

Machine learning-driven molecular dynamics unveils a bulk phase transformation driving ammonia synthesis on barium hydride

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 Check for updatesAxel Tosello Gardini ^{1,2}, Umberto Raucci ¹ & Michele Parrinello ¹ 

The modern view of industrial heterogeneous catalysis is evolving from the traditional static paradigm where the catalyst merely provides active sites, to that of a functional material in which dynamics plays a crucial role. Using machine learning-driven molecular dynamics simulations, we confirm this picture for the ammonia synthesis catalysed by BaH₂. Recent experiments show that this system acts as a highly efficient catalyst, but only when exposed first to N₂ and then to H₂ in a chemical looping process. Our simulations reveal that when first exposed to N₂, BaH₂ undergoes a profound change, transforming into a superionic mixed compound, BaH_{2-2x}(NH)_x, characterized by a high mobility of both hydrides and imides. This transformation is not limited to the surface but involves the entire catalyst. When this compound is exposed to H₂ in the second step of the looping process, ammonia is readily formed and released, a process greatly facilitated by the high ionic mobility. Once all the nitrogen hydrides are hydrogenated, the system reverts to its initial state, ready for the next looping cycle. Our microscopic analysis underlines the dynamic nature of this heterogeneous catalyst, which does not merely serve as static platform for reactions, rather it is a dynamic entity that evolves under reaction conditions.

The conventional approach to the study of heterogeneous catalysis strongly relies on the search for active sites^{1–3}. However, this restricted view is increasingly being challenged^{4–6}. Experimentalists, especially those closer to the industrial processes, have long questioned this traditional view^{7–9}. In this context, the words of Schlögl are particularly relevant: –Active centers are generated from the active phase by dynamic processes. These are not continuously present in general but rather result from fluctuations in the material structure and in the chemical bonds of the active phase–⁸.

Yet, there remains a notable lack of direct experimental or theoretical evidence to confirm this dynamical picture, since the standard approach has been to extrapolate the operando behavior from low temperature experiments and calculations. This gap is beginning to be filled by the emergence of advanced experimental technologies that

have enabled performing in situ and in operando analyses of catalytic materials, thus beginning to shed light on how operando conditions affect the catalyst structure and its activity^{10–13}.

At the same time, the advent of machine learning techniques, specifically machine learning-based interatomic potentials^{14–16} and enhanced sampling methods^{17,18}, has allowed performing accurate molecular dynamics simulations on realistic systems under operando conditions^{19–22}. With the help of these simulations, our group has recently shown that a non trivial change in catalytic behavior occurs in several systems as a function of temperature^{23–25} and/or after exposure to the reactants^{21,26}.

Here, as an example of such complex behaviors, we simulate the synthesis of ammonia on barium hydride (BaH₂). This compound has been recently experimentally investigated showing an ammonia

¹Italian Institute of Technology, Genoa, Italy. ²Università di Milano-Bicocca, Milan, Italy. ✉e-mail: michele.parrinello@iit.it

production rate comparable to that of some of the more traditional transition metal catalysts^{27,28}. Our interest in this system has been driven by several factors. Firstly, there is a pressing demand for more sustainable and efficient alternatives to the well-established but environmentally impactful Haber-Bosch process^{29,30}. Secondly, it is rather surprising that a transition metal-free ionic compound can be an active catalyst. Even more remarkably, in order to obtain significant ammonia yield, BaH_2 has to be alternately exposed to N_2 and H_2 in a chemical looping process³¹. In contrast, when exposed to a continuous N_2/H_2 gas mixture, BaH_2 exhibits very low catalytic activity. A microscopic understanding of this phenomenon is still lacking, but the very fact that it takes place, suggests that the exposure to N_2 changes in a dramatic way the catalyst structure, leading to a compound that stabilizes nitrogen fixation intermediates, and catalyzes the successive hydrogenation step.

Using state-of-the-art molecular dynamics simulations powered by enhanced sampling methods and driven by *ab initio* quality machine learning-based interatomic potentials, we provide a detailed microscopic explanation of the experimentally observed catalytic behaviour. Our simulations show that the initial step in the catalytic cycle is facilitated by the spontaneous release of hydrogen molecules from the surface at the operando temperature, which leave behind anionic vacancies acting as reducing agent during the N_2 adsorption process.

Furthermore, the temperature induces a high diffusivity of the hydride anions. Subsequently, when the catalyst is exposed to N_2 in the first step of the looping process, a series of intermediate reactions occurs, resembling those hypothesized for the nitrogenase enzyme³². This results in the formation of the mixed compound, $\text{BaH}_{2-2x}(\text{NH})_x$, in which the Ba^{2+} cations maintains their crystallographic positions whereas the hydrides are replaced by a mixture of hydrides and imides. This compound is stable at the operando temperature, and it is characterized by an high mobility of both hydride and imide anions. At the end of this first nitridation step, the compound is exposed to H_2 , and we have observed that the imides are easily hydrogenated, leading to the formation of ammonia. The superionic bulk behaviour of the mixed compound is crucial for its catalytic activity and for the regeneration of the catalysts after the H_2 looping cycle. This scenario could be considered an extreme version of the one suggested by Schlögl, where the transformation involves not just the catalyst surface, but the entire system.

Results

As we have recently shown in other catalysts, analyzing their bulk and surface dynamics is crucial to the understanding of the catalytic activity. For this reason, we start our investigation by examining the dynamics both in the bulk and on the (120) surface, which is its most stable surface²⁸.

