Exploring trimetallic clusters containing alkali and alkaline earth metal atoms with high activity for nitrogen activation

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Abstract
Activation of dinitrogen (N2) is the critical step in nitrogen reduction reaction (NRR) in ammonia synthesis. In this paper, reaction mechanisms of N2 activation on trimetallic clusters Mo2M (M = Li, Na, K, Mg, and Ca) and Mo3−xCa2x (x = 2–3) were systematically studied by density functional theory calculations. Unlike Mo2 which is inert to N2, clusters with alkali or alkaline earth metal atoms have much higher reactivity toward N2 in terms of both thermodynamics and kinetics. Particularly, in one reaction path of N2 with MoCa2, all the intermediates and transition states are well below the energy sum of the reactants, indicating that the dissociation of N2 on MoCa2 can take place spontaneously in gas-phase reactions. N2 transfers on clusters with different coordination modes, and the N−N bond is gradually activated. When N2 is bonded with three metal atoms with end-on: side-on: side-on coordination mode, it is fully activated and easily dissociated into two adsorbed N atoms. These results may serve as a prototype to design single-cluster catalysts with a trimetallic center for nitrogen activation and conversion.

Keywords Density functional theory · Nitrogen reduction reaction · Trimetallic clusters · Alkali metal · Alkaline earth metal

Introduction
Nitrogen-containing compounds are useful not only in agriculture [1] but also in new energy sources [2–6]. However, N2 is difficult to be activated because of its strong N≡N triple bonds, large highest occupied molecular orbital-lower unoccupied molecular orbital gap, and large ionization energy [7, 8]. At present, the most common large-scale nitrogen fixation process in the industry is Haber–Bosch, which requires a high temperature of up to 400 °C and high pressure of up to 15–25 MPa to produce ammonia through nitrogen reduction reaction (NRR) [9–14]. In the process of NRR, the environmental pollution caused by such a high temperature and pressure is very serious, so nitrogen fixation is a challenging and vital problem both in chemistry and industry. It is urgent to design new catalysts to convert N2 into nitrogen-containing compounds much more effectively under mild conditions [15, 16].

The development of single-atom catalysis (SAC) provides a new idea for catalyst design [17]. SAC can improve the atomic utilization of precious metals to the limit, and the active center is quite uniform, which improves the selectivity of catalytic reactions and reduces the occurrence of side reactions [18–20]. However, the coordination modes of N2 on the single metal atom are limited, only end-on or side-on, which is not conducive to the activation of N−N bond. It has been predicted that diatomic catalysts may have better NRR activity [21, 22]. Then, in 2018, Li et al. found that Fe3 clusters fixed on the surface of θ-Al2O3 can be good catalysts for heterogeneous ammonia synthesis [23]. The catalytic
mechanism of $\text{N}_2$ conversion to $\text{NH}_3$ on Fe$_3$/Al$_2$O$_3$ (010) was studied theoretically. They further studied the catalytic mechanism of $\text{N}_2$ to $\text{NH}_3$ on monodisperse Rh$_{10}$Co$_3$/CoO (011) [24]. A new concept of single-cluster catalysis (SCC) was proposed, which provides a new strategy for designing new catalysts especially for complicated reactions such as NRR. However, the catalytic mechanisms of the reaction on surfaces are very complicated, and the effect of the number of metal atoms on the reaction activity is not clear.

Gas-phase clusters are ideal models for simulating the active sites of related condensed phase systems, which can be used to understand the bond activation process under isolated and well-controlled conditions at a strictly molecular level [25–28], and is suitable to provide insights into the mechanisms of SAC and SCC [29]. A large number of experiments and theoretical work have explored the mechanism of $\text{N}_2$ activation by gas-phase clusters, mainly focusing on metal clusters [30–36], metal carbide clusters [37, 38], metal nitride clusters [39–41], and metal oxide clusters [42–44]. Coordination modes of $\text{N}_2$ on supporting atoms were found critical for $\text{N}_2$ activation. On bimetallic clusters, $\text{N}_2$ can first obtain the adsorption intermediate of side-on: side-on and then dissociate [35, 38], or it can pass through the intermediate of side-on: side-on and then dissociate [45–47]. On trimetallic clusters, $\text{N}_2$ is adsorbed on the center of the metal triangle in the form of side-on: side-on: side-on coordination modes before dissociation [48–51].

In the theoretical work of some bulk phases, it is predicted that trimetallic clusters can have good NRR activity [23, 52]. Some studies have shown that there are various coordination modes of $\text{N}_2$ on three metal atoms, which is beneficial for the dissociation of $\text{N}≡\text{N}$ triple bonds [23]. Experimental and theoretical studies on gas-phase clusters also showed that the clusters containing three active metal atoms can cleave the $\text{N}≡\text{N}$ triple bond under mild conditions [48–50, 53]. In addition, three atoms can reflect more comprehensively the complexity of the geometric and electronic structures of the active centers. The study of the reaction process of trimetallic clusters with nitrogen molecules is helpful to understand the activation mechanisms of nitrogen molecules deeply. Therefore, we will focus on $\text{N}_2$ activation on trimetallic clusters in this work.

