



Electronic structure and catalytic activity of TM@Mg₁₂O₁₂ nanocages for ambient ammonia synthesis

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ABSTRACT

The development of low-cost and efficient electrocatalysts for the ambient nitrogen reduction reaction (NRR) is essential for the synthesis of NH₃ and offers a substitute for the conventional Haber-Bosch process. In the present work, density functional theory (DFT) is employed to investigate the electrochemical nitrogen reduction reaction (NRR) catalysed by TM@Mg₁₂O₁₂ (TM = Sc ~ Zn) nanocages. All complexes exhibit chemisorption interactions with interaction energies ranging from −2.49 eV to −1.11 eV, except Zn@Mg₁₂O₁₂ (−0.48 eV) which shows physisorption. The energy gaps (*E_g*) of TM@Mg₁₂O₁₂ are significantly reduced compared with pristine Mg₁₂O₁₂ indicating enhanced conductivity. Electronic properties and interaction types were analyzed using density of states, natural bond orbital, interaction region indicator, and quantum theory of atoms in molecules analyses. The results reveal that TM doping notably enhances N₂ activation relative to pure Mg₁₂O₁₂. Among all candidates, Mn@Mg₁₂O₁₂ exhibits the highest NRR activity, with a limiting potential of −0.84 V along the alternating pathway. The stability and energetics of intermediates were further assessed to determine the optimal reaction mechanism for NH₃ synthesis. This study provides fundamental insights into the rational design of single-atom catalysts supported on three-dimensional nanocages, contributing to the development of efficient electrocatalysts for ambient ammonia synthesis.

1. Introduction

Ammonia (NH₃) is a key source of nitrogen for many biological molecules, including amino acids and nucleotides [1]. The conversion of atmospheric nitrogen (N₂) into ammonia is essential for sustaining life [2]. In addition to its biological significance, ammonia plays a major role in chemical manufacturing, particularly as a primary component of modern fertilizers [3]. Agricultural fertilizers, such as urea (NH₂)₂CO, ammonium phosphate, (NH₄)₃PO₄, ammonium sulfate (NH₄)₂SO₄ and ammonium nitrate NH₄NO₃ are made from the vast majority of the ammonia [4]. Rubber, plastics, explosives, synthetic fibers, pharmaceuticals, and numerous other products are produced as well [3]. It is also gaining attention as a potential carbon-free fuel and a carrier for renewable energy, making it important for future energy transportations [5]. Energy generated by non-renewable sources like fossil fuels and gasoline usually releases hazardous pollutants into the atmosphere, having adverse effects on human health. Extreme weather events [6], the thawing of permafrost in the Arctic [7], mass coral bleaching [8],

and other phenomena are thought to be associated with human-induced climate change. It is an ideal H₂ energy carrier due to its high energy density (17.6 % H content by mass) and relatively low transportation costs [9]. Bulk liquid NH₃ may be stored and transported using a well-established infrastructure. Therefore, the renewable NH₃ can be considered as a carbon-free chemical, and it might take the role of fossil fuel in a strategy to achieve zero carbon emissions.

At present, more than 90 % ammonia has been produced using the Haber-Bosch process, an innovation that has proven vital in sustaining the significant increase in the world's population in the last century [10]. This technique produces ammonia by reacting N₂ and H₂ at high temperatures (400–600 °C) and high pressures (20–40 MPa), using iron-based catalysts [10]. However, high temperatures are required to break the strong N≡N bond at significant rates due to its exceptionally high kinetic barrier [11]. Overall yields of around 97 % can be attained by recycling the unreacted N₂ and H₂ to the reaction chamber, even if only about 15 % conversion to ammonia is produced in a single reaction [12]. In light of its reliance on fossil fuels and high energy requirements,

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industrial ammonia synthesis has a detrimental effect on the environment. For instance, hydrogen gas is created in highly endothermic processes from fossil fuels like natural gas (72 %), coal, and petroleum [13], whereas cryogenic techniques are usually needed to extract the nitrogen feedstock from the atmosphere [14]. In addition to consuming 2–3 % of the world's energy supply and 2–5 % of natural gas, this process usually contributes to 3 % of global CO₂ emissions [15]. Therefore, finding alternatives to the energy-intensive Haber-Bosch process is essential.

Several approaches, such as plasma, chemical looping, electrochemical, and photochemical techniques, have been put forth to mitigate the Haber-Bosch energy consumption, pollution, and safety concerns, promoting sustainable green energy [16–18]. One of the most intriguing technique is the electrochemical reduction of the nitrogen molecule and it takes sustainability and energy consumption into consideration [4]. However, N≡N bonds in N₂ molecules are challenging to activate or break owing to their high ionization potential, cleavage energy and bond energy [11]. Additionally, competitive hydrogen evolution process (HER), which has a major impact on the efficiency of NH₃ synthesis, is one of the difficulties with nitrogen reduction reactions. To obtain a high efficiency and low energy consumption, it is crucial to design and use effective catalysts that can lower the bonding energy of N₂ molecules and activate the especially stable N≡N bonds.

Single-atom catalysts (SACs), an innovative technique that involves dispersing single atoms on a support, have garnered significant attention since their discovery in 2011 and are an emerging area in heterogeneous catalysis [19]. More significantly, compared to their nanoparticle counterparts, SACs exhibit unique catalytic activity, selectivity, and stability due to their distinct geometric and electronic structure [20]. It provides distinct active sites and optimizes atomic efficiency. Various SACs have synthesized experimentally by different methods such as the wet chemistry approach, atomic layer deposition method, and mass-selected soft-landing technique [21]. These SACs have spurred a significant utilization in the fields of CO₂ reduction, oxygen evolution and reduction [22], hydrogen evolution, water splitting [23] and nitrogen reduction reactions [24,25]. Single metal atoms are stabilized via forming strong bonds with anchoring sites on the support surface, which frequently include nanomaterials. They are the most efficient materials overall due to their high surface area and excellent electron mobility.

In this regard, finding reliable support compatible with single-atom catalysts (SACs) has become increasingly challenging. Liu *et al.* has theoretically investigated the transition metal atoms incorporated phthalocyanine monolayer (TM@Pc) catalysts for the N₂ activation and reduction and Mo@Pc exhibited the highest catalytic activity [26]. Three-dimensional nanocages, with their high surface area and abundant catalytic active sites, offer potential features that have captured the interest of many researchers. These materials effectively accelerate catalytic reactions and exhibit superior reactivity due to their unique properties. Among them, M₄@B₃₆N₃₆ (M = Sc-Cr, Y-Mo, Hf-W) has recently been investigated for nitrogen reduction reaction and shows a higher tendency to adsorb N₂. Notably, Mo₄@B₃₆N₃₆ requires only 0.19 V for the onset potential [27]. The NiCoS/C nanocage also demonstrates an excellent Faradaic efficiency of 12.9 %, attributed to the strong interaction between carbon and NiCoSe [28]. Furthermore, the Au-Ag-Pd nanocage, exhibits outstanding NRR performance with a high NH₃ yield rate and Faradaic efficiency as reported by Nazemi *et al.* [29]. These findings suggest that nanocages hold significant promise as catalytic substrate materials [30]. Their three-dimensional structure typically offers more active sites and a larger surface area than two-dimensional materials of the same size.