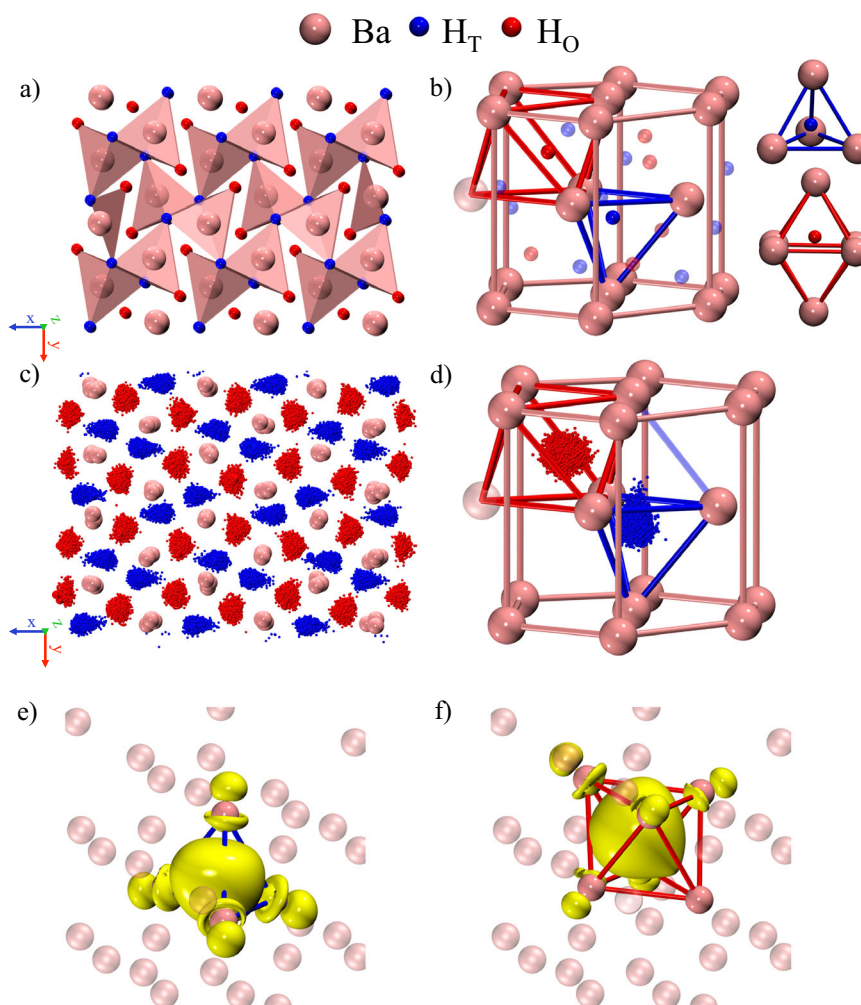


Fig. 1 | Bulk structure of BaH_2 . **a** Structure of orthorhombic BaH_2 at 0 K. **b** Distorted hcp unit cell of Ba^{2+} cations. Hydrides occupying tetrahedral (H_T) and octahedral (H_O) sites are shown in blue and red, respectively. **c** Scatter plot of H_T and H_O atom positions in orthorhombic BaH_2 at 550 K. Configurations are reported every 1 ps during a 5 ns long trajectory. **d** Anisotropic oscillations of H_T and H_O

anions highlighted in the hcp unit cell. Configurations are reported every 1 ps during a 5 ns long trajectory. **e** Charge density isosurface localized in a tetrahedral site after H_T removal, showing the overlap of Ba 5d orbitals. **f** Charge density isosurface localized in an octahedral site after H_O removal, showing the overlap of Ba 5d orbitals.

Bulk dynamics

Below the temperature of 770 K, BaH_2 crystallizes into an orthorhombic structure (space group Pnma) while at higher temperature it becomes hexagonal (space group $\text{P6}_3/\text{mmc}$)^{33–37}. In the orthorhombic arrangement, barium cations (Ba^{2+}) form a slightly distorted hexagonal close-packed (hcp) lattice in which the H^- anions occupy six of the twelve tetrahedral sites and all six octahedral sites. In the literature, these nonequivalent H^- sites are referred to as H_1 and H_2 but, in order to remark their different coordination, we refer to these anions as H_T and H_O , respectively. Each Ba^{2+} cation is coordinated by five H^- anions that form distorted squared pyramids of formula BaH_5 where four vertexes are occupied by H_T and the remaining vertex is occupied by one H_O . The H_T sites are shared among adjacent BaH_5 pyramids while H_O are located on the unshared vertexes (Fig. 1a, b).

In the absence of defects, only half of the possible twelve tetrahedral sites in the hcp unit cell are occupied by H_T anions. This leads to the presence of tetrahedral voids, ordered according to the crystal symmetry, which allow anisotropic oscillations of H_T from their crystallographic positions. Indeed, from our simulations of stoichiometric bulk, a difference in H_T and H_O dynamical behavior is observed.

In particular, the distribution of atomic displacements of H_O is isotropic while those of H_T are elongated along the x -direction, reflecting the existence at the H_T sites of a geometric frustration in agreement with neutron scattering measurements³⁶ (Figs. 1c, d and S1).

Like other alkali and alkaline earth metal hydrides, BaH_2 has the tendency to dehydrogenate leaving behind anionic vacancies^{28,33,38}. In such a defected system, H^- can now diffuse via a vacancy mechanism^{36,39} that involves jumps between H_T and H_O sites, as described in the Supplementary Information (SI) (Figs. S2 and S3). The electronic properties of the system are also modified. Stoichiometric BaH_2 has a band gap and behaves as a semiconductor. When anionic vacancies are present, electrons are called in to restore charge neutrality replacing the missing H^- (Fig. 1e, f). Thus, this compound is more properly described as an electride⁴⁰ with formula $[\text{Ba}_x\text{H}_{2x-2y}]^{2y+}(\text{e}^-)_{2y}$. This system is characterized by the presence of an electronic state near the Fermi level in which the electrons occupy the overlapping Ba^{2+} 5d orbitals (Figs. 1e, f, S4 and S5).

As described in the following section, when this electronic state is localized on the surface, it plays a crucial role in activating N_2 toward the NH_3 formation.

(120) surface dynamics and N_2 adsorption

The morphology of the (120) surface at 0 K is shown in Fig. 2. This surface is characterized by a periodic repetition of a particular complex polyhedral arrangement of Ba^{2+} . This motif results from the truncation of octahedral and tetrahedral units of the bulk building blocks. Within each of these cavities, four H^- are contained. We still classify these hydrides as H_T and H_O depending on the environment that they would have had in the perfect lattice.

A crucial feature of this structure is a square pyramid oriented toward the bulk (Ba^{2+} 1–5 in Fig. 2), resulting from an octahedron missing one vertex, and hosting a H_O hydride. This central square pyramid shares two of its edges with two triangles (Ba^{2+} 4,5,6 and 3,4,7, respectively), each derived from tetrahedrons that have lost one vertex and accommodate a H_T ion. Additionally, the square pyramid shares one of its vertices with an irregular polyhedron (Ba^{2+} 4,6,7,8) formed from an octahedral unit in which two vertices are missing, and that also contains one H_O .

Experimentally, one finds that the catalytic activity increases by a factor of 20 from 550 K to 700 K^{27,28}. For this reason we examine the surface behaviour at these two temperatures. The morphology of the surface is maintained at 550 K. In fact, only small fluctuations of Ba^{2+} around the equilibrium positions are observed while H^- can diffuse with a diffusion coefficient finite but small. In contrast, at 700 K some H^- and Ba^{2+} are promoted to the adlayer. In the adlayer, H^- anions are

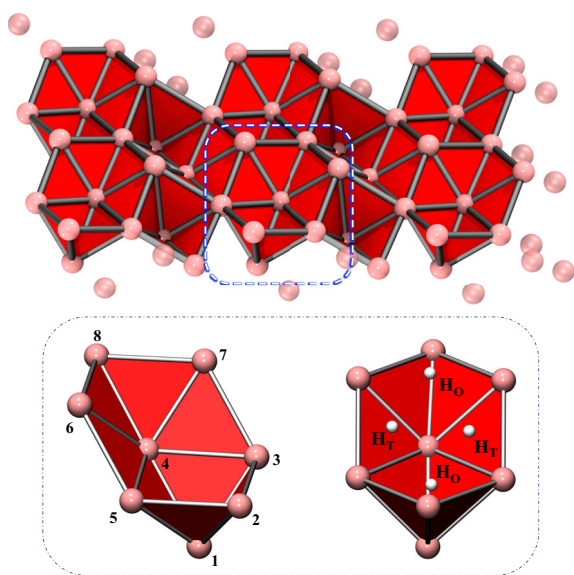


Fig. 2 | (120) surface of BaH_2 . Upper panel: top view of the pristine (120) surface at 0 K. The framed area highlights a representative cavity, while the red surfaces and bonds limit the polyhedra composing the cavities. Lower panel: arrangement of Ba^{2+} ions forming a complex polyhedral cavity. Ba and H atoms are coloured pink and white, respectively.