Previous experimental studies have found that the doping of alkali/alkaline earth metal atoms into the catalysts (e.g., Ru) can promote NRR sufficiently [54]. The reason is that the doping metals are easy to provide electrons so that the $\pi^*$ antibond orbitals of $\text{N}_2$ can obtain electrons to activate the $\text{N}≡\text{N}$ triple bonds. However, there are few studies on the interaction between alkali/alkaline earth metal atoms with $\text{N}_2$ [55], let alone the study of trimetallic clusters. Therefore, in this work, based on Mo$_2$ clusters, we try to introduce alkali and alkaline earth metal atoms into systems to investigate the microscopic mechanism of the $\text{N}≡\text{N}$ bond activation on these clusters and explore systems with high reactivity. The specific research systems include Mo$_2$, Mo$_2$M (M = Li, Na, K, Mg, and Ca), and Mo$_{3−x}$Ca$_x$ ($x = 2 − 3$).

### Calculation methods

Density functional theory (DFT) calculations using the Gaussian 09 program package [56] were carried out to investigate the structures of Mo$_2$, Mo$_2$M (M = Li, Na, K, Mg, and Ca), and Mo$_{3−x}$Ca$_x$ ($x = 2 − 3$) as well as the reaction mechanisms of Mo$_2$ + $\text{N}_2$, Mo$_2$M + $\text{N}_2$, and Mo$_{3−x}$Ca$_x$ ($x = 2 − 3$) + $\text{N}_2$. The Mo$_2$ + $\text{N}_2$, Mo$_2$M + $\text{N}_2$, and Mo$_{3−x}$Ca$_x$ ($x = 2 − 3$) + $\text{N}_2$ are optimized using the TPSS functional [57]. Polarized triple-$\zeta$ basis set (def2-TZVP) [58] for valence electrons with the corresponding effective core potential [59] is used for Mo to take into account the scalar relativistic effects, while all electron def2-TZVP basis sets are used for the other elements. The adsorption energy of $\text{N}_2$ on the Mo$_2$M cluster is defined as $E_{\text{ad}} = E_{\text{(Mo$_x$M$_{1−x}$N$_2$)}} − E_{\text{(Mo$_x$M$_{1−x}$)}} − E_{\text{(N$_2$)}}$, where $E$ is the total electron energy corrected with zero-point vibration energy (ZPE). It is clear that $E_{\text{ad}}$ is also the relative energy with respect to the separated reactants, which is also denoted as $\Delta H_{0\text{K}}$ in this work. All energies reported are for $\Delta H_{0\text{K}}$ unless specified in some cases where the relative Gibbs free energy at 298.15 K (denoted as $\Delta G_{298\text{K}}$) is reported. Harmonic vibration frequencies of the optimized structures are calculated at the same theoretical level to determine the properties of stagnation points (the minimum has no imaginary frequency, and the transition state has only one imaginary frequency). The N–N bond length ($R_{\text{N–N}}$), Mayer bond order ($\text{MBO}_{\text{N–N}}$), bond vibration frequency ($\nu_{\text{N–N}}$), and Hirshfeld charge transfer ($Q_{\text{N2}}$) of key intermediates and transition states were analyzed to measure the activation degree of $\text{N}_2$ during the reaction of $\text{N}_2$ with Mo$_x$M and Mo$_{3−x}$Ca$_x$ ($x = 2 − 3$), in which the values of MBO$_{\text{N–N}}$ and $Q_{\text{N2}}$ were obtained by using the Multiwfn program [60].

### Results and discussion

#### Activation of $\text{N}_2$ on Mo$_2$ cluster

Reaction mechanisms of $\text{N}_2$ activation on Mo$_2$ were studied at first to compare with subsequent investigations on Mo$_2$ doped with alkali or alkaline earth metal atoms. Figure 1 shows the reaction path between singlet Mo$_2$ and $\text{N}_2$. $\text{N}_2$ is adsorbed on a Mo atom in the end-on coordination mode to form an intermediate (11) with small adsorption energy ($E_{\text{ad}}$) of $−0.27$ eV and a weak activation of N–N bond length of circuits.
112 pm (N−N bond length of free N₂ molecule is 110 pm). The system forms a stable I₂ by overcoming a low energy barrier (TS1, 0.38 eV). In I₂, N₂ is adsorbed on a Mo atom in side-on mode, and the N−N bond length is 113 pm. Then, by overcoming a higher energy barrier (TS2, 0.72 eV), the coordination mode of N₂ changes from side-on to end-on: side-on (I₃). For I₃, the energy is above zero point (IS₁) by 0.82 eV, and the N−N bond is prolonged from 113 to 124 pm. The N−N bond in I₃ can be directly dissociated by transition state 3 (TS3) to obtain the final product I₅ (−0.48 eV), but it needs to overcome a very high energy barrier (TS3, 0.92 eV). Alternatively, it can also be converted to side-on: side-on structure adsorbed on two Mo atoms (I₄), and then, N−N dissociates through TS₄, but this step requires a higher energy barrier (1.48 eV).

