activation of the N-N bond, decreasing therefore the barrier for its dissociation (note that the bond dissociation enthalpy of N2 is very high, 945 kJ mol-1)35. The adsorption energies though of HN=NH and N=NH were found to be very similar. For all adsorption sites apart **site 4** the adsorption energy only differed by less than 5 kJ mol-1 for HN=NH and N=NH. However, for **site 4** the adsorption configuration was found not to be the same for HN=NH and N=NH. In fact although both HN=NH and N=NH had the same starting structure which is presented in Figure 3 (**site 4**) for NH=NH, the optimised structure for N=NH was such that it resided side-on in the four-fold hollow simultaneously bound to four Mn atoms (these are the 4 surface Mn atoms surrounding the N-vacancy), which is consistent with Scheme 1 for the adsorption configuration of N2. We, therefore, observe that for all adsorbates studied (i.e. N2, N=NH and HN=NH) it is only **site 4** that results in an adsorbed configuration where the N-N bond is significantly activated. Furthermore, in this adsorbed configuration the nitrogen is adsorbed close enough to the surface Mn atoms so that hydrogenation reactions can occur. These hydrogenation reactions should weaken the N-N bond as they withdraw electronic charge from the occupied p and d electrons of Mn which would become a facile route for activating the relatively inert triple bond of di-nitrogen.

To summarise, N2, N=NH and HN=NH can bind at nitrogen vacancy sites on the (100) surface of Mn3N2 and be significantly activated due to adsorption and subsequent hydrogenation reactions.



Figure 3. Side and top structures of HN=NH adsorbate on Mn3N2 surface. The N=NH adsorbate was bound to the same sites on this surface and the adsorption structures and energies are given in table 3.

**2.3 Reaction pathways for ammonia synthesis on Mn3N2-(100) surfaces**

Based on the reaction intermediates indetified in the previous sections we have modelled various potential mechanisms for ammonia synthesis on the (100) surface of Mn3N2. These reaction mechanism are given in Fig. 4 - 7 and described in schemes 2 - 5. In the first mechanism which synthesizes hydrazine via Langmuir-Hinschelwood chemistry and susequently ammonia via Eley-Rideal chemistry we find that the ammonia synthesis step is prohibitive as the barrier (i.e. **I** to **J**) is 153 kJ mol-1 which is relatively prohibitive at moderate temperatures. Suprisingly though the mechanism for hydrazine synthesis on this catalysts appears facile as all the barriers for the reaction are in the range of 38 kJ mol-1 (i.e **A** to **C**) to 64 kJ mol-1 (i.e. **D** to **E**) which are considerablly lower than the Eley-Rideal mechanism step for ammonia synthesis seen in Scheme 2 step **I** to **J**. It is intriguing that this mechanism occurs entirely at a nitrogen vacancy on the (100) surface of Mn3N2 and that the intermediate N2 and HN-NH both have the side on configuration as this is depicted in **site B** and **site F** of Figure 3. Molecular hydrogen dissociatively chemisorbs at nearly Mn sites as this can be seen in **C** and **D** of Scheme 2, which due to the presence of unpaired electrons bind atomic hydrogen better than molecular hydrogen. These atomic H species can from this position react very efficiently through low barrier process with N2 and subsequently with HN-NH forming hydrazine that is bound to the intrinsic nitrogen vacancy of Mn3N2. The subsequent further hydrogenation of hydrazine to ammonia appears energetically unfavourable and therefore this reaction mechanism is expected to saturate the surface of the catalysts with hydrazine which under high hydrogen feedstream should desorb the product hydrazine after flash annealing of the catalyst at moderate temperatures



Fig. 4 **Mechanism-1**: Potential energy diagram of hydrazine and ammonia synthesis reaction via a Langmuir–Hinshelwood and subsequent ammonia synthesis via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2



Scheme 2 **Mechanism-1**: Simplified schematic of the hydrazine synthesis reaction via a Langmuir–Hinshelwood mechanism and subsequent ammonia synthesis via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2



Fig. 5 **Mechanism-2**: Potential energy diagram of the hydrazine and ammonia synthesis reaction via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2



Scheme 3 **Mechanism-2**: Simplified schematic of the hydrazine and ammonia synthesis reaction via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2



Fig. 6 **Mechanism-3**: Potential energy diagram of the hydrazine and ammonia synthesis reaction via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2



Scheme 4 **Mechanism-3**: Simplified schematic of the hydrazine and ammonia synthesis reaction via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2

**Mechanism 4**



Fig. 7 **Mechanism-4**: Potential energy diagram of the hydrazine and ammonia synthesis reaction via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2



Scheme 5 **Mechanism-4**: Simplified schematic of the hydrazine and ammonia synthesis reaction via an Eley–Rideal mechanism at intrinsic nitrogen vacancies on η-Mn3N2

**Summary and Conclusions**

We have used dispersion-corrected hybrid DFT calculations to identify potential intermediates of the ammonia synthesis reaction on manganese nitride clusters and extended (100) surfaces. The calculated IR oscillator frequencies and intensities may assist in the experimental identification of the adsorbates on actual manganese nitride catalysts using surface IR spectroscopies. We have used a simple Lewis structure representation algorithm in order to locate various possible NxHy intermediates, using computationally inexpensive adsorbate-cluster calculations. Based on these cluster and surface calculations we have identified intermediates, (i.e. HN=NH and N=NH) for the ammonia synthesis reaction on Mn3N2. Both these intermediates adsorb side-on at the four-fold hollow of *intrinsic* nitrogen vacancies of this metal nitride. We hypothesize that the hydrogenation of dinitrogen, to N=NH and then to HN=NH is possible when it is bound side-on at intrinsic nitrogen vacancies which results in significant activation of the N-N triple bond. Therefore, our computational adsorption and IR calculations can act a guide for experimental efforts to identify these intermediates spectroscopically over metal nitride surfaces.

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Supporting Information

The Cartesian coordinates of the structure of the various cluster-adsorbates (Figure S1) and the fractional coordinates of the various surface-adsorbate slabs (Figure S2) are given as supporting information.

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