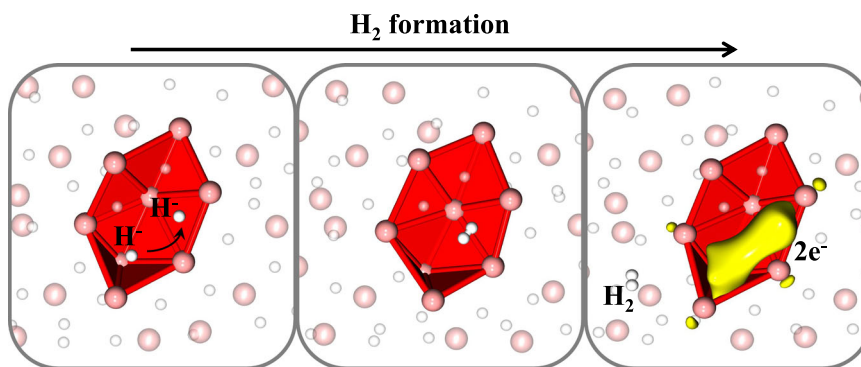


Fig. 3 | H_2 release from the pristine (120) surface. Schematic representation showing the release of H_2 from the (120) surface according to $2\text{H}^- \rightarrow \text{H}_2 + 2\text{e}^-$. The red area highlights the cavity in which the reaction takes place, while the yellow

isosurface indicates the charge density associated to the electride. Ba and H atoms are coloured pink and white, respectively.

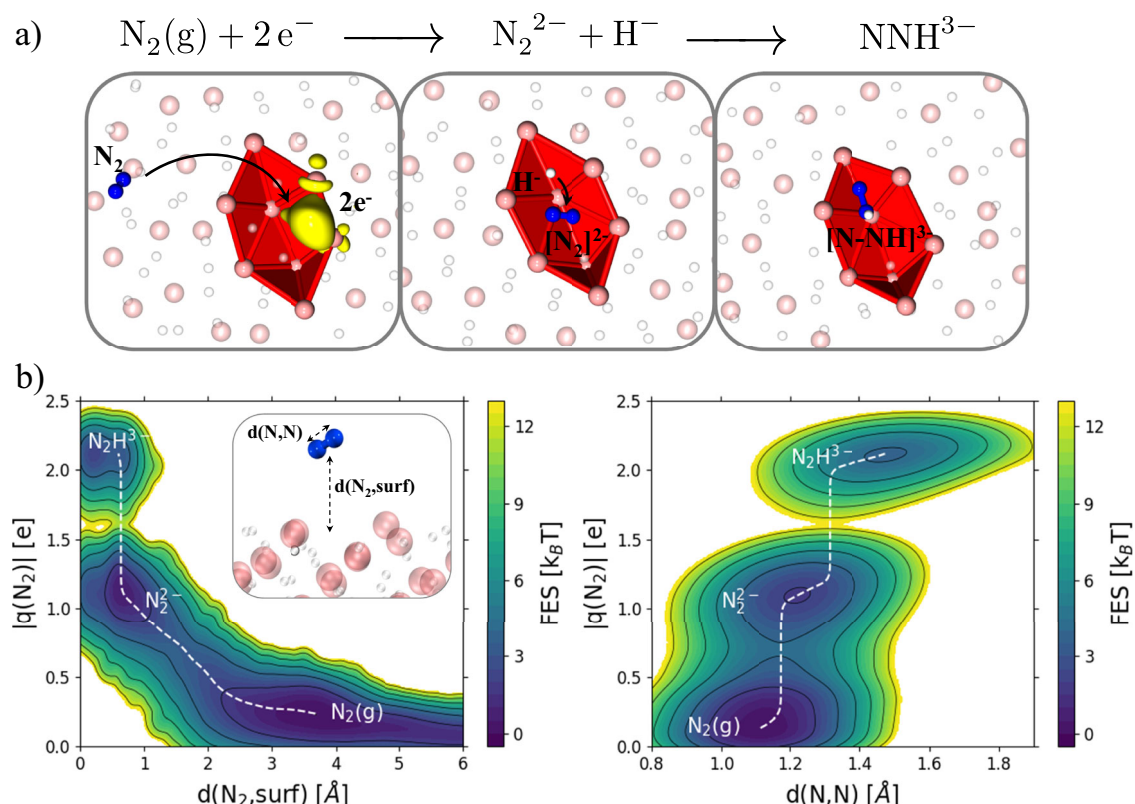


Fig. 4 | N_2 adsorption on the activated (120) surface. a Schematic representation of the adsorption of $N_2(g)$ in the cavity and the following reaction with superficial H^- to form NNH^{3-} . The red area highlights the cavity in which the reaction takes place, while the yellow isosurface indicates the charge density associated to the electride. **b** Free energy surfaces (FES) at 550 K for the adsorption of $N_2(g)$ and NNH^{3-} formation. In the left panel the FES is projected along the distance between N_2 and the surface ($d(N_2, surf)$) and the sum of N atoms Bader charges ($|q(N_2)|$). In right panel,

the FES is reported as a function of the N–N bond distance ($d(N_2)$) and the sum of N atoms Bader charges. The minimum free energy pathway is shown as white dashed line and it is computed using MEPSA (Minimum Energy Path Surface Analysis) package⁷⁶. Bader charges are predicted with a neural network, as detailed in the Method section. The $d(N_2, surf)$ is computed using the Alpha-Shape method, as implemented in OVITO⁷⁷ (see Supporting Information). Ba, H, and N atoms are coloured pink, white, and blue, respectively.

highly diffusive while Ba^{2+} cations oscillate around their putative hcp positions, occupying the missing vertexes of the tetrahedral and octahedral structures (Figs. S6–S8).

As anticipated in the previous section, BaH_2 tends to release H_2 and form anionic vacancies. The enhanced H^- anions fluctuations at high temperature promote the release of hydrogen following the reaction $2H^- \rightarrow H_2 + 2e^-$, as depicted in Fig. 3. Interestingly, the two reacting hydrides are situated in the surface cavity (Fig. 3). This reaction is facilitated by the Lewis acid character of the Ba^{2+} cations, that can use their $5d$ orbitals to accept the released electrons leading to a molecular orbital localized inside the cavity. If the atoms were in their perfect crystallographic positions, these electrons would be shared among the d orbitals of the Ba^{2+} ions surrounding the vacancy. However, due to thermal fluctuations and the high mobility of H^- , this ideal scenario is rarely observed, and the anionic electrons are typically localized in the d orbitals of just one or two barium cations (Fig. S9).