It can be seen that N₂ has different adsorption configurations on Mo₂ dimers, among which the energy of N₂ adsorption on end-on is the lowest, and the conversion of different adsorption configurations needs to overcome energy barriers. Although N₂ dissociation is an exothermic reaction (the head release is about 0.5 eV) on Mo₂ dimer, the dissociation of the N−N bond needs to overcome high energy barriers, so it is difficult for Mo₂ to react directly with N₂ to dissociate the N−N bond. Nitrogen adsorption sites and adsorption modes of diatomic metal clusters are relatively simple. Adding another metal atom to the diatomic can increase the diversity of nitrogen adsorption sites and adsorption modes. Next, we introduce alkali and alkaline earth metal atoms into Mo₂ clusters to explore more reactive clusters toward N₂ activation.

**Reaction of Mo₂M (M = Li, Na, K, Mg, and Ca) with N₂**

Optimized structures of Mo₂M (M = Li, Na, K, Mg, and Ca) clusters are all triangles, as shown in Fig. 2. Different spin multiplicities have been tested for each cluster in Table S1 in the Supplementary Information online (SI), and the doublet and triplet electronic states are found to have the lowest energy for Mo₂Li/Na/K and Mo₂Mg/Ca, respectively. The following calculations of N₂ adsorption and dissociation on
these clusters were just done with the same spin multiplicity as the clusters. Then, two possible initial adsorption sites of nitrogen molecules onto these clusters have been tested. One of the initial adsorption configurations is that N$_2$ is close to a Mo atom (Fig. 2a). After optimization, N$_2$ is adsorbed on a Mo atom in end-on coordination mode, and the N–N bond is extended from 110 to 113–114 pm. The adsorption energies ($E_{ad}$) of N$_2$ on this site for different clusters are similar, with $E_{ad}$ about −0.6 to −0.7 eV. The other initial adsorption configuration is that N$_2$ is close to the doping M, and two different adsorption modes are found after optimization (Fig. 2b). In the systems doped with alkali metal atoms Li, Na, or K, N$_2$ is adsorbed on the alkali metal atom with the end-on coordination mode, with an $E_{ad}$ relatively less negative (above −0.4 eV). The N≡N bond length is unchanged compared with that of the free N$_2$. In the systems doped with alkaline earth metal atoms Mg or Ca, N$_2$ is adsorbed on M and Mo; the coordination mode on the two metal atoms is side-on: end-on. $E_{ad}$ of Mo$_2$Mg is still less negative (−0.43 eV) while that of Mo$_2$Ca is as low as −0.90 eV. The N–N bond is extended from 110 to 119 pm, showing a certain degree of activation.

Compared with the case of Mo$_2$, when N$_2$ is adsorbed on Mo atoms of Mo$_2$M (M=Li, Na, K, Mg, and Ca) clusters, the adsorption energy is obviously more negative, and the N–N bond length increases slightly. When N$_2$ is adsorbed on M atoms (including on M-Mo), the adsorption energy on Mo$_2$Li/Mg/Ca is more negative than on Mo$_2$, and the N–N bond length of Mo$_2$Mg and Mo$_2$Ca increases surprisingly. It can be seen that the addition of alkali or alkaline earth metal atoms into Mo$_2$ will increase the stability of N$_2$ adsorption and the activation of N$_2$.

### Dissociation reaction path of N$_2$ on Mo$_2$M

Based on the study of nitrogen adsorption, we use TPSS functional to calculate the dissociation paths of nitrogen molecules at two different initial adsorption sites (Figs. 3 and 4). Taking the energy sum of the separated Mo$_2$M and N$_2$ as the reference, the relative energies ($\Delta H_{0K}$) of the intermediates and transition states are considered.