Nowadays, X₁₂Y₁₂ nanocages (where X = Al, B, Be, Mg and Y = N, O, P) have attracted considerable interest across various fields, including chemical sensing [31], hydrogen storage, nonlinear optics [32], drug delivery [33], and catalysis [34]. Their wide applicability is attributed to unique properties such as high chemical stability, a distinctive cage-like structure, and sufficient electrical conductivity. Ziemann and

Castleman demonstrated that Mg₁₂O₁₂ nanocages have exceptional stability in (MgO)_n, (n ≤ 90) nanostructures [35]. It has also shown promising applications in nonlinear optics, drug delivery, chemical sensing, and hydrogen storage. The potential of Be₁₂O₁₂, Mg₁₂O₁₂, and Zn₁₂O₁₂ nanocages for delivering the anticancer drug hydroxyurea was investigated by Fallahi *et al.* [36]. Additionally, Shakerzadeh *et al.* studied the alkali metal (Li, Na, & K) decorated Mg₁₂O₁₂ and Be₁₂O₁₂ nanocages for nonlinear optical applications. Their study revealed that encapsulating a Li atom inside the Mg₁₂O₁₂ cage significantly enhanced its hyperpolarizability of the nanocage [37]. Recently, Allangawi *et al.* theoretically investigated the suitability of late first-row transition metals (Fe-Zn) supported on Mg₁₂O₁₂ as SACs for the hydrogen evolution reaction [38]. These characteristics demonstrate that the Mg₁₂O₁₂ nanocage possesses the ideal properties to serve as support in single atom catalysis.

Despite of numerous breakthroughs in nitrogen reduction reactions (NRR), almost no endeavor has been made to describe transition metal (Sc-Zn) especially Mn based single-atom catalyst (SAC) for nitrogen activation and the reduction of Mg₁₂O₁₂ nanocage. To the best of our knowledge, the geometrical and thermodynamic stability, Gibbs free energy changes, and applied electrode potential of suggested system have not been explored yet. This gap motivates our interest in describing N₂ reduction to ammonia by using SAC based nanomaterials. Furthermore, our aim to investigate a detailed mechanistic pathway to elucidate the NRR mechanism and N₂ binding strengths on catalysts for practical applications. It is anticipated that our work will not only advance new insights into the N₂ reduction process but also provide sustainable NH₃ production.

2. Computational methodology

All the DFT calculations were carried out using Gaussian 16 [39] program package and structures were visualized by the Gauss View 6.0 [40] software. The hybrid B3LYP exchange correlation functional [41] along with the 6–31 + G (d,p) basis set [42] was employed for conducting various simulations. All intermediates involved in the process of NRR were considered with the DFT-D3 empirical dispersion correction method of Grimme to correct the van der Waals (vdW) interactions [43]. All of the single atom catalysts were first optimized to identify the stationary points. Frequency calculations were also carried out to distinguish between the transition state, intermediate and local minima of the reactant and products. To investigate the charge transfer between transition metal atoms and the substrate, natural population analysis was carried out. To evaluate the thermodynamic stability of designed complexes, binding energies were calculated as follows:

$$E_b = E_{\text{Metal@Mg}_{12}\text{O}_{12}} - (E_{\text{Mg}_{12}\text{O}_{12}} + E_{\text{Metal}}) \quad (1)$$

where, E_b is the total or binding energy of complex and $E_{\text{Mg}_{12}\text{O}_{12}}$ and E_{Metal} are the energies of nanocage.

To investigate the charge transfer between transition metal atoms and the Mg₁₂O₁₂ nanocage, natural bond orbital analysis was carried out. Further analysis including quantum theory of atoms in molecules (QTAIM) and interaction region indicator (IRI) were conducted at the same level of theory. Electron densities and related parameters were computed using Multiwfn [44] and visualized with visual molecular dynamics (VMD) [45]. In addition, partial density of states (PDOS) and total density of states (TDOS) spectra were analysed to evaluate the contribution of various fragments in the formation of frontier molecular orbitals.

To further confirm the thermodynamic and chemical stability of SACs complexes, ab initio molecular dynamics (AIMD) simulations are carried out by using built in atom-centered density matrix propagation (ADMP) technique as implemented in Gaussian 16. A thermostat is applied to retain the 300 K temperature, and the simulation trajectory is 250 fs with a 0.1 fs time step.

After designing the catalyst, N₂ molecule will be activated over the designed catalyst, and the adsorption energies can be calculated as:

$$E_{\text{Ads}} = E_{\text{Tot}} - (E_{\text{Metal@Substrate}} + E_{\text{Adsorbate(N}_2\text{)}}) \quad (2)$$

The activation barrier for N₂ has been calculated to assess the efficiency for N₂ activation and its reduction to NH₃. As a result, the change in Gibbs free energy (ΔG) for each step under study was determined by subtracting the Gibbs free energy of the reactants from products. The Gibbs free energy of each step will be calculated by using the following equation [46]:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} \quad (3)$$

Here, ΔE is the energy obtained via DFT simulations, ΔE_{ZPE} is zero point correction and $T\Delta S$ is the change in entropy at STP. Using vibrational computation, the entropies of each NRR intermediate were determined. Moreover, ΔG_U is the contribution of the electrode potential to Gibbs free energy and $\Delta G_{\text{pH}} = k_b T \times \ln 10 \times \text{pH}$, where, k_b is Boltzmann constant under standard reaction conditions. The activity of catalysts is determined by the limiting potential (U_L), which is $U_L = -\Delta G_{\text{max}}/e$, where ΔG_{max} is the most positive value of the six protonation steps. Beside this, to address the possibility of metal leaching, oxidation, and agglomeration, some explicit thermochemical analyses such as dissolution (ΔG_{Diss}), oxidation (ΔG_{Oxi}) and dimerization (ΔG_{Dim}) for Mn@Mg₁₂O₁₂ have also been carried out at the B3LYP-D3/6–31 + G(d, p) level of theory with aqueous solvation (CPCM).

3. Results & discussion

3.1. Geometry optimization and stability

The geometry optimization of pristine Mg₁₂O₁₂ nanocage has been carried out using DFT simulations. It consists of eight six-membered rings and six four-membered rings and the Mg–O bond lengths in these optimized 6-membered and 4-membered rings are 1.89 and 1.95 Å, respectively. These values also validate the reliability of the B3LYP-D3/6–31G+(d,p) level of theory and results align with previously reported work [37,47]. Six unique binding positions namely B64 (b is doping of TM on the bond fused between two rings), R4 (r shows doping of transition metal on ring), R6, B66, magnesium top and oxygen top of the Mg₁₂O₁₂ nanocage for transition metal doping are selected as depicted in Fig. 1.

All the six positions of the TM@Mg₁₂O₁₂ complex have been optimized at the same level of theory to determine the best location site for TM doping. After optimization, each of the six variants converged to the oxygen top position and preference of TM for the oxygen top position is somewhat expected as the first-row TMs are electropositive in nature [48] and are drawn to the strongly electronegative oxygen atom. Additionally, it is highly unfavourable for the TMs to diffuse to other sites, as evidenced by the convergence of the TMs from all sites toward

the oxygen top site and their TM@Mg₁₂O₁₂ complexes are shown in Fig. 2. Furthermore, a similar behaviour was described by Shakerzdeh et al., [37] and Allangawi et al., [38] when they observed the doping of metal atoms on the Mg₁₂O₁₂ nanocage.

Another significant factor is that, as the transition metal moves across the periodic table from Sc to Cr, its size decreases and its effective nuclear charge increases. This is demonstrated by the bond distances of O–TM as listed in Table 1, show a decreasing trend from Sc (1.93 Å) to Cr (1.90 Å) and then again increase for Mn. As the size of the Mn increases and the shielding effect increases, the bond length (1.98 Å) in Mn@Mg₁₂O₁₂ increases. This could be due to the bond between the Mn and Mg₁₂O₁₂ nanocage is weaker. When it comes to late transition metal atoms, the bond distance from Fe (1.89 Å) to Zn (2.35 Å) increases. This is due to the fact that electron–electron repulsion occurs in late transition metal atoms when the d-orbitals are partially or fully filled. This repulsion contributes to expand the electronic cloud and may results to an increase in the size of the metal atom.