Furthermore, these loosely bound electrons are stable on the surface (Fig. S9) and can be easily donated to electrophilic species^{41–43}, thereby acting as a hard Lewis base during the N_2 fixation process. The formed vacancy has notable reducing capability, similar to the anionic vacancies observed in related alkali and alkaline earth metal halides^{44–46}.

The role of this state can be immediately understood if we initiate the reactive process by exposing the surface to a nitrogen molecule simulating the N_2 -looping cycle. The N_2 molecule is not absorbed on the pristine (120) surface (Fig. S10). Instead, if the defect state is present on the surface, it can interact with the empty LUMO orbital of N_2 leading to the formation of a diazenido anion (N_2^{2-}) (Fig. 4a). This

anionic intermediate sits horizontally in the cavity previously occupied by the loosely bound electrons, and it is typically stabilized by five Ba^{2+} cations (Figs. S11 and S12). When sitting in this conformation the N–N bond lengthens from 1.1 Å to 1.2 Å acquiring an extra charge of $q \sim 1.1$, as measured by the Bader charge decomposition (Fig. 4b).

This finding explains why the looping process is necessary, and why exposing the surface to a mixture of N_2 and H_2 leads to a low ammonia yield. In fact, if one exposes BaH_2 to H_2 , the important electron-rich defective states would react with the hydrogen molecules, thereby poisoning the surface and making it catalytically inactive to N_2 fixation^{28,47}.

The formation of N_2^{2-} is the first step in a process that leads first to the weakening of the $N \equiv N$ triple bond and eventually, after a series of reduction steps, to its breaking.

In the first of these steps the diazenetriide anion (NNH^{3-}) is formed (Figs. 4a and S13–S15). This reaction can be interpreted by examining the frontier molecular orbitals. In fact, upon adsorption, the N_2^{2-} LUMO orbital (Fig. S14) is oriented in such a way that it can be attacked by a nucleophilic H^- present within the cavity. The high mobility of the hydrides facilitates this step, ensuring that the surface cavity is always occupied by reacting H^- . Additionally, the Ba^{2+} cations help also to stabilize this intermediate (Fig. S12). A further lengthening of the N–N bond (1.4 Å) takes place after this process and the total Bader charge of the nitrogen atoms increases to a value of $q \sim 2.1$ (Fig. 4b).

We perform a detailed characterization of this process by calculating the free energy surface (FES) for nitrogen adsorption and diazenetriide formation at 550 K and 700 K, using the change in

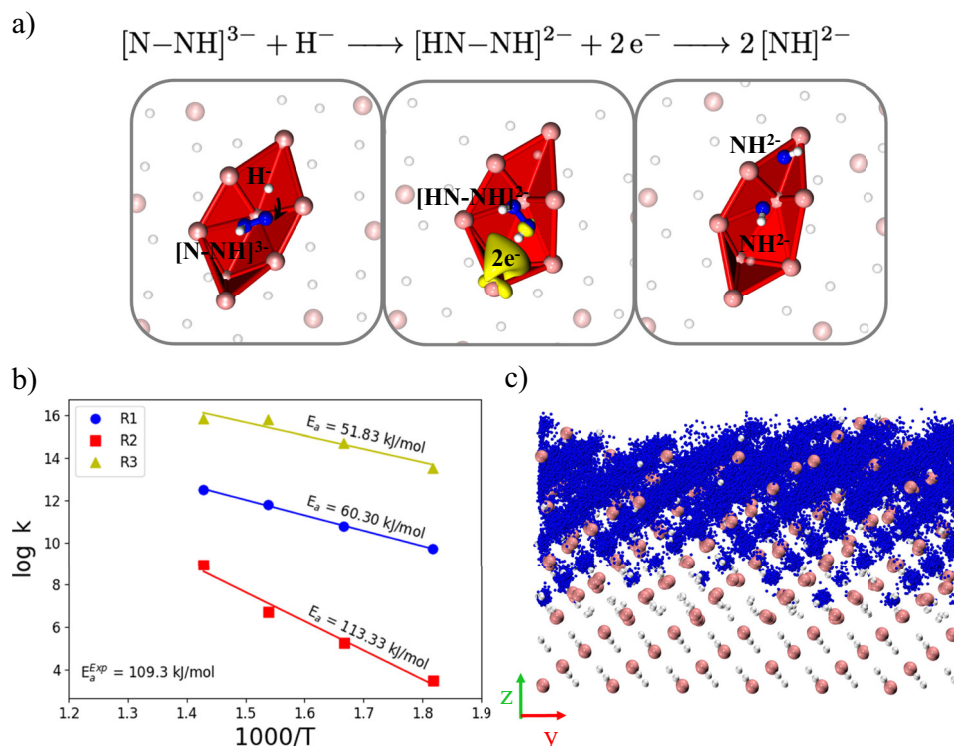


Fig. 5 | N–N bond cleavage. **a** Schematic representation of the reduction of NNH^{3-} to form two NH^{2-} . The red area highlights the cavity in which the reaction takes place, while the yellow isosurface indicates the charge density associated to the electrode. **b** Arrhenius plot for the different steps involved in the nitridation process computed with the OPES flooding method. The activation energy (E_a) is obtained from the slope of the logarithm of the kinetic constant (k) versus $1000/T$. The experimental value of the global activation energy (E_a^{Exp}) for the process is taken from ref. 27. We refer to the following reactions: R1: $N_2(g) + 2e^- + H^- \rightarrow NNH^{3-}$; R2: $NNH^{3-} + H^- \rightarrow HNNH^{2-} + 2e^-$; R3: $HNNH^{2-} + 2e^- \rightarrow 2NH^{2-}$. We combined N_2 absorption

and NNH^{3-} formation into a single step to compute the kinetics, as the shortened lifetime of the N_2^{2-} intermediate at elevated temperatures makes it challenging to accurately determine the reaction rate for the second step ($N_2^{2-} + H^- \rightarrow NNH^{3-}$). The number of replicas for each simulation is reported in Table S1. **c** Scatter plot of N atom positions in the imidized surface at 700 K. Configurations are reported every 1 ps during a 60 ns long trajectory. To simplify reading, a single instantaneous configuration is chosen to represent Ba and H atoms. Ba, H, and N atoms are coloured pink, white, and blue, respectively.

Bader charges^{48,49} of N atoms as a sensitive indicator of electronic structural variations during the reaction. With the increase in temperature, we observe a decrease in the barrier for the formation of NNH^{3-} from N_2^{2-} of about $4.3 k_B T$ going from 550 K to 700 K. This is related to the greater disorder of the surface which destabilize the N_2^{2-} state, thus lowering the barrier. More details can be found in Figs. S16–S18.

