Heterogeneous Fe\textsubscript{3} single-cluster catalyst for ammonia synthesis via an associative mechanism

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The current industrial ammonia synthesis relies on Haber–Bosch process that is initiated by the dissociative mechanism, in which the adsorbed N\textsubscript{2} dissociates directly, and thus is limited by Brønsted–Evans–Polanyi (BEP) relation. Here we propose a new strategy that an anchored Fe\textsubscript{3} cluster on the θ-Al\textsubscript{2}O\textsubscript{3}(010) surface as a heterogeneous catalyst for ammonia synthesis from first-principles theoretical study and microkinetic analysis. We have studied the whole catalytic mechanism for conversion of N\textsubscript{2} to NH\textsubscript{3} on Fe\textsubscript{3}/θ-Al\textsubscript{2}O\textsubscript{3}(010), and find that an associative mechanism, in which the adsorbed N\textsubscript{2} is first hydrogenated to NNH, dominates over the dissociative mechanism, which we attribute to the large spin polarization, low oxidation state of iron, and multi-step redox capability of Fe\textsubscript{3} cluster. The associative mechanism liberates the turnover frequency (TOF) for ammonia production from the limitation due to the BEP relation, and the calculated TOF on Fe\textsubscript{3}/θ-Al\textsubscript{2}O\textsubscript{3}(010) is comparable to Ru B5 site.
Ammonia synthesis is one of the most important industrial catalytic reactions, which is based on the Haber–Bosch process \( \text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3 \) since the World War II, and it plays a key role in the growth of human population \(^{1,2}\). Although the process using Fe and Ru metal-based catalysts with promoters has been developed for more than one hundred years, it still requires high pressure (~100 bar) and moderately high temperature (~700 K) \(^3\), which is dictated by the compromise between thermodynamic equilibrium and kinetics \(^4\). Ammonia synthesis on Fe and Ru metal surfaces is widely regarded as a classical example of correlating the experimentally observable turnover frequency (TOF) with the predicted atomistic mechanism \(^5\), where the N\(_2\) activation is confirmed to be a direct N=N dissociation process \(^6-8\). The performance of promoted Fe- and Ru-based catalysts clearly shows a site dependence of the N\(_2\) dissociation and NH\(_x\) desorption \(^9\). N\(_2\) molecules are firstly dissociated on specific active sites, such as the B5 site of Ru(0001) step and the C7 site of Fe(111) or Fe(211) surface \(^9,10,11\), then the adsorbed *N is hydrogenated step by step to produce *NH\(_x\). This is the well-studied dissociative mechanism.

Previous theoretical studies discussed the possibility of ammonia synthesis at low temperature and low pressure \(^12,13\), but the TOF was limited, due to the Brønsted–Evans–Polanyi (BEP) relation \(^14,15\). The BEP relation regulates that the dissociation barrier of N\(_2\) and the desorption energies of NH\(_x\) scale linearly with the adsorption energy of N atom \(^12,14,16\). Stronger adsorption of N atom implies lower N\(_2\) dissociation barrier but higher NH\(_x\) desorption energies, such as on Re, Mo, Fe metal surfaces; while weaker adsorption of N atom indicates higher N\(_2\) dissociation barrier and lower NH\(_x\) desorption energies, such as on Pd, Co, Ni metal surfaces. Thus a good metal catalyst for ammonia synthesis must have a moderate atomic N adsorption energy, around where the top of volcano plot locates \(^15,16\).

Several molecular catalysts and naturally occurring nitrogenase enzymes are capable of reducing N\(_2\) under ambient conditions \(^17-21\), and the associated mechanisms are likely initiated by the associative adsorption or hydrogenation of N\(_2\), rather than the dissociative adsorption that is the key to the Haber–Bosch process. Recently, there were some theoretical indications showing that in the electrochemical ammonia synthesis the N\(_2\) molecule did not dissociate upon adsorption, but was hydrogenated to "*NNH instead" \(^22-29\). Even for the thermal catalytic process, Skułason et al. \(^30\) showed that the proportion of associative process (i.e., *N\(_2\) + *H → *NNH + *) is underestimated based on Bayesian statistics. For heterogeneous catalysis, O\(_2\) and CO can be hydrogenated via an associative mechanism to *OOH and *HCO, respectively, which have been proved to be key intermediates for O\(_2\) and CO activation \(^30-36\). When the N\(_2\) hydrogenation becomes the dominating process, the N–N bond is much weakened, and consequently the dissociation barrier no longer obeys the BEP relation. Thus, designing a catalyst with surface active centers that hydrogenate N\(_2\) first can be a new strategy to accomplish ammonia synthesis at low temperature and pressure.