Figure 3 shows the reaction paths for the initial adsorption site of N$_2$ on a single Mo atom, including the structures of the intermediates and transition states (Fig. 3a) and their relative energy with respect to the separate reactants (Fig. 3b). The reaction paths of systems with three kinds of alkali metal atoms (Li, Na, and K) are similar, so we discuss them by taking Mo$_2$Li-N$_2$ as an example. When N$_2$ approaches the Mo atom of Mo$_2$M, it is adsorbed on the Mo atom in the form of end-on coordination (forming the intermediate I6). By overcoming the energy barrier of 0.16 eV, N$_2$ is transferred to Li and Mo atoms, and the intermediate I7 is obtained, in which N$_2$ is adsorbed on Li and Mo atoms in the form of side-on: end-on coordination. Next, a relatively high energy barrier (0.97 eV) needs to be overcome to obtain the key intermediate I8. In I8, N$_2$ connects with three metal atoms of Mo-Mo-Li in the coordination mode of end-on: end-on: side-on. In order to dissociate the N–N bond completely, it is necessary to overcome a very low energy barrier (0.04 eV) to form a stable configuration (I9). Note that I9 structures contain M–N=Mo bonds without M-Mo bonds, while TS7 structures contain M-Mo bonds and N atoms are at the bridge sites of M-Mo. The N–N bond dissociates completely (I10) with a high energy barrier (0.62 eV). From the change of reaction energy (Fig. 3b) for five systems, it can be seen that the barriers for N$_2$ transfer on Mo$_2$Li, Mo$_2$Na, and Mo$_2$K clusters are 0.97, 1.10, and 1.10 eV, respectively, at I7 → TS6 → I8, and 0.62, 0.65, and 0.67 eV to dissociate the N–N bond at I9 → TS8 → I10, respectively. In addition, from the point of view of thermodynamics, the energy gains of the three reaction systems are −1.86, −1.42, and −1.44 eV, respectively. Therefore, no matter from the point of view of thermodynamics or kinetics, Mo$_2$Li/Na/K clusters have similar reactivity toward N$_2$, and Mo$_2$Li is the most reactive one.

The reaction paths of clusters with two kinds of alkaline earth metal atoms (Mg, Ca) are similar to alkali metal systems. The only difference is that in the process of dissociating the N–N bond, the alkaline earth metal system does not need to go through the intermediate I9, and only needs one step (I8 → TS8 → I10) to get the dissociated product. For N$_2$ transfer process on the cluster (I7 → TS6 → I8), the energy barrier (1.14 eV) of Mo$_2$Mg cluster is higher than those of the alkali metal system, while that of the Mo$_2$Ca cluster (0.98 eV) is lower than those of the Na/K systems and only 0.01 eV higher than that of the Li system. In the process of N$_2$ dissociation (I8 → TS8 → I10), the energy barriers (0.56 and 0.44 eV) that Mo$_2$Mg and Mo$_2$Ca clusters need to overcome are lower than that for the complete dissociation of N–N bond in the systems doped with alkali metals in the step I9 → TS8 → I10 (> 0.6 eV). In terms of the energy relative to the reactants, the energies of the transition states of the Mo$_2$Ca system during N$_2$ transfer (TS6) and N–N bond dissociation (TS8) are 0.08 and 0.01 eV, respectively, which are much lower than those of Mo$_2$Li (0.20 and 0.38 eV). In addition, the energy gain of the whole reaction for Mo$_2$Ca system reaches 2.28 eV, which is also the largest. Therefore, Mo$_2$Ca has relatively the highest reactivity toward N$_2$ among all studied clusters. However, it can also be seen that the N$_2$ transfer process in Mo$_2$Ca system has a global energy barrier of +0.08 eV, and the relative energy barrier is still quite large especially for the N$_2$ transfer process (0.98 eV). Therefore, the reaction processes need to be further optimized. Changing the initial adsorption site may affect N$_2$ transfer.
process. In the following study, we will explore whether we can change the \( N_2 \) transfer process by changing the initial adsorption site, to reduce the energy barrier of the reaction process.

To take thermal contributions into account, reaction paths in Fig. 3 are also drawn with the data of \( \Delta G_{298K} \) in Fig. S3 in the SI, together with the values of both \( \Delta H_{0K} \) and \( \Delta G_{298K} \) in Table S2. Because the adsorption of \( N_2 \) on clusters causes the reduction of entropy of the whole system, the values of \( \Delta G_{298K} \) are generally higher than those of \( \Delta H_{0K} \) by as large as 0.5 eV. Therefore, if a reaction species (including both intermediates and transition states) has \( \Delta H_{0K} > 0 \), it must have also \( \Delta G_{298K} > 0 \). A species with negative \( \Delta H_{0K} \) may still have positive \( \Delta G_{298K} \) if \( \Delta H_{0K} \) is not well below zero. In both cases, the reaction is kinetically forbidden. For example, in the reaction of Mo\(_2\)Li with \( N_2 \), TS6 has \( \Delta H_{0K} = 0.20 \text{ eV} \) while its \( \Delta G_{298K} \) is as high as 0.61 eV; I8, TS7, and I9 have negative \( \Delta H_{0K} \) as \(-0.16\), \(-0.12\), and \(-0.25 \text{ eV} \), respectively, while their \( \Delta G_{298K} \) values are 0.27, 0.32, and 0.16 eV. On the other hand, the difference \( \Delta R = \Delta G_{298K} - \Delta H_{0K} \) is quite similar for different species (except the reactants), in a narrow range of 0.36–0.49 eV in Table S2. Thus, the energy profiles of \( \Delta G_{298K} \) of the reaction paths can be roughly obtained by shifting those of \( \Delta H_{0K} \) upward as a whole, and the relative energies of different species in a reaction path are generally similar for \( \Delta H_{0K} \) and

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Fig. 3  Reaction paths of Mo\(_2\)M (M = Li, Na, K, Mg, and Ca) with \( N_2 \) when the initial adsorption site is on a single Mo atom (Mo\(_2\)M–1). a The structure of intermediates and transition states, and the N–N bond length (pm) in intermediates. b Relative energy (\( \Delta H_{0K} \)) with respect to the reactants.
For example, energy barriers for two critical steps of each reaction path are listed in Table S3 for both $\Delta H_{0K}$ and $\Delta G_{298K}$. The difference ($\Delta B = \Delta G_{298K} - \Delta H_{0K}$) is less than 0.06 eV for all studied reaction paths.