Cleavage of the N–N bond and imide formation

The successive step is the cleavage of the N–N bond, leading to the formation of imide (NH^{2-}) anions. The diazanetriide HOMO orbital (Fig. S15) is oriented to facilitate the next reductive protonation reaction in which an H^- ion reacts with NNH^{3-} , according to $NNH^{3-} + H^- \rightarrow HNNH^{2-} + 2e^-$ (Fig. 5a)⁵⁰. This reduction process is favoured by the Ba^{2+} cations that also in this case act as Lewis acid accepting the released electrons in a localized state resulting from the overlap of their $5d$ orbitals. The formation of the diazanediide anion ($HNNH^{2-}$), effectively reduces the N–N bond order, which extends further its length to 1.5 Å. Interestingly, a competing pathway leading to NNH_2^{2-} (where two protons are bound to the same N atom) has not been observed in our simulations, emphasizing the preference for an alternating-like mechanism.

The newly formed diazanediide lies horizontally on the surface cavity stabilized by five barium cations (Fig. S12). Following this step, $HNNH^{2-}$ can be further reduced by the anionic electrons, which can populate its antibonding σ^* orbital thus facilitating the cleavage of the N–N bond. This process results in the formation of two imide ions ($HNNH^{2-} + 2e^- \rightarrow 2NH^{2-}$), as depicted in (Fig. 5a).

By using the on-the-fly probability enhanced sampling flooding method (OPES_f), we estimated the kinetic rates of the three steps leading to the N–N bond cleavage at various temperatures. The activation energy for each step, was then evaluated from the slope of the Arrhenius plot (Fig. 5b, and Methods section for computational details). The reduction of NNH^{3-} to $HNNH^{2-}$ is the rate-determining step with the highest activation energy, of about 110 kJ/mol. In contrast, the formation of NNH^{3-} and the dissociation of $HNNH^{2-}$ proceed with a lower and similar activation energy, of around 60 and 50 kJ/mol, respectively. Our activation energy is comparable with the one experimentally reported for the nitridation process^{27,28}.

Thus far, it appears that we are dealing with a standard catalytic process involving a well-defined catalytic site. Its structure can be viewed as a complex exposed cavity permeable to H^- , and works as a sort of nanoreactor where the catalytic steps take place. Indeed, the undercoordinated hydrides present inside the cavity serve as reactants in various reactive events.

However, these steps alone cannot explain the working of this catalyst, which involves a significant change in chemical composition and dynamics, as hypothesized by Schlögl and discussed in the following section.

Formation and characterization of the hydride-imide compound after N_2 exposure

The NH^{2-} ions can diffuse across the surface and penetrate into the bulk (Fig. 5c), where they can be hosted in octahedral sites (Fig. 6a). As the exposure to N_2 continues, a gradual replacement of the hydrides by imides occurs, leading to the formation of a mixed compound with

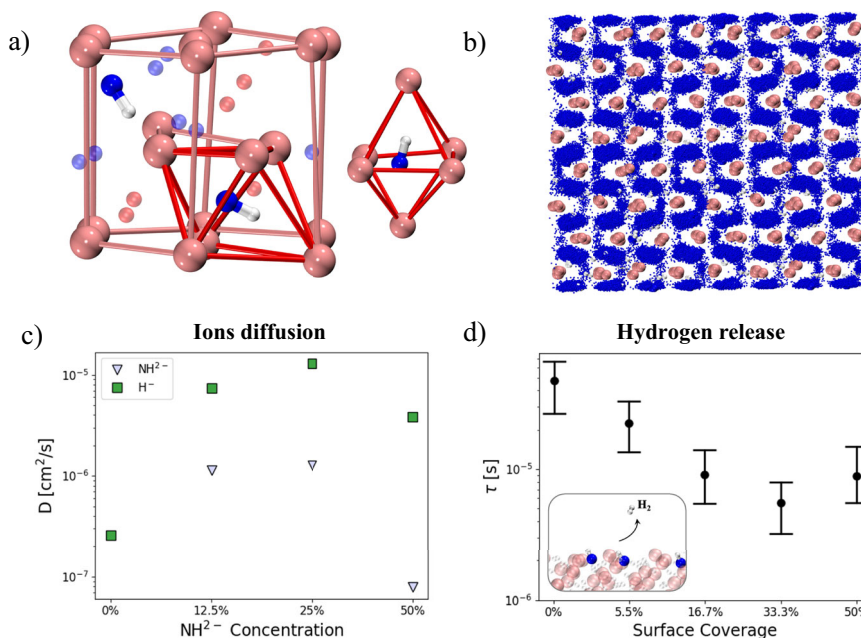


Fig. 6 | Structure of the $\text{BaH}_{2-2x}(\text{NH})_x$ mixture. **a** Hcp unit cell for $\text{BaH}_{2-2x}(\text{NH})_x$. In the reported example, two octahedral sites are occupied by two NH_2^- anions. The red bonds highlight the octahedral coordination for the NH_2^- anion. **b** Scatter plot of N atom positions in the bulk $\text{BaH}_{2-2x}(\text{NH})_x$ at 700 K with $x = 0.125$. Configurations are reported every 10 ps during a 90 ns long trajectory. **c** Diffusion coefficients (D) of H^- and NH_2^- at 700 K for different concentration x of imides. The error bar falls within the size of the data point. We have performed 4 replicas for each

concentration (Table S1). **d** Transition times (τ) for H_2 release at different values of NH_2^- surface coverage, computed using OPES flooding method. The uncertainties of τ were estimated by computing the 95% confidence intervals as reported in ref. 78. We have performed 20 replicas for each value of surface coverage (Table S1). The inset shows a simplified representation of the H_2 formation and release from the imidized surface. Ba, H, and N atoms are coloured pink, white, and blue, respectively.

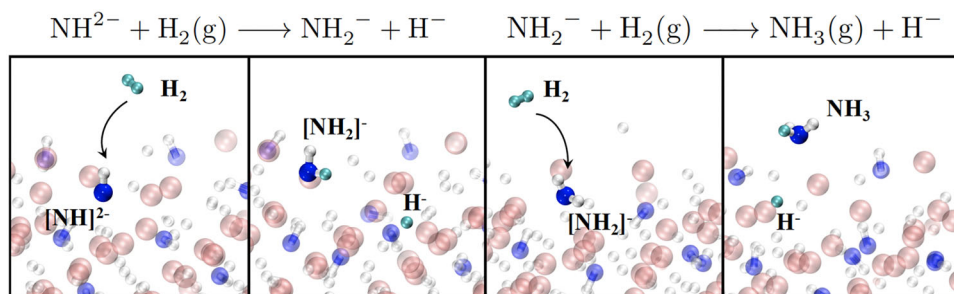


Fig. 7 | Hydrogenation of $\text{BaH}_{2-2x}(\text{NH})_x$ and ammonia release. Schematic representation of the hydrogenation of NH_2^- to NH_2^- and the following hydrogenation to NH_3 . Ba, H, and N atoms are coloured pink, white, and blue, respectively. The H_2 molecules introduced during the hydrogenation cycle are colored in cyan.

general formula $\text{BaH}_{2-2x}(\text{NH})_x$. Hence, the reaction that occurs during the N_2 looping process can be written as $2\text{BaH}_2 + x\text{N}_2 \rightarrow 2\text{BaH}_{2-2x}(\text{NH})_x + x\text{H}_2$. Experimental evidences indicate that the nitridation yield is $\sim 50\%$ at 700 K and it reaches a plateau of $\sim 65\%$ at 750 K²⁷. For this reason, we have investigated the bulk properties of $\text{BaH}_{2-2x}(\text{NH})_x$ at 700 K, considering x values of 0.125, 0.25, and 0.50. Our findings indicate that the cell remains stable even after permitting the cell size to vary using the Parrinello-Rahman Lagrangian⁵¹.