The remarkable recent development of surface single-atom catalyst (SAC) and single-cluster catalyst (SCC) demonstrates the possibility to build homogeneous catalytic active centers on heterogeneous solid surfaces \(^37-41\). Inspired by nitrogenase, in which the FeMoco is responsible for N\(_2\) activation and ammonia synthesis \(^42-45\), Holland and co-workers designed a series of multinuclear iron complexes to mimic the nitrogenase, and showed that the formally Fe(I) and Fe(0) complexes can weaken or even break N\(_2\) triple bond at or below room temperature \(^18,19,46\). Hosono and co-workers also reported a series of stable electrides as efficient electron donor for loaded Ru metal, which is proved to be more reactive than the bare metal surface \(^47\).

**Fig. 1** Homogeneous and heterogeneous Fe\(_3\) cluster with N\(_2\) adsorption. a Schematic representation of N\(_2\) coordinated with three Fe(I)-ion homogeneous complexes in the side-on/end-on/end-on (\(\mu_5-\eta^2-\eta^1\)) configuration; b schematic representation of N\(_2\) coordinated with heterogeneous Fe\(_3\)/\(\theta\)-Al\(_2\)O\(_3\)/(010) in the same configuration; c optimized Fe\(_3\) cluster on \(\theta\)-Al\(_2\)O\(_3\)/(010); d, e optimized configurations of N\(_2\) adsorption on Fe\(_3\)/\(\theta\)-Al\(_2\)O\(_3\)/(010); f N\(_2\) adsorption configuration on the C7 site of Fe(211) surface.
In this work, we propose an active center of Fe$_3$ cluster that is anchored on the θ-Al$_2$O$_3$(010) surface, and we predict that the direct dissociation of *N$_2$ on this center is difficult (dissociative mechanism), but the *N$_2$ is easily hydrogenated to form the *NNH species (associative mechanism), which has a much lower N–N bond dissociation barrier than that of *N$_2$. We further reveal that the large spin polarization of Fe$_3$ is responsible for N$_2$ activation, and the low oxidation state iron atom works as an electron reservoir, regulating the charge variation of the whole process. The surface-anchored Fe$_3$ SCC renders a robust multi-electron reservoir, regulating the charge variation of the whole process. The surface-anchored Fe$_3$ SCC renders a robust multi-electron reservoir, regulating the charge variation of the whole process.

**Results**

N$_2$ adsorption on supported Fe$_3$ cluster. The FeMoco site of nitrogenase has been considered responsible for biological nitrogen fixation. Its performance in activating N$_2$ molecule originates from the highly efficient redox cycle between Fe(II) and Fe(III) of the Mo-Fe-S-C cluster of FeMoco. Based on the model of FeMoco, various Fe containing complexes are designed to mimic the N$_2$ activation process on FeMoco.$^{19,20,44,48-51}$ A general implication for designing such complex is to keep the Fe center at a reduced state to facilitate electron donation to the N$_2$ molecule.

In recent years, embedded Fe clusters with low oxidation state, such as three diketiminate-bound Fe(I) ions in Fig. 1a, are shown to synergistically facilitate N$_2$ reduction.$^{18,19,46,48,52}$ Inspired by this finding, we conceive that the small Fe clusters supported by θ-Al$_2$O$_3$(010) surface should be capable of efficient N$_2$ activation (Fig. 1b, c), because the inert support has little electronic interaction with the Fe cluster and thus retains Fe in an even more reduced state for metal-metal bonded Fe clusters.$^{3,35}$ This type of Fe clusters on alumina surface may be experimentally prepared by soft-landing cluster method or thermal treatment of ligated tri-iron cluster (e.g., Fe$_3$(CO)$_{12}$)$^{34,55}$. By testing the binding energies for Fe$_n$ clusters ($n = 1–5$) (Supplementary Fig. 1 and 2), we have shown that the triangular Fe$_3$ and the pyramidal Fe$_4$ are the most stable clusters on Al$_2$O$_3$ substrate, with the Fe$_3$ cluster kinetically stable against aggregation.