Figure 4 shows the reaction paths of $\text{Mo}_2\text{M}$ ($\text{M} = \text{Li, Na, K, Mg, and Ca}$) when the initial adsorption site is on the doping M atoms. Drawing of reaction paths with $\Delta G_{298K}$ and the values of both $\Delta H_{0K}$ and $\Delta G_{298K}$ are given in the SI (Fig. S4 and Table S4). When $\text{N}_2$ is initially put near the alkali metal M ($\text{M} = \text{Li, Na, and K}$), it will be end-on adsorbed on M (I11). Then, $\text{N}_2$ transfers to a more stable adsorption intermediate I12 by overcoming a small energy barrier (TS9). In I12, $\text{N}_2$ is adsorbed on M and Mo with the end-on: side-on coordination mode. Although $\text{N}_2$ is far away from Mo atoms in the initial setting, the structures will be optimized directly to I12 without any energy barriers for the systems doped with Mg and Ca. The relative energy of I12 of Li and Ca systems is lower than that of the other three systems. Starting from I12, all systems need to pass through a high energy barrier (TS10) to obtain the pre-decomposition intermediate I13. The $\text{N}_2$ transfer barriers of Li, Na, K, Mg, and Ca systems are 0.95, 1.10, 1.08, 0.87, and 0.85 eV, respectively. Compared with the values for the reaction paths with $\text{N}_2$ initial adsorption on Mo, as shown in Fig. 3 (0.97, 1.10, 1.10, 1.14, and 0.98 eV), the transfer energy barriers on alkali metal systems are similar in both cases, which are about 1.00 eV, while for alkaline earth metal systems, lower transfer barriers (ca. 0.9 eV) are obtained. Note that the I13 structure of the $\text{Mo}_2\text{Ca}$ system is the same as the I8 in Fig. 3a, in which $\text{N}_2$ is adsorbed on the three metal atoms of Mo-Mo-Ca with the coordination mode of end-on: side-on: end-on. $\text{N}_2$ is adsorbed on Mo-Mo-M as side-on: end-on: side-on. $\text{N}_2$ dissociation products can be obtained from I13 through a N–N dissociation barrier (TS11). The $\text{N}_2$ dissociation barriers of the Li, Na, K, Mg, and Ca systems are 0.27, 0.35, 0.41, 0.29, and 0.44 eV, respectively. Compared with the values for the reaction paths with $\text{N}_2$ initial adsorption on Mo (0.62, 0.65, 0.67, 0.56, and 0.44 eV), the energy barrier decreases by about 0.3 eV for all systems, except $\text{Mo}_2\text{Ca}$. Thus, different reaction paths and lower energy barriers are obtained by changing the initial adsorption configuration of $\text{N}_2$. Besides, from a thermodynamic point of view, the energy gain of reaction has generally increased, from $-1.86$, $-1.42$, $-1.44$, $-1.44$, $-1.42$, and $-2.28$ eV (Fig. 3) to $-2.04$, $-1.73$, $-1.77$, $-1.64$, and $-2.28$ eV (Fig. 4).

Dissociation paths of $\text{N}_2$ on $\text{MoCa}_2$ and $\text{Ca}_3$

In the above studies on $\text{Mo}_2\text{M}$ cluster systems, $\text{N}_2$ transfer barriers (TS10) and dissociation barriers (TS11) in each reaction path are all higher than the initial energy of the reactants, except $\text{Mo}_2\text{Ca}$. $\text{Mo}_2\text{Ca}$ has the highest reactivity toward $\text{N}_2$, but the energy of the transition state for N–N dissociation is still higher than the initial energy by 0.01 eV. Therefore, $\text{N}_2$ dissociation may not occur in all these systems because it may be kinetically forbidden. Considering that the introduction of one Ca atom has excellent promoting effects on the reaction process, it is desired to further explore the systems with more Ca atoms to achieve even higher reactivity toward $\text{N}_2$ activation. Therefore, the reactions of $\text{N}_2$ with $\text{MoCa}_2$ and $\text{Ca}_3$ clusters were studied and the results are shown in Fig. 5.