Moreover, spin state analysis for all complexes has been carried out as TM atoms have valence electrons in d-orbitals, they may reside in multiple spin states. In d-orbitals, valence electrons can reside as unpaired electrons when the corresponding energies of orbitals are similar or as pairs when they are far separated [48]. Only the most stable spin state is taken into consideration for additional analysis after spin-polarized computations. The values of the spin polarized computations ($\langle S^2 \rangle$) in Table 1 demonstrate that there is no spin contamination. A stable spin state of any transition metal may be different from that of its surrounding elements because of its odd or even number of electrons. Additionally, middle transition elements have more unpaired electrons than early or late transition metals, they are more likely to show higher multiplicities [49]. As a result, the spin states increase monotonically from doublet (for Sc@Mg₁₂O₁₂) to sextet (for Mn@Mg₁₂O₁₂) and then decrease from quintet (for Fe@Mg₁₂O₁₂) to singlet (for Zn@Mg₁₂O₁₂) as listed in Table S1. A similar trend of spin states variation has been observed previously by Ayub et al., on transition metal-doped Al₁₂N₁₂ nanocage [50]. Another significance of performing spin-polarized calculations is highlighted by the observation that the energy differences between the spin states can reach 3.31 eV.

The stability of SACs supported Mg₁₂O₁₂ nanocages has been estimated by computing the interaction energy of each complex. Stability of the structures is determined by negative interaction energy values; higher stability is implied by a larger negative interaction energy value. It is evident from the Table 1 that all transition metal doped complexes exhibit chemisorption interaction, as evidenced by the interaction energies, which range from –2.49 eV for Cr@Mg₁₂O₁₂ to –1.11 eV for Cu@Mg₁₂O₁₂ complexes whereas physisorption is observed for the Zn@Mg₁₂O₁₂ with an interaction energy of –0.48 eV. The monotonic trend was not followed by interaction energies due to several competing factors, including metal size, nature, interaction distance, and various spin states. To prevent aggregation and ensure that the metal atoms in the SACs are evenly distributed on the support, the E_{int} values must be less than the TM–TM bond. As a result, SACs with finely distributed single-atom sites and lower interaction energies should be more effective. Strong interaction energies from Sc@Mg₁₂O₁₂ to Ni@Mg₁₂O₁₂ indicate that these metals will be easier to disperse on the nanocage. However, owing to the possibility for aggregation, care must be taken when synthesizing SACs based Cu@Mg₁₂O₁₂ and especially Zn@Mg₁₂O₁₂ complexes. The E_{int} values found in the present study coincide with those reported in the previous literature [51–53].

3.2. Natural bond orbital analysis

The charge transfer between the single transition metals and Mg₁₂O₁₂ support for SACs has been determined via the natural bond orbital (NBO) [54]. The transition metal atoms are electropositive, and it is assumed that they can be polarized on interaction with the oxygen atoms of pristine Mg₁₂O₁₂ that has high negative NBO charges (–1.825 |

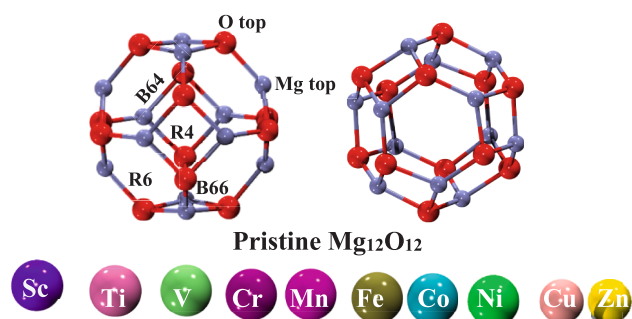


Fig. 1. Schematic structures of the Mg₁₂O₁₂ nanocage and transition metal atoms are shown in different colors.

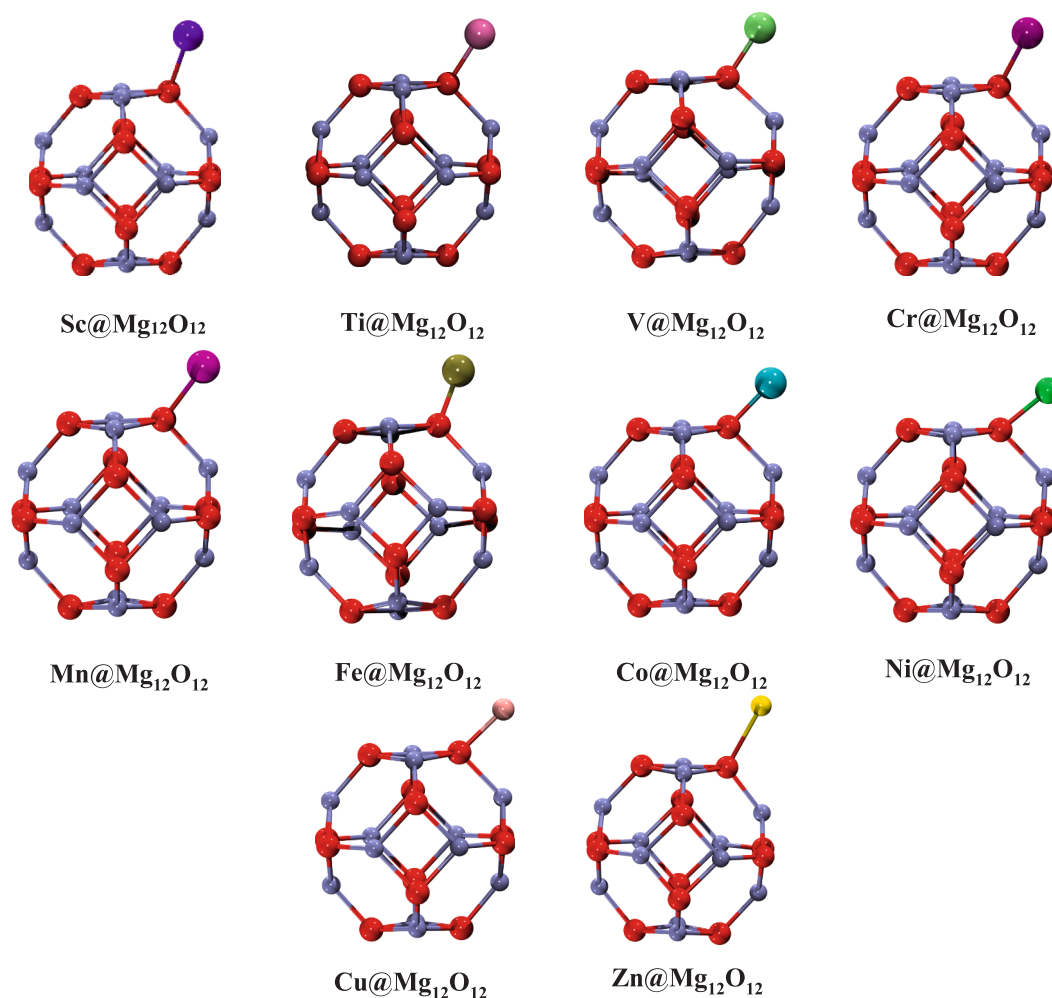


Fig. 2. Optimized complexes of transition metals (Sc-Zn) doped Mg₁₂O₁₂ nanocages.

Table 1

Optimized complexes of TM@Mg₁₂O₁₂ with first frequencies ν_1 (cm⁻¹), interaction distances between metal atom and nanocage D_{O-TM} (Å), symmetry and E_{int} interaction energies (eV).