Here we focus on the catalytic performance of Fe$_3$ on ammonia synthesis, while we have also proved that the pyramid Fe$_4$ cluster, consisting of four triangular planes, exhibits similar catalytic activity to that of Fe$_3$ cluster (Supplementary Fig. 3). Fe$_3$/θ-Al$_2$O$_3$(010) with magnetic moment of 10 μB is the most stable, and the state of 8 μB is only 0.08 eV less stable (Supplementary Fig. 4), which is consistent with the ab initio molecular dynamics (AIMD) simulations in which the magnetic moment oscillates between 10 and 8 μB (Supplementary Fig. 5g). Such large spin polarization on Fe sites is thought to be one of the key factors to activate N$_2$ on FoMoco and Fe complexes.$^{19,43,56}$

Two of the most stable configurations of N$_2$ adsorption on the Fe$_3$ site are shown in Fig. 1d and e, which are denoted as μ$_3$−η¹−η¹ (side-on/end-on/end-on) and μ$_3$−η¹−η¹ (end-on/end-on/end-on), respectively. These two configurations are also observed in the AIMD simulations (Supplementary Fig. 5). N$_2$ can also adsorb at single or double Fe sites as μ$_2$−η¹−η¹, μ$_1$−η¹, and μ$_1$−η¹ configurations$^{37,38}$, but these are less stable here (Supplementary Fig. 6). The Bader charge on N$_2$ decreases to −1.13 |e| with its bond length significantly stretched from 1.10 Å in gas phase to 1.26 Å, close to that in N$_2$F$_2$. In comparison, the N–N bond length on C7 site of Fe(221) surface with high surface energy is 1.33 Å with Bader charge of −1.55 |e| (Fig. 1f).

**Competition between dissociative and associative hydrogenation.** Lots of efforts have been made to investigate the mechanism of ammonia synthesis on metal surfaces. It is found that the N$_2$ molecule dissociates directly at specific sites of the surface, such as the B5 site of Ru(0001) step surface and the C7 site of Fe(111) or Fe(211) surface.$^{5,10,59}$ The barrier of N$_2$ direct dissociation over close-packed Ru(0001) surface is as high as 1.9 eV but lowers to 0.4 eV on the step site.$^{6}$ Different from on the Fe(C7) site, the binding energy of *NH$_x$ on Ru surface is lower. According to the BEP relation, the dissociation barrier of N$_2$ (ΔG($N_2$)) and desorption energies of *NH$_x$ (ΔG(*NH$_x$)) scale linearly with the
amsythesis. a The dissociative mechanism, and three pathways of associative mechanism with N–N bond dissociation at *NNH, *HNNH, and *HNNH₂ intermediates by the alternating hydrogenation route. b Two pathways of associative mechanism by the distal hydrogenation route. c Initial, transition, and final states of *N₂ and *NNH dissociation step. d Schematic depiction of the six reaction pathways for conversion of N₂ to NH₃ catalyzed by Feₓ/Al₂O₃(010). Reaction energies are shown for every step and barriers are enclosed in brackets. The dissociation steps of *N₂, *NNH, *HNNH, and *HNNH₂ intermediates are enclosed with dashed lines

ad sorption energy of N atom (ΔG(N)) on the same type of sites, so the dependence of ΔG*N₂(N₂) and ΔG*NNH* on ΔG(N) can be fitted into lines. It is found that the intercepts of such lines for step sites are lower than those for terrace sites, but the slopes are similar for different kinds of sites. Thus, with the N₂ dissociative mechanism on metal surfaces (the slopes of ΔG*N₂(N₂) and ΔG*NNH* against ΔG(N) are of opposite signs), high temperature and high pressure are intrinsically needed to overcome ΔG*N₂(N₂) and ensure the desorption of NHₓ simultaneously.