The research experience of the previous systems shows that different initial adsorption configurations may lead to different reaction paths and reactivities. Therefore, for $\text{MoCa}_3$ system, we also consider two initial adsorption configurations of $\text{N}_2$. The ground state of $\text{MoCa}_3$ is septet, while reaction paths with different spin multiplicities have been tested and shown in Figs. S1 and S2 in the SI. It can be seen that only the $\text{MoCa}_2$–1 path with the triplet and quintuplet states can satisfy that all the intermediates and transition states have negative $\Delta G_{298K}$, thus can happen in...
gas-phase experiments. Considering that the path with the triplet state has lower energies for both the first adsorption complex (I15) and the last product (I18), only the results of the triplet state are discussed below.

In the MoCa$_2$−1 path, N$_2$ is first adsorbed on the Mo atom in the form of end-on (I15), and then after passing through two tiny energy barriers (TS12 and TS13, < 0.01 eV), two intermediates are obtained, in which N$_2$ is end-on: side-on adsorbed on Mo−Ca two atoms in I16 and end-on: side-on: side-on adsorbed on Mo−Ca−Ca three atoms in I17. I17 in MoCa$_2$−1 is very stable with the adsorption energy of N$_2$ as −1.75 eV, which is the largest absolute value for the adsorption energy of molecular N$_2$ on the studied clusters in this work. For comparison, the largest value for Mo$_2$M clusters is −0.90 eV of I12 in Mo$_2$Ca reaction system. The N−N bond in I17 is then dissociated to produce the final product I18. This dissociation process needs to overcome a relatively high energy barrier (TS14, 0.97 eV), which is the rate-determining step of the whole reaction, and the relative energy is higher than that of the reactants (+0.14 eV), so this reaction path cannot be realized in gas-phase experiments. After passing through a small energy barrier (TS16, 0.07 eV), I20 transfers to be side-on: end-on adsorbed on trimetallic Mo−Ca−Ca (I21). By overcoming a relatively high energy barrier (TS17, 0.69 eV), the N−N bond dissociates and the final product I22 is obtained, in which the two N atoms are at the hollow position of three metal atoms and the bridge site of Ca−Mo, respectively. It is worth noting that the relative energy of I22 is extremely low (−4.41 eV). The significant heat release here may provide enough energy for the subsequent reactions, thus promoting the follow-up reactions.

Finally, we studied the N$_2$ dissociation reaction path on Ca$_3$ with singlet state, the same as the ground state spin multiplicity of Ca$_3$. For Ca$_3$, N$_2$ first combines onto the cluster with a very weak physical adsorption mode to form I23, and the calculated adsorption energy is only −0.007 eV. After that, N$_2$ molecules adjust the adsorption mode with a negligible barrier. In I24, N$_2$ molecules are perpendicular to the Ca$_3$ plane and adsorbed at the center of the Ca$_3$ triangle, but the adsorption energy is still small (−0.16 eV). As a result, when the adsorption mode is further adjusted, the overall energy is slightly higher than the initial reactant energy (TS24, +0.02 eV). The stable adsorption structure obtained after that has a remarkable adsorption energy (I25, −1.03 eV), and N$_2$ is end-on: side-on adsorbed on three Ca atoms. The relative dissociation barrier of N−N is quite small, only 0.32 eV (TS20), further indicating that Ca atoms are beneficial for N−N bond activation. The whole reaction path is exothermic by −1.78 eV, just similar to the case in the MoCa$_2$−1 path.

Analysis of intermediates and transition states in typical reaction systems

In order to better understand the activation process of the N−N bond on clusters, we studied the variation of four properties of the N−N bond in the reaction process, namely, N−N bond length ($R_{N-N}$), Mayer bond order (MBO$_{N-N}$), N−N bond vibration frequency ($\nu_{N-N}$), and Hirshfeld charge transfer onto N$_2$ ($Q_{N2}$). Compared with the values
of free-state $N_2$ molecules calculated by DFT at the same theoretical level, if the N−N bond in the system has an increased $R_{N,N}$, decreased MBON–N and $\nu_{N,N}$, and enlarged $Q_{N_2}$, it means that the N−N bond is activated to some extent. Therefore, these four properties are selected as index properties to measure the $N_2$ activation degree. Four reaction paths, namely, reactions on Mo$_2$ (Fig. 1), Mo$_2$Ca (initial $N_2$ adsorption on Ca, i.e., Mo$_2$Ca–2 in Fig. 4), MoCa$_2$ (initial $N_2$ adsorption on Mo, i.e., MoCa$_2$–1 in Fig. 5), and Ca$_3$ (Fig. 5), were selected. The variation of four properties is shown in Fig. 6 (data for other systems are given in the SI).