Complexes	ν_1 (cm ⁻¹)	D _{O-TM} (Å)	Symmetry	E _{int} (eV)	<S ² >
Sc@Mg ₁₂ O ₁₂	22.61	1.93	C ₁	-2.23	0.75
Ti@Mg ₁₂ O ₁₂	20.50	1.91	C ₁	-2.35	2.01
V@Mg ₁₂ O ₁₂	23.61	1.91	C ₁	-2.09	3.81
Cr@Mg ₁₂ O ₁₂	53.78	1.90	C ₁	-2.49	6.01
Mn@Mg ₁₂ O ₁₂	32.42	1.98	C ₁	-1.17	8.75
Fe@Mg ₁₂ O ₁₂	30.78	1.89	C ₁	-2.24	6.01
Co@Mg ₁₂ O ₁₂	29.25	1.90	C ₁	-1.56	3.75
Ni@Mg ₁₂ O ₁₂	39.46	1.91	C ₁	-1.41	2.01
Cu@Mg ₁₂ O ₁₂	32.95	1.94	C ₁	-1.11	0.75
Zn@Mg ₁₂ O ₁₂	28.77	2.35	C ₁	-0.48	—

e|). In the Sc@Mg₁₂O₁₂ and Mn@Mg₁₂O₁₂ complexes, the charges on the TMs are positive and fall between 0.052 and 0.039 |e|. The amount of charge transfer on all other complexes is negative; Ti@Mg₁₂O₁₂, V@Mg₁₂O₁₂, Cr@Mg₁₂O₁₂, Fe@Mg₁₂O₁₂, Co@Mg₁₂O₁₂, Ni@Mg₁₂O₁₂, Cu@Mg₁₂O₁₂ and Zn@Mg₁₂O₁₂ have -0.013, -0.042, -0.009, -0.025, -0.026, -0.186, -0.014, and -0.002 |e|, respectively, as depicted in Table 2.

The charge that has been shifted from the TM to the Mg₁₂O₁₂ support and back from nanocage to the single metal atoms. The Sc@Mg₁₂O₁₂ exhibits the highest positive charge transfer on metal atom due to the

Table 2

NBO charges Q_M (|e|), HOMO energies (eV), LUMO energies (eV), HOMO-LUMO energy gap (eV), and percentage E_g of designed complexes.

Complexes	Q _M (e)	E _(HOMO) (eV)	E _(LUMO) (eV)	E _g (eV)	%E _g (eV)
Mg ₁₂ O ₁₂	—	-6.59	-1.78	4.81	—
Sc@Mg ₁₂ O ₁₂	0.052	-3.61	-1.76	1.83	61.8
Ti@Mg ₁₂ O ₁₂	-0.013	-4.33	-1.78	2.54	47.1
V@Mg ₁₂ O ₁₂	-0.042	-4.55	-1.77	2.77	42.29
Cr@Mg ₁₂ O ₁₂	-0.009	-4.91	-1.90	3.01	37.47
Mn@Mg ₁₂ O ₁₂	0.039	-4.33	-1.91	2.42	49.55
Fe@Mg ₁₂ O ₁₂	-0.025	-4.23	-1.88	2.35	51.08
Co@Mg ₁₂ O ₁₂	-0.026	-4.18	-1.87	2.31	51.99
Ni@Mg ₁₂ O ₁₂	-0.186	-4.15	-1.85	2.30	52.09
Cu@Mg ₁₂ O ₁₂	-0.014	-4.05	-1.84	2.21	54.11
Zn@Mg ₁₂ O ₁₂	-0.002	-5.12	-1.89	3.22	32.93

biggest size of metal atom. The negative charge transfer shows increasing order from Ti to V and then decreases for Cr the shielding effect, size of metal atom and increase in effective nuclear charge. In the case Mn@Zn₁₂O₁₂, charge transfer is positive and follow an abnormal trend due to all unpaired electrons. In the case of late TM atoms, the negative charge value increases from Fe to Ni and then decreases from Cu to Zn as d orbitals in these metals are nearly filled and ability to gain or lose electrons is energetically less favourable.

3.3. Molecular orbitals analysis

Frontier molecular orbital analysis has been performed to compute the electronic environment and *iso*-densities of TM doped Mg₁₂O₁₂ nanocage. The energy gap (E_g) between the HOMOs (highest occupied molecular orbital) and LUMOs (lowest unoccupied molecular orbital) usually provide the information about the microelectronic characteristics, including their conductance, semi-conductance, and insulating qualities [55]. Low energy gap values are preferred in electrocatalysts because they improve the conductivity of a catalyst [54]. Therefore, the E_g values of the pristine and TM@ Mg₁₂O₁₂ complexes have been computed and are listed in Table 2.

In pristine nanocage, the E_g value is 4.81 eV indicating its semi-conducting behaviour and is in line with earlier findings [38,56]. The results clearly depict that doping Mg₁₂O₁₂ with TM atoms significantly reduces the energy gap. The smallest E_g value is observed for Sc@Mg₁₂O₁₂ (1.83 eV) and the highest E_g value is observed for Zn@Mg₁₂O₁₂ (3.22 eV). The main cause of the decrease in the E_g is the addition of extra electrons from transition metal atoms to the nanocage or *vice versa*. Another major factor for the reduction in E_g is the increase in the HOMO energy of the doped systems, whilst the LUMOs show a little change in energy. The previous HOMO is now categorized as HOMO-1, and a new HOMO orbital is formed because of this phenomenon. Overall, all designed catalysts showed a significant decrease in energy, which is indicative of increased conductivity of designed complexes. Furthermore, the HOMO-LUMO *iso*-surfaces are also computed and are shown in Fig. S1.

The results indicate that the electron densities of HOMOs are located on the respective transition metal atoms whereas in the LUMOs and pristine nanocage are mostly dispersed on the Mg₁₂O₁₂ substrate. A similar trend of energy gap has also been observed in prior work on transition metal atom doping Al₁₂N₁₂ nanocage carried out by Ayub et al., [50].

3.4. Density of states analysis

The density of states (DOS) refers to the number of states that electrons can occupy at a specific energy level. The TDOS (total density of states) and PDOS (partial density of states) spectra are analysed in this work to validate the electronic properties, particularly the contribution of individual fragments and the creation of new HOMOs in the newly designed TM@Mg₁₂O₁₂ nanocluster. The DOS spectra of pure and TM doped Mg₁₂O₁₂ nanocages are depicted in Fig. S2.

The TDOS spectrum of pristine Mg₁₂O₁₂ nanocage demonstrates that the occupied and virtual regions yield energy levels at lower energies. The peak intensity of PDOS exhibits a significant variation by the doping of nanocage with transition metal atoms. New high-energy HOMO orbitals are thus produced because of the interaction between the TM atoms and Mg₁₂O₁₂. The shifting of energy levels in the DOS spectra of these complexes validate the creation of new HOMOs, and the presence of new HOMOs is shown by a vertical dashed line. These molecular orbitals range from -3.8 eV to -4.3 eV in the high energy zone as compared to the -6.7 eV of pristine nanocage. In all TM doped Mg₁₂O₁₂ complexes, the TM (Sc-Zn) (blue line contribution) contribute significantly to the formation of new HOMOs. Additionally, it appears that intensities of transition metal atoms play a significant role in the complexes being studied. The DOS spectra of transition metal doped nanoclusters demonstrate a notable enhancement in their electrical and conductive properties.

3.5. Quantum theory of atoms in molecules (QTAIM) analysis

Transition metal atom doping on Mg₁₂O₁₂ generates a variety of intermolecular interactions, including van der Waals forces and hydrogen bonds. The Virial theorem and the QTAIM are effective methods for understanding different kinds of interactions

(intermolecular or intramolecular) at the bond critical sites (BCPs) [57]. Electron density $\rho(\mathbf{r})$, kinetic electron energy density $G(\mathbf{r})$, potential electron energy density $H(\mathbf{r})$, and Laplacian electron density ($\nabla^2\rho$) are the primary topological aspects utilized to reveal the bond type at the bond crucial points (BCPs). The BCPs can be expressed by the following equations:

$$H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r}) \quad (4)$$

$$\left(\frac{1}{4}\right)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + V(\mathbf{r}) \quad (5)$$

The strength of interactions is significantly influenced by the value of electron density ($\rho(\mathbf{r})$). The negative Laplacian $\nabla^2\rho(\mathbf{r})$, $H(\mathbf{r}) < 0$, $-G(\mathbf{r})/V(\mathbf{r}) < 1$ and $\rho(\mathbf{r}) > 0.1$ *au* all show strong bonding's (i.e., electrostatic interactions and H-bonding). However, partial covalent and partial electrostatic forces only have $H(\mathbf{r}) < 0$ with positive Laplacian $\nabla^2\rho(\mathbf{r})$ value, while weak interactions like van der Waals are shown to have a positive Laplacian $\nabla^2\rho(\mathbf{r})$, $H(\mathbf{r}) > 0$, $-G(\mathbf{r})/V(\mathbf{r}) > 1$ and $\rho(\mathbf{r}) < 0.1$ *au*, respectively. The topological diagrams with the corresponding BCPs of designed complexes are displayed in Fig. 3 and their interaction parameters are provided in Table S2.