When N₂ adsorbs on Fe(211) surface, the anti-bonding π* orbitals of N₂ interact strongly with Fe metal surface, and each N is coordinated with four surface Fe, so N₂ cannot be hydrogenated without reconstruction. As shown in Fig. 2, the *NNH species (B2) has to rotate from the original *N₂ (B1), with the N–N bond length increased to 1.40 Å. Although the dissociation barrier of *NNH (i.e., from B2 to B3) is only 0.32 eV, the hydrogenation barrier of *N₂ (from B1 to B2) is as high as 1.38 eV, which is much higher than the *N₂ direct dissociation barrier. Thus, it is the high hydrogenation barrier initiating the associative mechanism that makes the dissociative mechanism dominate on Fe(211) surface.

Based on the mechanism on metal catalysts, we investigate the reaction pathways of N₂ activation on single-cluster catalyst Feₓ/θ-Al₂O₃(010), as shown in Fig. 3 and Supplementary Fig. 8. The calculated barrier of *N₂ direct dissociation is 1.89 eV (Fig. 3c, d), but the associative hydrogenation of *N₂ to *NNH only has a barrier of 0.98 eV, which can be driven over with relatively low temperature. Note that the H₂ dissociative adsorption barrier is as low as 0.05 eV (Supplementary Fig. 9), which can be neglected comparably. The *N₂ dissociation is a structure-sensitive process, which usually needs more than 5 surface metal atoms’ cooperation. The geometry of Feₓ cluster is similar to a close-packed Fe(111) surface, where the dissociation of *N₂ is not favored. However, the electronic structure of supported Feₓ cluster is distinct from that of metal surface, which will be
discussed in the electronic structures section. On metal surface sites, such as Ru B5 site, the barrier of $^{*}$N$_2$ hydrogenation is about 0.2 eV higher than that of $^{*}$N$_2$ dissociation, which leads to around three orders of magnitude difference between the rate constants$^{25}$. On the contrary, on Fe$_3$/θ-Al$_2$O$_3$(010), the barrier of $^{*}$N$_2$ hydrogenation is 0.91 eV lower than that of $^{*}$N$_2$ dissociation, and the calculated rate constants are $9.8 \times 10^{-3}$ s$^{-1}$ and $5.2 \times 10^{-1}$ s$^{-1}$ at 700 K and 100 bar, respectively.

**Reaction mechanisms.** As is shown earlier (see also the movie file in the supplementary material), N$_2$ is first activated on Fe$_3$ active center followed by attacking by dissociated H atom, which differs from the procedure in electrochemical condition where proton attacks the adsorbed N$_2$ in solution. With thermochemical condition, after the first N$_2$ hydrogenation step, it is more favorable for $^{*}$NNH to dissociate into $^{*}$N and $^{*}$NH rather than further hydrogenation to $^{*}$HNHH or $^{*}$NNH$_2$. Such associative process is believed to occur in the homogeneous catalysis and enzymatic mechanism$^{44,50,60,61}$. As shown in Fig. 3d, the $^{*}$NNH can migrate from Fe$_3$ to the Fe$_3$/θ-Al$_2$O$_3$(010) interface (i.e., b2 to b2') with a barrier of 0.45 eV, where the N-end coordinates with two Fe atoms and the NH-end coordinates with one Fe and one substrate Al ion. The dissociation barrier of $^{*}$NNH in b2 is only 0.45 eV with an exothermic reaction energy of $-1.20$ eV (Fig. 3c, d). Afterwards, the upper $^{*}$N atom moves to the Fe$_3$ 3-fold site, while the lower $^{*}$NH is anchored at the Fe$_3$/θ-Al$_2$O$_3$(010) interface by coordinating with one surface Al ion and two Fe atoms.

The $^{*}$NNH can also be hydrogenated further via the alternating or the distal pathway$^{49,51,56}$. In the alternating pathway, $^{*}$NNH is hydrogenated to $^{*}$HNHH with a barrier of 1.16 eV (b2 to c1), and the N–N bond length is elongated to 1.42 Å with the N–N stretching frequency of 1012 cm$^{-1}$, suggesting a single bond between N atoms. The formed $^{*}$HNHH species can either dissociate into two $^{*}$NH group or be hydrogenated to $^{*}$H$_2$NNH that can again dissociate into $^{*}$NH$_2$ and $^{*}$N. The $^{*}$NH$_x$ ($x = 1$–2) species can be ultimately hydrogenated to $^{*}$NH$_3$.