In Fig. 6, I$_3$ (similar for I$_{13}$, I$_{17}$, and I$_{25}$) is the last intermediate just before N−N bond dissociation. Before I$_3$ is the transfer process of $N_2$ on these clusters, while after I$_3$ the $N_2$ dissociates. Generally, $N_2$ on Mo$_2$ clusters has shorter $R_{N,N}$, larger MBON–N and $\nu_{N,N}$, and less $Q_{N_2}$ than that on the other clusters, especially for I$_3$ and TS3. This indicates that the clusters containing Ca atoms have a higher ability to activate $N_2$ bonds than Mo$_2$ clusters. Taking MoCa$_2$ as an example, the activation process of $N_2$ is as follows (see also Fig. 5). When $N_2$ is adsorbed on MoCa$_2$ cluster in the form of end-on: side-on, the corresponding $R_{N,N}$, MBON–N, $\nu_{N,N}$, and $Q_{N_2}$ are changed from free $N_2$ (1.10 Å, 2.82, 2373 cm$^{-1}$, and 0 e) to I$_{15}$ (1.14 Å, 2.29, 1971 cm$^{-1}$, and −0.23 e), indicating that activation of $N_2$ is not very evident. After I$_{15}$ is TS$_{12}$, which has a similar structure to I$_{15}$, and the activation of $N_2$ in TS$_{12}$ (1.15 Å, 2.22, 1932 cm$^{-1}$, and −0.27 e) is also similar to that in I$_{15}$. This is just corresponding to the tiny energy barrier from I$_{15}$ to TS$_{12}$. After TS$_{12}$, I$_{16}$ is obtained in which $N_2$ is adsorbed on two metal atoms in the form of end-on: side-on. The corresponding four index properties become 1.21 Å, 1.58, 1588 cm$^{-1}$, and −0.44 e, indicating that the N−N bond has been activated to some extent. $N_2$ further changes the adsorption mode on MoCa$_2$ to get I$_{17}$ through TS$_{13}$. TS$_{13}$ is similar to I$_{16}$, just as the previous case of TS$_{12}$ to I$_{15}$. I$_{17}$ is the last intermediate before N−N dissociation, in which $N_2$ is end-on: side-on: side-on adsorbed on Mo-Ca-Ca three atoms. The interaction

![Fig. 6](image-url)
between $N_2$ and the cluster is strong according to the highest adsorption energy among all studied clusters. The four index properties of I17 are 1.27 Å, 0.91, 1332 cm$^{-1}$, and −0.68 e, indicating that the N−N bond has been activated to a high enough level, and the N=N triple bond now becomes an N=N single bond. The following N−N dissociation becomes not too hard with a relatively low energy barrier for the transition state TS14. The activation degree of N−N bond in TS14 is further improved to 1.91 Å, 0.45, 758 cm$^{-1}$, and −0.78 e, and finally N−N dissociates into adsorbed two N atoms.

Conclusions

In this work, we explored clusters with high activity for nitrogen activation by using DFT calculations on reactions of $N_2$ with well-designed metal clusters. The reaction of $N_2$ on Mo$_2$ cluster was calculated at first, and the results show that Mo$_2$ is inert to $N_2$. Then, the reactions of $N_2$ with Mo$_2$M (M = Li, Na, K, Mg, and Ca) were calculated. Two initial adsorption sites for $N_2$ have been tested, which may cause different reaction paths. The results show that doping with one alkali or alkaline earth metal atom can promote the reactions by increasing the adsorption energy of $N_2$ and reducing the energy barriers for both transfer and dissociation of $N_2$ on clusters. Among them, Mo$_2$Ca cluster has the highest ability to activate $N_2$, although the dissociation barrier is still above the energy sum of the reactants. Finally, we tried to increase the number of Ca atoms to obtain clusters with even higher reactivity, and MoCa$_2$ and Ca$_3$ were tested. In one reaction path of $N_2$ on MoCa$_2$, all the intermediates and transition states are well below the energy sum of the reactants, for both $\Delta H_{0K}$ and $\Delta G_{298K}$, indicating the dissociation of $N_2$ on MoCa$_2$ can take place spontaneously in gas-phase reactions. The process of N−N bond activation on these clusters was analyzed by investigating the variation of four index properties which can reflect the activation degree of N−N bond (the bond length, the vibrational frequency, Mayer bond order, and Hirshfeld charge of $N_2$). On the clusters, N$_2$ is gradually activated by changing the adsorption mode, and the adsorption mode of N$_2$ on three metal atoms with end-on: side-on: side-on coordination is beneficial to the final dissociation of N−N bond. This work shows a practical process to search for model systems with high activity. Trimetallic active sites with alkali or alkaline earth metal atoms are suggested to have high reactivity toward $N_2$ activation, which may be used as a guide to design the active sites of single-cluster catalysts for nitrogen activation and conversion.