The results revealed that all complexes exhibit shared interactions with $\rho(\mathbf{r}) > 0.1$ *au* at the BCPs between oxygen and transition metal atoms (Sc-Zn). Moreover, positive Laplacian and relatively large coupled with the negative $H(\mathbf{r})$ values indicate the presence of strong interactions, possibly partial covalent interactions. The confirmation of these partial covalent interactions is further confirmed by the $-G(\mathbf{r})/V(\mathbf{r}) < 1$ for all TM doped Mg₁₂O₁₂ complexes.

3.6. Interaction region indicator analysis

Intramolecular and intermolecular interactions are identified, and their nature is better analyzed using the IRI approach proposed by Lu et al., in 2021 [58]. Several interactions within chemical systems can be simultaneously identified by the recently introduced real-space function. A constant pre-factor separates the IRI from the RDG (reduced density gradient), which is necessary to maintain equilibrium between covalent and non-covalent forces. It consists of 3D *iso*-surfaces and 2D-IRI plots. The IRI expression can be written as:

$$IRI(r) = \frac{|\nabla\rho(\mathbf{r})|}{[\rho(\mathbf{r})]^a} \quad (6)$$

where ρ is electron density, $(\mathbf{r})$ is the vector constant, $\nabla\rho$ is the Laplacian of electron density, and a is an adjustable parameter. Strong attractive forces are represented by $(\sin\lambda_2)\rho < 0$, weak van der Waals (vdW) interactions by $(\sin\lambda_2)\rho \approx 0$, and dispersive or steric repulsive forces by $(\sin\lambda_2)\rho > 0$. Additionally, the colour pattern indicates the different types of interactions, with blue, red, and green representing strong electrostatic forces of attraction, steric repulsive forces, and van der Waals forces, respectively. The 3D *iso*-surfaces and 2D-IRI graphs of TM Doped Mg₁₂O₁₂ are displayed in Fig. 4 & S3.

The results depict that the covalent bond areas between the oxygen atom of the Mg₁₂O₁₂ nanocage and the transition metal atoms (Sc to Zn) are displayed in blue colour rings on the IRI isosurface, signifying a high electron density and interaction strength. In the same way, the green area shows the weak van der Waals forces between the atoms of Mg₁₂O₁₂ nanocage. The blue spots in the 2-D IRI scattered graphs in the electron density $(\sin\lambda_2)\rho$ ranging from -0.04 to -0.05 *au*. further demonstrate the presence of covalent interaction between the transition metal atoms and oxygen atoms of the Mg₁₂O₁₂ nanocage. Additionally, the chemisorption of transition metal atoms on the Mg₁₂O₁₂ surface is confirmed by the existence of covalent bonds. The findings from the NBO, QTAIM, and FMOs investigations are corroborated by the current IRI analysis.

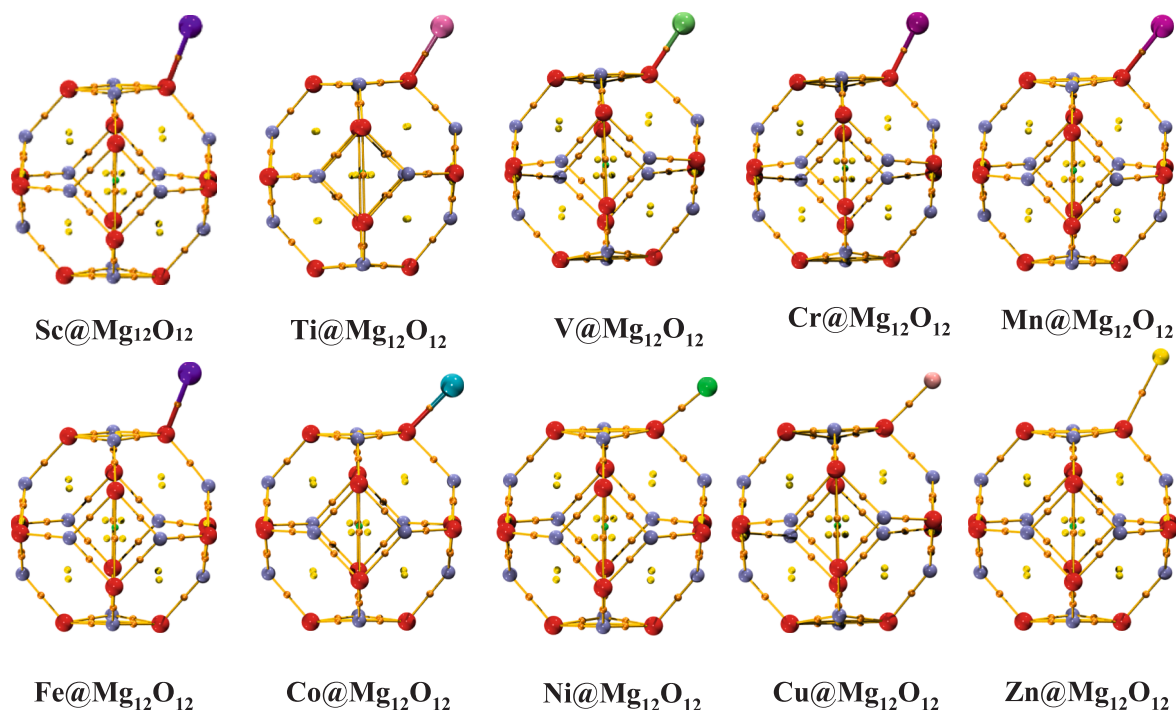


Fig. 3. Topological diagrams of complexes of TM@Mg₁₂O₁₂ nanocages.

3.7. Nitrogen (N₂) molecule activation on the TM@Mg₁₂O₁₂

The nitrogen reduction reaction (NRR) requires activation of N₂, and the free energy must be less than zero ($\Delta G_{(N_2)} < 0$) for effective adsorption. Adsorption of N₂ on TM@Mg₁₂O₁₂ can occur via either end-on or side-on adsorptions. The most stable adsorption geometry is determined by comparing the relative stabilities of both configurations and performing structural refinements. To identify the most stable spin states, spin-polarized computations are performed. The results indicate that the triplet state is the most stable for both geometries and are displayed in Fig. 5.

The computed ΔG values for N₂ adsorbed on TM@Mg₁₂O₁₂ (TM=Sc–Zn) are presented in Table S3. The results indicate that N₂ is more likely to adsorb in the end-on configuration, as its adsorption free energies are more negative than those of the side-on configuration, which even shows some positive values. Therefore, only end-on adsorption is considered in this study.

A moderate level of interaction between the adsorbent and the substrate is essential in accordance with the Sabatier principle [59], whereas weak adsorption may lead to reduced catalytic activity, whereas excessively strong adsorption can hinder catalyst turnover. The adsorption energy of Mn@Mg₁₂O₁₂ for the end-on approach falls within a moderate range, as shown in Table S3. It can be inferred that the Mn@Mg₁₂O₁₂ catalyst can effectively activate the N₂ molecule.