In the distal pathway, $^{*}$NNH is hydrogenated to $^{*}$NNH$_2$, where both H atoms are on the same end of N–N bond. This process requires a barrier of 1.31 eV, slightly higher than that of the alternating pathway. Next, $^{*}$NNH$_2$ can be further hydrogenated to $^{*}$HNHH or $^{*}$N$^{+}$ $^{*}$NH$_2$. The latter step features spontaneous N–N bond dissociation with a barrier of 0.95 eV, while the former step drives the distal pathway back to the alternating one with a barrier of 1.24 eV.

Overall, we find that the most hydrogenation steps experience barriers ranging from 1.0 to 1.3 eV, which are close to those on metal surfaces$^{5,6}$, but the indirect N–N bond breaking via $^{*}$NNH has only a barrier of 0.45 eV, much lower than the direct N–N dissociation. As a result, the N–N bond breaking step is not the rate-determining step (RDS) of ammonia synthesis on surface-supported Fe$_3$ cluster, distinct from on the traditional metal catalyst surfaces.

The N–N bond dissociation via $^{*}$NNH bypasses the direct dissociation of $^{*}$N$_2$ that is one of the severe limitations for the Haber–Bosch process. On the Sabatier volcano curve$^{14}$, the $^{*}$N$_2$ dissociation is replaced by the $^{*}$NNH dissociation, which has a lower barrier that can be driven over with moderate thermodynamic conditions. Therefore, the RDS is no longer the dissociation of N$_2$ but desorption of NH$_x$ species. Such an associative mechanism for N$_2$ activation is what nitrogenase does in nature$^{25}$, and has been reproduced by metal complexes for homogeneous catalysis, where the N$_2$ triple bond is first weakened by single-metal or multiple-metal center, and then hydrogenated by protons and electrons toward NH$_3$ formation$^{42}$. The surface-anchored Fe$_3$ center with multi-step redox capability, large spin polarization and low oxidation state metal provides a heterogeneous single-cluster catalyst design to mimic the FeMoco in nature.

We further tracked the Bader charges of Fe$_3$ cluster and the N-containing adsorbates along the reaction pathway with associative mechanism, as shown in Fig. 4. The highly reducing Fe$_3$ cluster is strongly oxidized during the whole process. When N$_2$ and H$_2$ are adsorbed on Fe$_3$ cluster, the Bader charge of Fe$_3$ increases from 0.59 to 2.97 [e], while N$_2$ and H$_2$ are reduced to $^{*}$N$_2$ and $^{*}$H$^{2+}$ adsorbates. The bond order of N$_2$ is reduced to 2.5, with its bond length of 1.26 Å and stretching vibrational frequency of 1384 cm$^{-1}$. Then, one $^{*}$H$^{2+}$ combines with $^{*}$N$_2$ to form a $^{*}$NNH species, with one electron released back to Fe$_3$ simultaneously. The N–N bond length is then lengthened to 1.36 Å with stretching frequency of 1099 cm$^{-1}$, and the N–N bond order becomes 2.0 with around two electrons occupying its $\pi^*$ orbitals. Bader charges on Fe$_3$ and $^{*}$NNH turn to 2.45 and $-1.13$ [e], respectively. When $^{*}$NNH migrates from the Fe$_3$ cluster to the Fe$_3$/θ-Al$_2$O$_3$(010) interface, the N–N bond length is further stretched to 1.40 Å with Bader charge of $-1.47$ [e]. As shown in Fig. 4, Fe$_3$ is a bifunctional multi-step redox active center for donating electrons at the adsorption steps and accepting electrons at the hydrogenation steps. Thus, the surface-anchored Fe$_3$ single cluster serves as an electron reservoir that regulates the charge variation of the whole process.