The most striking feature of this compound is its superionic behavior. Both H^- and NH_2^- are highly mobile (Figs. 6b and S19–S20), with H^- exhibiting a diffusion coefficient of $\sim 10^{-5} \text{ cm}^2/\text{s}$, comparable to that of water at room temperature (Fig. 6c). The diffusion mechanism is similar to that observed in pristine BaH_2 , with H^- moving from tetrahedral to octahedral sites.

This mixed phase is stabilized at the operando temperature by entropic effects associated to the high diffusivity of hydrides and imides. At lower temperature, the diffusivity decreases (Fig. S20) and the phase coexistence of barium hydride and imide is likely to be

expected⁵² in line with the X-ray diffraction patterns recorded at room temperature²⁷.

The superionic behavior plays a critical role in enhancing hydrogen release during the nitridation process. Experimental findings indicate an increase in hydrogen release during the N_2 looping cycle, exceeding that observed when increasing the temperature under Ar flow^{27,28}. Our simulations show that the marked increase in the H^- mobility in $\text{BaH}_{2-2x}(\text{NH})_x$ significantly facilitates the formation of H_2 in agreement with experiments. In particular, we performed OPES_f simulations (computational details are reported in the Methods section) observing that the transition time (τ) for hydrogen release decreases with the rising concentration of imides on the surface (Fig. 6d). This indicates a faster kinetics, although this trend is not strictly linear at higher surface coverage. Furthermore, comparing the transition times for H_2 release and HNNH^{2-} formation (the rate-determining step of the nitridation process, with a τ of $1.3 \times 10^{-4} \text{ s}$ at 0% surface coverage), hydrogen release is consistently faster than the reductive protonation leading to HNNH^{2-} .

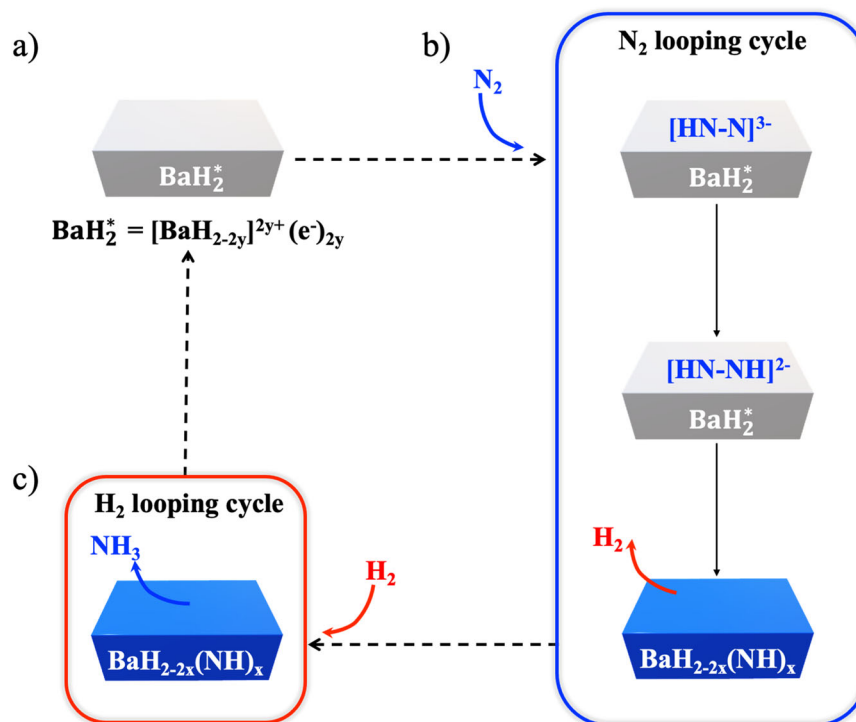


Fig. 8 | Simplified scheme outlining the catalytic process. Schematic representation of the ammonia synthesis process through nitridation of BaH_2 and hydrogenation of $\text{BaH}_{2-2x}\text{NH}_x$ to produce NH_3 . **a** Thermal activation of the catalyst facilitates the formation of electrides. **b** N_2 looping cycle leads to nitrogen

reduction and imides formation. In this step BaH_2 is transformed into the mixed compound $\text{BaH}_{2-2x}\text{NH}_x$. **c** H_2 looping step closes the catalytic process by hydrogenating the mixed compound $\text{BaH}_{2-2x}\text{NH}_x$, resulting in the formation of NH_3 and regeneration of the catalyst.

Hydrogenation and NH_3 release

After the formation of this new solid state compound $\text{BaH}_{2-2x}(\text{NH})_x$, we proceed to simulate the next stage in the looping process, which involves the exposure of the catalyst to H_2 . In the initial phase of this step, imides on the catalyst surface are transformed into amides, while a hydride ion is simultaneously released according to: $\text{NH}_2^- + \text{H}_2 \rightarrow \text{NH}_2^- + \text{H}^-$ (Fig. 7). At this stage the catalyst becomes a mixture of NH_2^- , NH_2^- , and H^- .

The newly formed amides can be further hydrogenated leading to the formation of ammonia, following the reaction: $\text{NH}_2^- + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}^-$ (Fig. 7).

This process can continue until, in principle, all the NH_x groups are hydrogenated, and the original BaH_2 catalyst is reconstituted: $\text{BaH}_{2-2x}(\text{NH})_x + 2x\text{H}_2 \rightarrow \text{BaH}_2 + x\text{NH}_3$. The catalyst recovery is facilitated by the high mobility of the anions in $\text{BaH}_{2-2x}(\text{NH})_x$. Interestingly, our simulations did not show ammonia formation through the reductive protonation of imides, consistent with experimental evidence indicating no ammonia release during the nitridation process.

Discussion

A simplified outline of the catalytic process is reported in Fig. 8. A crucial feature of this process is the dynamic transformation of the catalyst during the catalytic cycle. This transformation affects the whole system, and it is not confined to only the surface. Indeed, as catalyst BaH_2 transcends a traditional role of static support for electron exchange, and actively participates in the catalytic process by providing hydrides to both reactants and intermediates, thus moving the reactive process forward. The highly mobile hydrides can attack the adsorbed N_2 molecules aiding in the weakening of the $\text{N} \equiv \text{N}$ triple bond, until its final cleavage and eventual imide formation. These steps closely resemble the mechanism engineered by nature in the nitrogenase enzyme, where the $\text{N} \equiv \text{N}$ bond is hydrogenated prior to breaking. While the exact mechanism in nitrogenase remains a subject

of debate, in this system, hydrides are able to directly attack the adsorbed N_2 molecules. This behavior closely resembles that of certain homogeneous catalysts, where hydride transfer facilitates bond activation and reduction⁵³.