To assess the operational (electrochemical) stability under NRR conditions, the possibility of metal leaching, oxidation, and agglomeration, thermochemical analyses have also been carried out for Mn@Mg₁₂O₁₂ at the B3LYP-D3/6–31 + G(d,p) level of theory with aqueous solvation (CPCM). The overall computed free energy for the dissolution of Mn into aqueous Mn²⁺ (modelled as [Mn(H₂O)₆]²⁺), is strongly endergonic ($\Delta G_{\text{Diss}} = +153$ kcal/mol), corresponding to a dissolution onset potential of $U_{\text{Diss}} = 3.3$ V (Table S4). This indicates that Mn leaching is highly unlikely under the negative potentials relevant for NRR.

Oxidation of Mn@Mg₁₂O₁₂ is also strongly unfavorable, with ΔG_{oxi} of -141.8 kcal/mol, yielding an absolute oxidation potential of $+6.15$ V (≈ 1.7 – 1.9 V vs SHE) (Table S4). Although Mn detachment from the

oxidized Mn@Mg₁₂O₁₂⁺ state requires only a moderate energy ($\Delta G \approx +11.1$ kcal/mol, $\sim +0.48$ V), but such oxidation requires potentials well beyond NRR operating conditions and is therefore not accessible during catalysis. Agglomeration was evaluated by computing the Mn–Mn dimerization free energy. The value obtained ($\Delta G_{\text{Dim}} = +124.6$ kcal/mol) shows that Mn–Mn dimer formation on Mg₁₂O₁₂ is strongly endergonic. Thus, Mn atoms do not thermodynamically favor aggregation on the support, demonstrating excellent resistance to agglomeration (Table S4). Overall, dissolution, oxidation, and aggregation pathways are all strongly disfavored under NRR-relevant potentials, supporting the electrochemical stability of Mn@Mg₁₂O₁₂ as an operationally stable single-atom catalyst.

The structural robustness of Mn@Mg₁₂O₁₂ was assessed through deformation energies. The small deformation of 0.14 eV indicates minimal structural distortion upon metal binding, further confirming the intrinsic stability of the SAC. Moreover, by using AIMD simulations and the built-in ADMP method, the stability of Mn@Mg₁₂O₁₂ is further confirmed. The results show that the designed SACs have significant kinetic and thermodynamic stabilities. The trajectory of total energy (au) vs time of evolution (fs) for Mn@Mg₁₂O₁₂ is shown in Fig. S4. The complexes are thermodynamically and kinetically stable, as evidenced by the proposed SAC's energy oscillations, which are limited to a certain area and remain constant across a 250 fs trajectory.

3.8. Comprehensive catalytic activity of TM@Mg₁₂O₁₂

The affinity of pristine Mg₁₂O₁₂ for the N₂ molecule has been examined previously to determine whether the pristine nanocage can catalyse the NRR. It was found that the N₂ molecule cannot adsorb to the pristine Mg₁₂O₁₂ nanocage and it has been observed to move away from the nanocage throughout the optimization process, ultimately lead to failed convergence [60]. The nitrogen reduction reaction involves the progressive addition of H atoms to the adsorbed N₂ through the addition of H⁺ and electron (e[−]). Therefore, every stage of the NRR is regarded as a proton-coupled electron transfer (PCET) phase. The H atom can be added to any of the nitrogen atoms in the adsorbed N₂ in each PCET step causing the NRR to have distinct catalytic routes, such as dissociative,

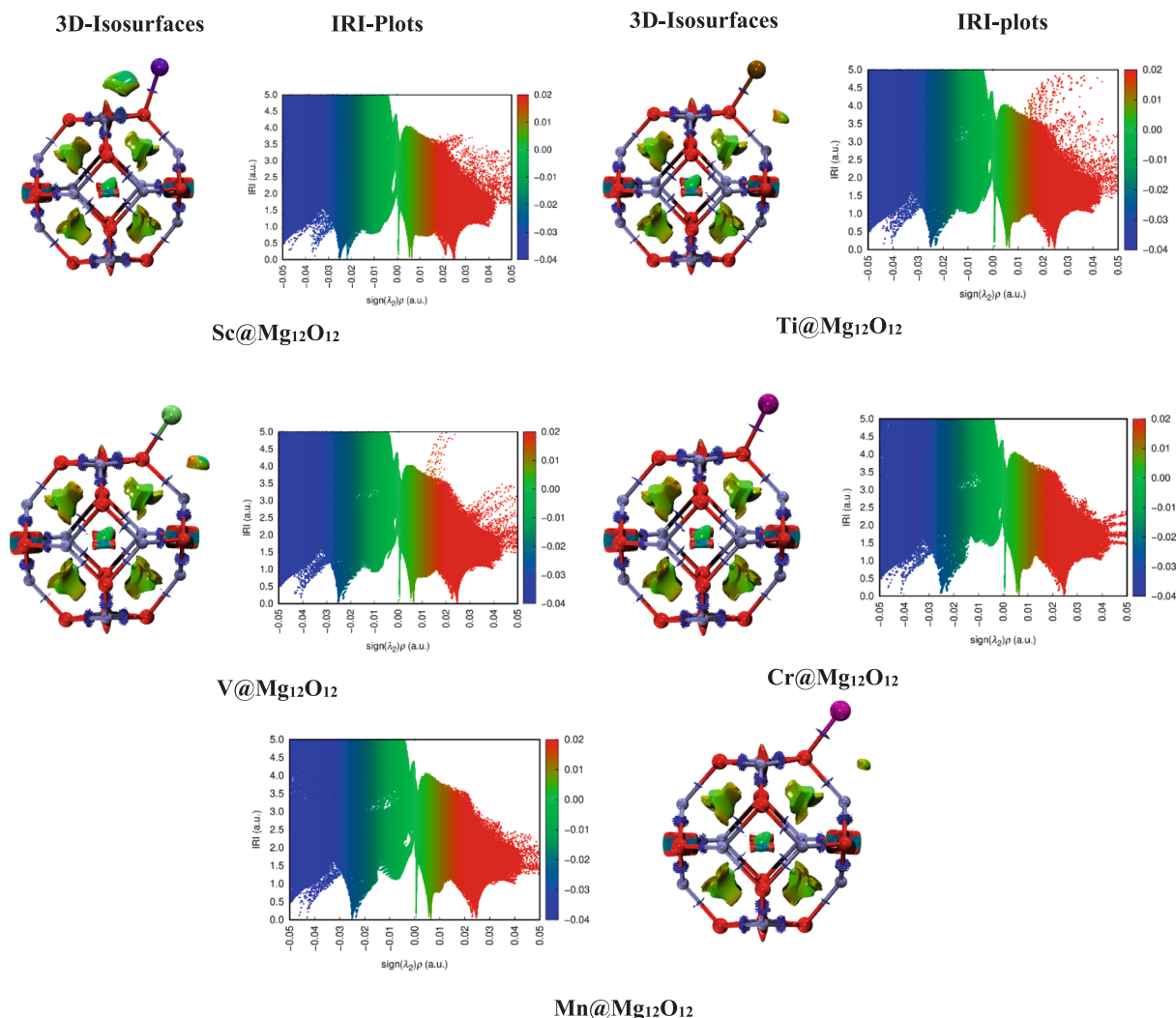


Fig. 4. 3D iso-surfaces and 2D IRI plots of TM(Sc-Mn) @Mg₁₂O₁₂ nanocages.

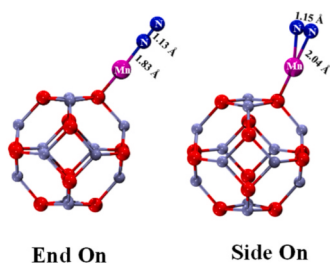


Fig. 5. Optimized geometries of nitrogen molecule adsorbed Mn@Mg₁₂O₁₂.

associative distal, and associative alternating pathways [60]. The most effective and ideal catalytic pathway is found and followed throughout the NRR process by assessing every potential isomer at every PCET step, including the initial N₂ adsorption, and choosing the most stable intermediate at each stage. Furthermore, the H atoms are doublets, their addition may result in a decrease or an increase in the overall spin-state of the system. Spin polarized calculations are carried out to optimize the structures and determine the most stable spin state for each intermediate under consideration. The various phases and reaction mechanisms involved in the distal and alternating pathways are depicted in Fig. 6.