**Electronic structures.** To elucidate the bonding nature of the species involved in the associative mechanism, we investigate the densities of states (DOS) of N$_2$ adsorption on Fe$_3$/θ-Al$_2$O$_3$(010) (with the most stable configuration $\mu_3$–$\pi_1^1$–$\pi_1^1$–$\pi_1^1$) and C7 site of Fe(211) (Fig. 5a and Supplementary Fig. 10) for comparison. The energy levels of Fe$_3$ minority $\beta$-spin d orbitals and N$_2$ $\pi^*$ orbitals are well matched, leading to partial occupation of the formed $d$-$\pi^*$ orbitals. While the strong spin polarization provides large exchange stabilization energy for the majority $\alpha$-spin orbitals, leading to that the energy levels of Fe$_3$’s $\alpha$-spin d orbitals are about 2.5 eV lower than the $\pi^*$ orbitals of N$_2$, and thus no obvious interaction of a orbitals is observed. This indicates that only the $\beta$ $\pi^*$ orbitals of $^{*}$N$_2$ are partially occupied, and thus forcing $^{*}$N$_2$ to be of radical nature (with unpaired electron, Fig. 5c) that is active for hydrogenation. Therefore, the large spin polarization on Fe$_3$ cluster is responsible for the activation of N$_2$. When $^{*}$N$_2$ is hydrogenated to $^{*}$NNH, one electron transfers from hydrogen to the $\alpha$ $\pi^*$ orbitals of $^{*}$N$_2$, and now both $\alpha$ and $\beta$ DOS of Fe$_3$’s d orbitals overlap with NNH’s $\pi^*$ orbitals, which further weakens
the N–N bond. Therefore, the more interaction and thus larger occupation of the π* orbitals in NH3 leads to a lower N–N bond order, and is thus responsible for the lower dissociation barrier than that of *N2.

Fragment orbital analysis is further performed to provide more details of such interaction between isolated Fe3 and N2 (Fig. 5e, Supplementary Fig. 11 and Supplementary Table 1). The main contribution to the interaction is from the tangential σ, πt molecular orbitals of Fe3 and N2 π* orbitals, which lead to two bonding orbitals and two anti-bonding orbitals. This bonding model shows that the electrons from metal d orbitals partially transfer to the empty π* orbitals of N2, which is consistent with the electron transfer shown in the charge density difference (Fig. 5d) and the DOS analysis. Remarkably, in homogeneous catalysis, the N2 activation process is also initiated with the electron transfer from the electron-rich metal center to the empty π* orbitals of N2, which lowers the bond order in N2 and facilitates the hydrogenation process.

**Microkinetic simulations.** To explore the reactive performance of ammonia synthesis under realistic conditions, we performed comparative kinetic analysis of Fe3/Al2O3, Fe surface, and Ru surface based on the free energy calculations. (Supplementary Fig. 12 and 13) The TOF map (Fig. 6a) is calculated under the pressure range of 1–100 bar and the temperature range of 300–1000 K. The TOF of ammonia production on Fe3/Al2O3 is less than 10−10 s−1 site−1 below 400 K because of too stable adsorption of NH3 species (Supplementary Fig. 14a). At high temperature and low pressure, the conversion of NH3 is lower than 10%, and the decomposition of ammonia occurs. With the increase of temperature, the concentrations of NH3 decrease and that of bare sites increase, since the entropy of free gas molecules becomes dominant. The calculated TOF on Fe3/Al2O3 is 1.4 × 10−2 s−1 site−1 at 100 bar and 700 K, which is comparable to that on the Ru B5 site. As shown in Fig. 6b, the contribution from the associative mechanism is six orders of magnitude larger than from the dissociative mechanism. While on the Ru step surface, the TOF of the dissociative mechanism is calculated to be three orders of magnitude lower than that of the dissociative mechanism.

Based on the above microkinetic analysis of the ammonia synthesis on Fe3/Al2O3(010), we further compare it with the widely reported cases on Fe C7 site and Ru B5 site (Fig. 6c). The coverages and free energy diagrams for surface species are shown in Supplementary Fig. 13 and 14. For Fe C7 site, although the transition state energy of *N2 dissociation is only −0.10 eV with respect to the gas phase N2 and clean surface, the adsorption energy of two *N is as high as −2.4 eV (Fig. 2), which results in dominant coverage of *N on the active center (Supplementary Fig. 14). Thus, the RDS on Fe C7 site is the desorption of NH3 species. For Ru B5 site, the transition energy of *N2 dissociation is 0.4 eV, with two *N adsorption energy of −0.8 eV. At low (<450 K) and high (>450 K) temperature, the Ru B5 site is covered by *NH2 and *H, respectively. Thus, Ru B5 site is the closest to the top of volcano curve, which balances the *N2 dissociation and *NH3 desorption processes.