Furthermore, the system proximity to phase transitions is a key characteristic of this catalyst, which contributes to amplifying the system's overall fluctuations and creates a state of frustration crucial for its catalytic functions. Indeed, the approach to the orthorhombic-hexagonal phase transition, occurring at approximately 770 K, results in a substantial increase in hydride mobility on the pristine surface. These high fluctuations of surface hydrides are essential for the release of H_2 and the formation of the electride, thereby facilitating the catalyst's thermal activation. Additionally, the formation of the hydride-imide mixture, which is an intermediate state in the BaH_2 to BaNH phase transition, results in a superionic state characterized by large mobility of both imides and hydrides. This highly fluctuating environment is crucial for the stabilization of the imides following the N-N bond cleavage, and for the catalyst recovery after the hydrogenation step.

Finally, another key catalytic property of this system is its ability to facilitate electron exchange through anionic vacancies. This mechanism stands in contrast to that of traditional transition metal-based catalysts, which modulate the catalytic process by transferring electrons via their partially occupied d orbitals. We have recently reported the important role of F-centres in the ammonia decomposition on lithium imide, and it is significant that the ammonia synthesis on BaH_2 follows the same main steps but in the reverse direction. Furthermore, also recent experimental studies support the critical role of F-centres in ionic catalysts. Indeed, Ping Chen et al. have shed light on the catalytic behavior of lithium hydride (LiH) in ammonia synthesis when exposed to ultraviolet (UV) light⁴⁷. It has been observed that LiH undergoes a photolytic reaction upon UV irradiation, resulting in the release of H_2 and the transfer of electrons generated from photon

absorption to surface hydrogen vacancies, effectively creating F-centres, and thus activates LiH for nitrogen fixation. Similar intuitions for the reducing ability of surface defects were proposed for CaH_2 , where the vacancies on the surface reduce the work function of the material, making it a plausible reducing agent⁵⁴.

Furthermore, the interplay between alkali and alkaline earth metal hydrides with transition metals can lead to an enhanced catalytic activity due to the facilitated electron exchange through the d orbitals of the transition metals. This synergistic effect is evidenced by the significant boost in ammonia synthesis observed in Ru/CaH_2 , $\text{Ru/Ca}_2\text{N:e}^-$ ⁵⁵, and Ni-BaH_2 ⁵⁶ catalysts. Hypothetically, in these systems, the metal hydride serves as a second catalytic site that removes activated nitrogen from the transition metal, hence breaking the traditional scaling relationship between the nitrogen dissociation energy and the formation energy of reduced intermediates.

In conclusion, the ammonia synthesis on BaH_2 is another example that clearly underscores the importance of considering the catalyst dynamics and how it is influenced by the reaction conditions. Traditional approaches in computational catalysis typically model the surface as a static system at 0 K, failing to capture this dynamic behavior, and highlighting the limitations of such static calculations in accurately representing the catalytic system under operando conditions. Only by adopting a dynamic microscopic view of catalysis, made possible by advances in machine learning-based molecular dynamics simulations, one can create new opportunities to improve the understanding and design of catalytic systems for industrial applications.

Methods

All the MD simulations were performed using a machine learning-based interatomic potential combined with enhanced sampling methods to sample reactive events. A full description of the performed simulations is reported in Supplementary Table S1. The following sections provide a complete description of the training process, and molecular dynamics simulations.

Machine learning-based interatomic potential

To accurately simulate heterogeneous catalytic processes, it is critical to properly describe the formation and cleavage of chemical bonds, while considering the dynamic behavior of the surface. Ab initio molecular dynamics (AIMD), where interatomic forces are derived from accurate first principle electronic structure calculations, would be the method of choice for such a complex endeavor. Nevertheless, its prohibitive computational cost limits its use for realistic large-scale structures and long simulation time. However, since Behler and Parrinello's work¹⁴, machine learning (ML)-based interatomic potentials have emerged as a valuable solution to reconcile the accuracy of ab initio methods with the efficiency of classical force field. These ML potentials are trained to reproduce the energy and forces from a large set of quantum mechanical calculations, and thanks to the locality of the energy decomposition employed, they can be trained on small system sizes and then used to simulate much larger systems for long timescales (e.g., nanoseconds). Despite their promise, ML methods excel at interpolation rather than extrapolation, making it challenging to predict energies and forces for configurations significantly different from those in the training set. Therefore, the construction of these potentials for complex, multicomponent reactive systems represents a complex endeavor, requiring a comprehensive training set that incorporate all relevant configurations, including a broad spectrum of chemical species, from reactants to products and transition states, across all possible reaction pathways. Sampling configurations within the transition state region for such reactions with high energy barriers is computationally demanding, making it challenging without the use of enhanced sampling techniques. Indeed, enhanced sampling methods such as metadynamics or the On the fly probability enhanced

sampling (OPES) method, allow to speed up the process of collecting reactive configurations and generating uncorrelated structures which cover the complete reactive landscape including all relevant transition states.

In this work, the configurations of the training set were collected using an active learning approach augmented with the OPES method similar to that of refs. 21,26. This procedure can be briefly summarized as follows:

1. **Initial Geometry Collection:** The training process starts with the acquisition of initial geometries extracted from short AIMD trajectories.
2. **DFT Labeling and Initial Training:** These structures are labeled via DFT single-point calculations to determine energy and forces. This data forms the preliminary training set for training an initial model.
3. **Active Learning and Model Refinement:** An active learning methodology is then applied, involving the training of four models initialized with different seeds. One of these models is used to perform MD simulations, while the others are employed to evaluate the model uncertainty quantified as the maximal standard deviation of the atomic forces ($\sigma = \max_i \sqrt{\frac{1}{4} \sum_{\alpha=1}^4 \|\mathbf{F}_i^\alpha - \mathbf{F}_i\|^2}$). Structures exhibiting significant force deviations are singled out, whereas other geometries are selected for relabeling based on the criteria described in ref. 21.
4. **Ab Initio Relabeling:** Energies and forces are computed at ab initio level on the identified geometries, and then these relabeled points are incorporated into the training dataset.
5. **Dataset Expansion and Final Model:** Steps 3 and 4 are iteratively repeated to improve the accuracy and generalizability of the ML potential. As a result of the active learning cycle, the training set is enlarged, allowing the construction of a robust machine learning potential, able to predict atomic energy and forces with an accuracy comparable to that of the reference DFT method.

To capture configurations within the transition region, which are challenging to obtain through unbiased simulations, enhanced sampling techniques are employed in the steps 1 and 3 to ensure comprehensive coverage of the potential energy surface.

We have built a training set composed of 224876 configurations encompassing bulk BaH_2 , the pristine (120) surface, intermediates and transition states of all the reaction steps of the nitridation and hydrogenation processes. Furthermore, it also includes configurations of the mixed $\text{BaH}_{2-2x}(\text{NH})_x$ system across different values of x (the whole composition of the training set is reported in Supplementary Table S2).