3.8.1. Distal pathway for N₂ reduction

The Gibbs free energy profiles for nitrogen reduction in distal pathways show a stepwise hydrogenation process in which one nitrogen atom is hydrogenated at a time while the other stays inactive until NH₃ is formed. The catalytic performance of these systems is varied. The NRR starts with the formation of HNN-Mn@Mg₁₂O₁₂, which is the result of adding a H atom to the N₂-Mn@Mg₁₂O₁₂ system. The incorporation of the H atom on either side of N₂ results in the formation of the same structure due to the symmetry of N₂-Mn@Mg₁₂O₁₂. The optimized structure of HNN-Mn@Mg₁₂O₁₂ is shown in the Fig. 7. Moreover, the spin-state analysis was carried out to verify the most stable spin-state for all steps of distal pathways of Mn@Mg₁₂O₁₂ are computed and the most stable are considered for further analyses. The Gibbs free energy profile showed very favourable catalytic behaviour for the Mn@Mg₁₂O₁₂ catalyst as shown in Fig. 7.

The results depict that the hydrogenation of N₂ to N₂H is slightly exergonic at zero potential ($V = 0$), with the Gibbs free energy dropping from 0.00 eV to 0.88 eV. With the Gibbs free energy dropping from 0.88 eV to -0.13 eV, indicating an energy difference of -1.01 eV, the transition from NNH to NNH₂ is exergonic. The potential-determining step (PDS), which is the next hydrogenation step from NNH₂ to NNH₃, has the highest energy barrier at 1.49 eV (from -0.13 eV to 1.36 eV). The path becomes more advantageous after the PDS. As the Gibbs free energy drops from 1.36 eV to -1.85 eV, further advancement to N and NH₃ via NNH₃ necessitates further energy reduction. In addition to being

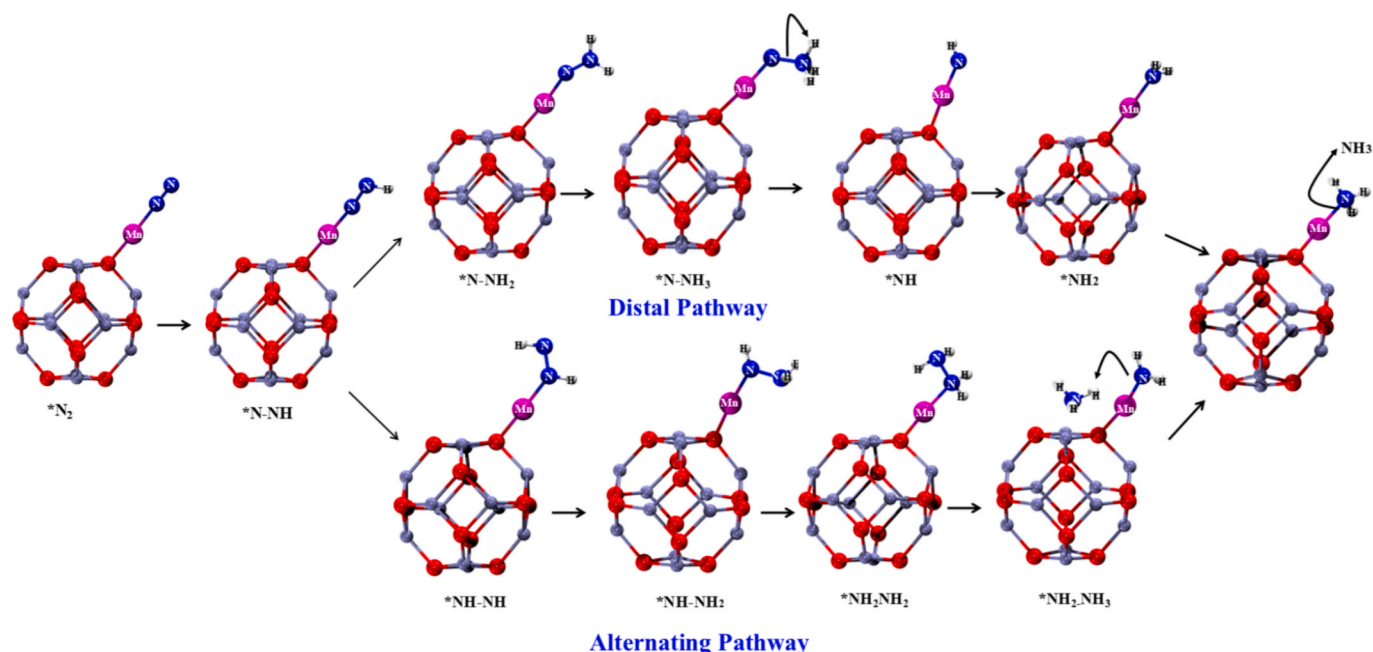


Fig. 6. Schematic diagrams of distal and alternating pathways for NH_3 synthesis (* is for $\text{Mn@Mg}_{12}\text{O}_{12}$ SAC).

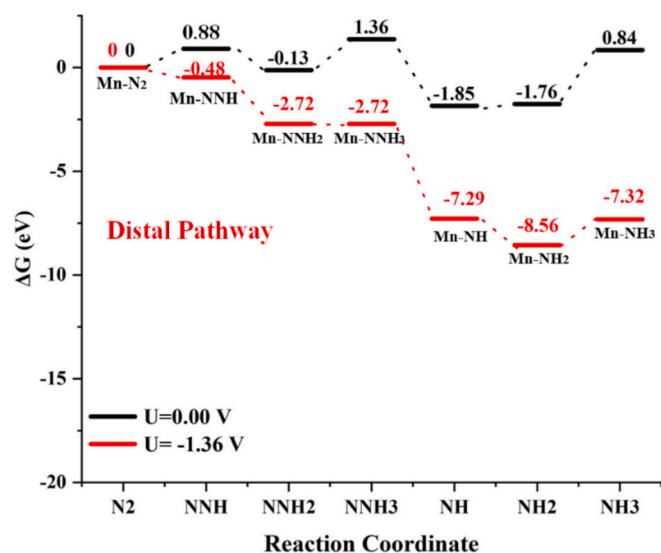


Fig. 7. The free energy plots of the distal NRR pathway for $\text{Mn@Mg}_{12}\text{O}_{12}$ and limiting potential.

exergonic, the hydrogenation of atomic nitrogen (N) to NH results in a -3.21 eV difference in the Gibbs free energy, which goes from 1.36 eV to -1.85 eV. The system is further stabilized by the subsequent synthesis of NH_2 , which lowers the energy to -1.76 eV a notable energy drop of -1.85 eV from the NH intermediate. In the last stage, ammonia desorption, the Gibbs free energy increases from -1.76 eV to 0.84 eV, making it endergonic. There is no longer an energy barrier for the NNH_2 to NNH_3 transition because the complete chemical pathway is exergonic at an applied potential of -1.32 eV. Ammonia is released efficiently due to the stabilization of the intermediates, which also makes the reaction pathway proceed efficiently. Due to its favourable thermodynamics for NRR and low energy barriers, these results demonstrate that $\text{Mn@Mg}_{12}\text{O}_{12}$ is an extremely effective electrocatalyst.

3.8.2. Alternating pathway for N_2 reduction

A unique hydrogenation mechanism where both nitrogen atoms undergo alternating hydrogenation during the reduction process is depicted by the Gibbs free energy diagrams for the alternating pathway. Due to the relatively uniform thermodynamic demand at each step, this pathway displays a more balanced energy distribution than the distal pathway. Similar to distal pathways, spin-state analyses were carried out to identify the most stable spin state for all steps of the alternating pathways of $\text{Mn@Mg}_{12}\text{O}_{12}$. The Gibbs free energy profile for the alternating pathway of $\text{Mn@Mg}_{12}\text{O}_{12}$ catalyst is shown in Fig. 8.