For our single-cluster catalyst Fe3/Al2O3(010), the Fe3 active site is covered by *NH2 and *NH3 at low temperature, and at constant temperature or pressure (Supplementary Fig. 14), the TOF on Fe3/Al2O3(010) is comparable to that on Ru B5 site.
and is about two orders of magnitude larger than on Fe C7 site. (Supplementary Fig. 15) By plotting the TOF against the partial pressure of N₂ as shown in Fig. 6d, the maxima for Fe C7, Fe₃/θ-Al₂O₃(010), and Ru B5 site are 0.06, 0.44, and 0.78, respectively. As the Fe C7 site is mainly covered by *N, lowering the N₂ partial pressure from 25% to 6% increases the TOF. On the contrary, for Ru B5 site, the main surface species is *H at 700 K and 100 bar, and thus increasing the proportion of N₂ accelerates the reaction. For Fe₃/θ-Al₂O₃(010), to reach a high TOF, one should balance the partial pressure of N₂:H₂, because the associative mechanism requires the co-adsorption of N₂ and H₂ to form the *NNH species, which is the key intermediate as discussed above.

As shown in Fig. 6e, for most active sites on metal surfaces, there is a linear relation (i.e., BEP relation) between the adsorption energies of N atom (Eₐ) and the transition state energies (Eₜₐₜ) as well as the nitrogen adsorption energy (Eₐₐₜ). The partial occupation of N₂ π* orbitals to N₂ π* orbitals. The partial occupation of N₂’s β-spin π* orbitals both lowers the N–N bond order and also grants *N₂ a spin-polarized charge transfer from Fe’s 3d orbitals to N₂ π* orbitals. The partial occupation of N₂’s β-spin π* orbitals both lowers the N–N bond order and also grants *N₂ a novel radical nature that leads to an associative mechanism for N₂ activation, which mimics the initiation process in the nitrogenase as well as artificial metal complexes for homogeneous catalysis involving nitrogen fixation.

Discussion
We propose a surface-anchored Fe₃ single-cluster active center for ammonia synthesis by first-principle calculations and microkinetic analysis. This Fe₃ cluster can be stably anchored on the θ-Al₂O₃(010) surface, and its multi-step redox capacity, large spin polarization and low oxidation state metal enable efficient N₂ activation, due to the spin-polarized charge transfer from Fe’s 3d orbitals to N₂ π* orbitals. The partial occupation of N₂’s β-spin π* orbitals both lowers the N–N bond order and also grants *N₂ a novel radical nature that leads to an associative mechanism for N₂ activation, which mimics the initiation process in the nitrogenase as well as artificial metal complexes for homogeneous catalysis involving nitrogen fixation.

We predict the whole catalytic mechanism for ammonia synthesis on Fe₃/θ-Al₂O₃(010) that is distinctly different from on the industrially used Fe and Ru metal surfaces. The dissociative mechanism dominates the ammonia synthesis on metal surfaces, where *N₂ dissociates directly. Thus, the TOF of ammonia synthesis on metal surfaces obeys the BEP relation that demands the balance between N₂ dissociation and NH₃ desorption. However, we find that in our associative mechanism at the single-cluster catalyst the first hydrogenation of N₂ to *NNH is much
faster than the dissociative mechanism on Fe₃/Al₂O₃(010), and the following dissociation of \( \text{NNH} \) only has a barrier of 0.45 eV. Remarkably, the associative mechanism bypasses the BEP relation and thus the limitation underlying one side of the volcano curve. Such surface-anchored Fe₃ center represents a class of new catalyst—single-cluster catalysts become the promising candidate heterogeneous catalysts for highly selective ammonia synthesis via the associative mechanism. In the future work, we will conduct extensive investigation of various surface-anchored metal trimers and polyatomic clusters, in order to find the optimum of such design for ammonia synthesis toward high TOF at low temperature and low pressure. Highly tunable single-cluster catalysts with well accommodating support hold promises for rational design of highly selective and active catalysts for complicated catalytic reactions such as N₂-to-NH₃ conversion.