In the following we provide the computational details for the steps 1–5.

AIMD simulations. AIMD simulations were performed with CP2K (version 9.1)^{57,58} in order to build the initial training set. Simulations were performed in the canonical ensemble (NVT) with periodic boundary conditions, and a time step of 0.5 fs. The temperature was controlled using the stochastic velocity rescaling thermostat⁵⁹ with a coupling constant of 0.05 ps. Energy and forces were computed using the PBE exchange-correlation functional⁶⁰. The Kohn-Sham orbitals were expanded in a triple- ξ plus polarization Gaussian basis sets and the plane wave expansion of the electronic density was truncated at an energy cut-off of 240 Ry. The core electrons were treated using the Goedecker-Teter-Hutter pseudopotentials^{61,62} optimized for PBE.

Labeling configurations via DFT calculations. The DFT energies and forces needed for training the neural network were calculated using the Quantum Espresso (QE) software (version 7.2)^{63–65}. The PBE exchange-correlation functional together with the RRRJUS PBE pseudopotentials⁶⁶ taken from the QE pseudopotential library were

used. The Kohn-Sham orbitals were expanded on a plane wave basis set up to a kinetic-energy cut-off of 60 Ry and a density cut-off at 240 Ry. The convergence threshold for self-consistency was set to 1.0×10^{-7} a.u.

Training of the ML-based interatomic potential. The Deep Potential Molecular Dynamics Smooth Edition scheme, as implemented in the DeePMD-kit software (version 2.1)⁶⁷, was used for training the deep potential models. An embedding and a fitting network with [30, 60, 120] and [240, 240, 240, 240] nodes per layer were used, respectively. A cut-off of 7 Å was used to describe the local environment of each atom. The ADAM optimizer was used to train the network with an exponentially decaying learning rate from 1×10^{-3} to 5×10^{-8} . The prefactors used in the loss function for the energy and force terms are varied during the optimization process from 0.05 to 5 and from 1000 to 1, respectively. The batch size was set to 8 and the final models used for the production runs were trained for 2×10^6 steps.

Accuracy of the ML-based interatomic potential. The mean absolute errors (MAEs) of energies in the training and test set are 2.11 and 2.74 meV per atom, respectively. The MAEs of forces in the training and test set are 64.8 and 54.8 meV/Å, respectively (Fig. S21). Relevant frames along the reactive pathways and the transition states were included in the test set. We also carefully verified the accuracy of the forces predicted by the ML potential on the atoms involved in the reactions, confirming that the errors were small and consistent with the overall accuracy of the ML potential.

Molecular dynamics simulations

The bulk dynamics of BaH₂ was studied in an orthorhombic supercell of edges 27.278, 25.376, 31.508 Å, containing 1152 atoms, which amounts to replicate $4 \times 6 \times 4$ times the conventional unit cell. The ammonia synthesis on the (120) surface was modelled using a slab made of 756 atoms with edges 32.398, 23.648, 77.325 Å. In this setup, we left enough distance (about 20 Å) between replicas along the z direction to minimize interactions. In all the simulations of the (120) surface, we fixed the atoms in the 2 bottom layers to their ideal crystal lattice positions to mimic the bulk environment.

For reactive events where a N₂ or H₂ gaseous molecule is involved, we constrained the z-position of the molecule using a reflective wall⁶⁸. In this way the molecule can move in a volume of $32.398 \times 23.648 \times 10 \text{ Å}^3$.

Deep Potential molecular dynamics simulations were performed with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software (version 24Mar2022)⁶⁹, patched with DeePMD-kit and PLUMED (version 2.9)⁷⁰. NVT simulations were performed with an integration time step of 0.5 fs. The temperature was controlled using stochastic velocity rescaling thermostat⁵⁹ with a coupling constant of 50 fs.

MD simulations within the NPT ensemble were conducted using the Parrinello-Rahman formalism^{51,71} to ensure the stability of the BaH_{2-2x}(NH)_x system. We used a pressure damping parameter of 250 fs and a scalar external pressure of 1 bar. All the simulations were performed on the deuterated system.

Enhanced sampling simulations

The PLUMED library⁷⁰ is used to calculate the collective variables and the OPES⁷² bias potentials for both ab initio and deep potential molecular dynamics simulations. The formation of H₂ from the pristine surface was obtained by biasing the minimum of the distance between H atoms $d = d(\text{H}, \text{H})$:

$$\min(d) = \frac{\beta}{\log \sum_i \exp\left(\frac{\beta}{d_i}\right)} \quad (1)$$

The biased simulations regarding the formation of the various hydrogenated nitrogen species (i.e., NNH³⁺, HNNH²⁺, NH²⁺, NH₂⁺, NH₃) were performed by biasing the maximum of the coordination number (C.N. = C.N.(N,H)) between N and H atoms:

$$\text{C.N.} = \sum_{i \in \text{H}} \frac{1 - \left(\frac{d_{\text{N,H}}}{d_0}\right)^6}{1 - \left(\frac{d_{\text{N,H}}}{d_0}\right)^{12}} \quad (2)$$

$$\max(\text{C.N.}) = \beta \log \sum_i \exp\left(\frac{\text{C.N.}_i}{\beta}\right) \quad (3)$$

where $d_{\text{N,H}}$ is the distance between N and H atoms. Details regarding the bias settings are reported in Table S3.

Neural network model for predicting Bader charges

The training of the neural network for Bader charges inference is performed using a DeepDOS model⁷³ with an attention mechanism⁷⁴. Bader charges were computed processing the DFT charge density obtained from QE with the code by Henkelman et al.⁷⁵. The embedding network is composed of three layers with 25, 50, and 100 nodes, while the fitting network has three hidden layers with 240 nodes in each layer. The radius cut-off is chosen to decay from 0.5 Å to 6.0 Å. The number of layers in the attention scheme is set to 2, whereas the size of the embedding matrix to 12. Since we want to train only the scalar atomic properties, i.e., Bader charges per atom, we set the weight of the global loss to 0, whereas the weight of the atomic loss is set to 1. The training set and test set are composed by 23746 and 290 configurations, respectively. The RMSE on the test set is $1.71\text{e-}2 e$ and the MAE is $6.79\text{e-}3 e$ (Figs. S22 and S23).

Data availability

Inputs and instructions to reproduce the results presented in this manuscript can be found in the Zenodo repository (<https://doi.org/10.5281/zenodo.14789082>). Source data are provided with this paper.

Code availability

Results described in this manuscript have been obtained with publicly available software packages such as CP2K, Quantum Espresso (<https://www.quantum-espresso.org>), LAMMPS (<https://docs.lammps.org>), Plumed (<https://www.plumed.org>) and DeePMD-kit (<https://docs.deepmodeling.com/projects/deepmd>).

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Author contributions

A.T.G., U.R., and M.P. made substantial contributions to the design and implementation of the work and wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Michele Parrinello.

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