Notably, the first PCET step in the distal and alternating pathways such as hydrogenation of N_2 to NNH is the same. But in later stages, the alternating pathway changes course as both nitrogen atoms undergo hydrogenation in turn. The essential intermediates in this pathway are NNH, NH-NH, NH-NHH, $\text{NH}_2\text{-NH}_2$, $\text{NH}_2\text{-NH}_3$ and NH_3 for NH_3 synthesis

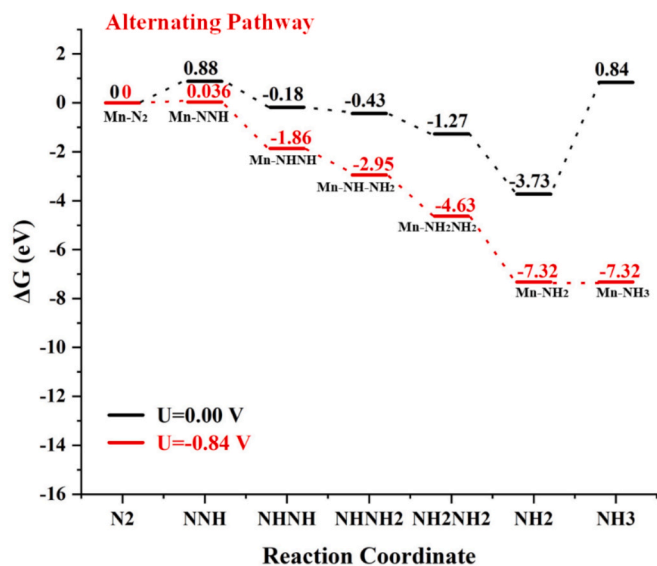


Fig. 8. The free energy plots and limiting potential for the alternating NRR pathway of $\text{Mn@Mg}_{12}\text{O}_{12}$.

and are displayed in Fig. 6. The incorporation of a hydrogen atom in the second PCET stage may result in the formation of HNNH-Mn@Mg₁₂O₁₂. In this context, the Gibbs free energy values of both structures are calculated and optimized. The addition of H atom in HNNH-Mn@Mg₁₂O₁₂ can be in either a trans or cis configuration, both isomers are optimized, and the more stable stereoisomer is taken into consideration. Thus, the HNNH-Mn@Mg₁₂O₁₂ intermediate facilitates the continuation of the NRR. Only one structure can be produced by adding a hydrogen atom to the symmetric HNNH-Mn@Mg₁₂O₁₂ intermediate. Consequently, the only structure for the third PCET step of the NRR is the H₂NNH-Mn@Mg₁₂O₁₂ intermediate. The H atom can be added to the NH group in the fourth PCET stage, generating H₂NNH₂-Mn@Mg₁₂O₁₂. A remarkable −0.84 eV is the computed Gibbs free energy of H₂NNH₂-Mn@Mg₁₂O₁₂. In the fifth PCET step, the hydrogen atom is added to the H₂NNH₂-Mn@Mg₁₂O₁₂ and results in the formation of H₃N...NH₂-Mn@Mg₁₂O₁₂. The computed free energy for this step is −2.46 eV as it increased from −1.27 eV to −3.73 eV and first NH₃ molecule is released. In the sixth and final PCET step, the development of the second NH₃ molecule and the regeneration of the Mn@Mg₁₂O₁₂ occur immediately. It is the potential-determining step (PDS) and has the highest energy barrier at 4.57 eV (from −3.73 eV to 0.84 eV).

The optimal reaction pathway obtained for the Mn@Mg₁₂O₁₂ SACs can be considered as a hybrid pathway of the associative distal, and associative alternating pathways. The reason being is that the initial N₂ adsorption was found to be most stable in the end-on geometry. Moreover, the first, second, and third PCET steps (potential determining step in this pathway) were found to be thermodynamically favoring the distal addition of the H atom, resembling the associative distal pathways. Additionally, the addition of the H atom in the NH₂-Mn@Mg₁₂O₁₂ initiated the sixth PCET step, which is the potentially deciding step of all the steps and indicates an alternating pathway addition. A single pathway may result in the production of unfavourable isomer intermediates during the NRR, the resulting reaction pathway emphasizes the significance of considering all potential sites for the addition of the H atom in each PCET step.

To demonstrate the intrinsic activity of the catalyst, the U_L value under the optimal path of the chosen catalyst is determined using the equation $U_L = -\Delta G_{PDS}/e$ regarding the limiting potential (the limit potential is the lowest negative potential that promotes PDS becoming exothermic) For distal and alternating pathways of Mn@Mg₁₂O₁₂ catalyst, the corresponding U_L values are −1.36 V and −0.84 V, respectively. The rate of proton-electron pair transfer in the protonation stage is greatly influenced by the applied electrode potential because of the presence of electrons. All electron transfer steps can be downscaled following the application of U_L to the catalyst surface, which is advantageous for NH₃ generation. Thus, when the potential is applied to the electrode, the Gibbs free energy curve will be significantly reduced. It can be concluded from the above results that among all the examined systems, the sixth step of alternating pathway has a limiting potential of −0.84 V demonstrating exceptional reactivity of Mn@Mg₁₂O₁₂ catalyst for NRR.

To evaluate the competition between HER and NRR, the hydrogen adsorption free energy ΔG_{H^*} on Mn@Mg₁₂O₁₂ has been computed and the corresponding HER limiting potential using the computational hydrogen electrode (CHE). The obtained adsorption free energy is $\Delta G_{H^*} = -2.40$ eV, indicating exceptionally strong hydrogen binding at the Mn site (Table S4). Using this value, the HER limiting potential was calculated to be U_L (HER) = −4.80 V (vs SHE), which is significantly more negative than the NRR limiting potentials (−1.36 V for the distal pathway and −0.84 V for the alternating pathway). These results show that, although hydrogen adsorption is favorable, the subsequent H₂ formation steps are highly uphill, effectively suppressing HER activity on Mn@Mg₁₂O₁₂. Therefore, HER is unlikely to compete with NRR under electrochemical conditions, supporting the high NRR selectivity of this catalyst.

The literature indicates that various PCET steps have been identified

by investigating the potential determining steps (PDS) [61–63]. The stability of NRR intermediates, which is correlated with the ability of a single atom catalyst to stabilize these NRR intermediates, essentially determines the PDS. In the present study, the Mn@Mg₁₂O₁₂ SAC exhibits a limiting potential of −0.84 V, making it a better catalyst than the Fe-doped nanocage (−1.39 V) [60]. Moreover, the potential determining step of the current system is comparable to that of the Ru@Al₁₂N₁₂ electrocatalyst [64].

4. Conclusion

The present investigation reveals that decorating Mg₁₂O₁₂ nanocages with transition metals (Sc-Zn) dramatically enhances their ability to activate nitrogen, transforming an inert nanocage into a highly active electrocatalyst system. With strong chemisorption energies, narrowed bandgaps, and pronounced charge transfer effects, these TM@Mg₁₂O₁₂ systems exhibit superior N₂ activation compared to pristine Mg₁₂O₁₂. Strikingly, Mn@Mg₁₂O₁₂ achieves a remarkably low limiting potential of −0.84 V via the alternating pathway, positioning it as a highly promising candidate for ambient ammonia synthesis. Moreover, results confirm that HER is thermodynamically inaccessible on Mn@Mg₁₂O₁₂, making NRR the dominant reaction pathway. Beyond identifying a standout catalyst, this work opens new avenues for the rational design of three-dimensional nanocage-supported single atom catalysts, offering a sustainable and energy-efficient alternative to the Haber-Bosch process.

CRediT authorship contribution statement

Rehana Bano: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Béla Viskolcz:** Writing – review & editing, Resources, Funding acquisition, Formal analysis. **Béla Fiser:** Writing – review & editing, Validation, Supervision, Resources, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2025.115370>.

Data availability

Data will be made available on request.

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