Methods

DFT parameters. Energetics calculations for reaction mechanisms were carried out by using spin-polarized density functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation as implemented in VASP 5.3.4. The cutoff energy of plane-wave basis set is 400 eV and single gamma-point grid sampling was used for Brillouin zone integration. Atomic positions were optimized until the forces were less than 0.02 eV Å⁻¹. Transition states were searched by climbing image nudged elastic-band method (CI-NEB) and further optimized until the forces were less than 0.02 eV Å⁻¹. The slab lattice parameters were obtained by vibrational frequency analysis. The slab consists of seven O₁-Al₂O₃ planes, in order to mimic the support bulk. The trinuclear Fe clusters were anchored by coordinating with surface oxygen as shown in Fig. 1c, and Supplementary Fig. 1. The formation energy of adsorbed iron clusters is defined as \( E_f = E(\text{Fe}_3/\text{Al}_2\text{O}_3) - E(\text{Al}_2\text{O}_3) - nE(\text{Fe}) \), where \( E(\text{Fe}_3/\text{Al}_2\text{O}_3) \) is the total energy of Al₂O₃ surface with Fe₃ adsorbed, \( E(\text{Al}_2\text{O}_3) \) is the energy of pristine Al₂O₃ surface, and \( E(\text{Fe}) \) is the energy per atom of Fe metal. So the formation energy includes both the formation energy of gas Fe₃ cluster and its binding energy on surface. Therefore, we can directly evaluate the stability by \( E_f \). The binding energy of Fe₃ cluster is defined as \( E_{\text{bind}} = E(\text{Fe}_3/\text{Al}_2\text{O}_3) - E(\text{Al}_2\text{O}_3) - nE(\text{Fe}) \), where \( E(\text{Fe}_3/\text{Al}_2\text{O}_3) \) is the energy of gas phase Fe₃ cluster. The adsorption energies of molecules are defined as \( E_{\text{ads}}(\text{M}) = E(\text{Fe}_3/\text{Al}_2\text{O}_3) - E(\text{Al}_2\text{O}_3) - E(x) \), where \( x \) is H₂, N₂, and NH₃. The adsorption energy of N atom is defined as \( E_{\text{ads}}(\text{N}) = 1/2 \left( E(2 \text{Fe}_3/\text{Al}_2\text{O}_3) - E(\text{Al}_2\text{O}_3) - E(\text{Fe}) \right) \). The binding energy of N₂ is the total energy for N₂ desorption.

Chemical bonding analysis. Electronic structure analyses were performed using spin-unrestricted DFT with PBE exchange-correlation functional and TZ2P Slater basis sets as implemented in the Amsterdam Density Functional (ADF 2016.101) program. Frozen core approximations were applied to N [1s²] and Fe [1s²-2p²]. The scalar relativistic (SR) effect was included by the zero-order-regular approximation (ZORA)²⁶. Fe and N₂ were optimized under D₃h and C₃v point-group symmetries, respectively, at all possible spin configurations. Molecular orbitals (MOs) of Fe₃ and N₂ and their corresponding contributions from Fe₃ and N₂ were obtained from fragment MO analyses.

Microkinetic method. Microkinetic modeling was carried out using the CatMAP software package. The model was constructed by numerically solving the differential equations that describe the coverage of each surface intermediates under the steady-state approximation. The rate equations of each elementary step was calculated by using harmonic transition state theory. The free energies for gas molecules were estimated using the ideal gas approximation considering the vibrational, rotational, and translational contributions to both entropy and enthalpy, while the free energies for surface adsorbates were approximated using the harmonic approximation that treats all degrees of freedom as vibrational modes. The steady-state TOFs were calculated based on the steady-state surface coverages.

Data availability. All other data supporting the findings of this study are available in the article and its Supplementary Information files and from the corresponding author on request.

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Author contributions
J.-L. conceived and directed the research. J.-C.L. performed all the calculations. J.-C.L., X.-F. and J.L. co-wrote the paper. All the authors discussed the results and commented on the manuscript.

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