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Availability of data and material The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

References

1. Erisman J-W, Sutton M-A, Galloway J, Klimont Z, Winiwarter W (2008) Nat Geosci 1:636–639
2. Guo J, Chen P (2017) Chem 3:709–712
3. Canfield D-E, Glazer A-N, Falkowski P-G (2010) Science 330:192–196
4. Jia H-P, Quadrelli E-A (2014) Chem Soc Rev 43:547–564
5. Cheng Q (2008) J Integr Plant Biol 50:786–798
6. Thamdrup B (2012) Annu Rev Ecol Evol S 43:407–428
7. Shilov A-E (2003) Russ Chem Bull 52:2555–2562
8. Himmel H-J, Reihert M (2006) Angew Chem Int Ed 45:6264–6288
9. Schlögl R (2003) Angew Chem Int Ed 42:2004–2008
10. Schlögl R (2008) In: Ertl H-K-G, Scheth F, Weitkamp J (Eds) Handbook of heterogeneous catalysis. Wiley-VCH, Weinheim, pp 2501–2575
11. Honkalä K (2005) Science 307:555–558
12. Logadóttir Á, Nørskov J-K (2003) J Catal 220:273–279
13. Ertl G, Lee S-B, Weiss M (1982) Surf Sci 114:515–526
14. Fryzuk M-D, Johnson S-A (2000) Coord Chem Rev 200–202:379–409
15. Chekerasov N, Ihabadon A-O, Fitzpatrick P (2015) Chem Eng Prog 90:24–33
16. Chen J-G, Crooks R-M, Seefeldt L-C, Bren K-L, Bullock R-M, Darenbourg M-Y, Holland P-L, Hoffmann B, Janik M-J, Jones A-K, Kannatidis M-G, King P, Lancaster K-M, Lymar S-V, Pfromm P, Schneider W-F, Schrock R-R (2018) Science 360:eaa06611
17. Qiao B, Wang A, Yang X, Allard L-F, Jiang Z, Cui Y, Liu J, Li J, Zhang T (2011) Nat Chem 3:634–641
18. Yang W, Zhao M, Ding X-L, Ma K, Wu C, Gates I-D, Gao Z (2020) Phys Chem Chem Phys 22:3983–3989
19. Gao Z-Y, Yang W-J, Ding X-L, Lv G, Yan W-P (2018) Phys Chem Chem Phys 20:7333–7341
20. Wang D, Ding X-L, Liao H-L, Dai J-Y (2019) Acta Phys-Chim Sin 35:1005–1013
21. Chen Z-W, Yan J-M, Jiang Q (2018) Small Methods 3:1800291
22. Guo X, Gu J, Lin S, Zhang S, Chen Z, Huang S (2020) J Am Chem Soc 142:5709–5721
23. Liu J-C, Ma X-L, Li Y, Wang Y-G, Xiao H, Li J (2018) Nat Commun 9:1610
24. Ma X-L, Liu J-C, Xiao H, Li J (2018) J Am Chem Soc 140:46–49
25. Lang S-M, Bernhardt T-M (2012) Phys Chem Chem Phys 14:9255–9269
26. O’Hair R-A-J, Khairallah G-N (2004) J Cluster Sci 15:331–363
27. Schwarz H (2017) Catal Sci Technol 7:4302–4314
28. Yin S, Bernstein E-R (2012) Int J Mass Spectrom 321:49–65
29. Liu J (2017) ACS Catal 7:3–59
30. Sugawara K-i, Yamaguchi W, Shimo Y, Murakami J (2017) Chem Phys Lett 667:267–271
31. Kumar D, Pal S, Krishnamurthy S (2016) Phys Chem Chem Phys 18:27721–27727
32. Kerpal C, Harding D-J, Lyon J-T, Meijer G, Fielicke A (2013) J Phys Chem C 117:12153–12158
33. Geng C, Li J, Weiske T, Schwarz H (2018) Proc Natl Acad Sci USA 115:11680–11687
34. Dillinger S, Mohrbach J, Niedner-Schatteburg G (2017) J Chem Phys 147:184305
35. Wang Y-Y, Ding X-L, Gurti J-I, Chen Y, Li W, Wang X, Wang W-J, Deng J-J (2021) ChemPhysChem 22:1645–1654
36. Ding X, Yang J, Hou JG, Zhu Q (2005) J Mol Struct (THEOCHEM) 755:9–17
37. Mou L-H, Liu Q-Y, Zhang T, Li Z-Y, He S-G (2018) J Phys Chem A 122:3489–3495
38. Li Z-Y, Mou L-H, Wei G-P, Ren Y, Zhang M-Q, Liu Q-Y, He S-G (2019) Inorg Chem 58:4701–4705
39. Geng C, Li J, Weiske T, Schwarz H (2019) Proc Natl Acad Sci USA 116:21416–21420
40. Cheng X, Li Z-Y, Mou L-H, Ren Y, Liu Q-Y, Ding X-L, He S-G (2019) Chem Eur J 25:16523–16527
41. Hu J-C, Xu L-L, Li H-F, Valdivielso DY, Fielicke A, He S-G, Ma J-B (2017) Phys Chem Chem Phys 19:3136–3142
42. Xue W, Yin S, Ding X-L, He S-G, Ge M-F (2009) J Phys Chem A 113:5302–5309
43. Wang C, Zhuang J, Wang G, Chen M, Zhao Y, Zheng X, Zhou M (2010) J Phys Chem A 114:8083–8089
44. Zhou M, Zhuang J, Zhou Z, Li ZH, Zhao Y, Zheng X, Fan K (2011) J Phys Chem A 115:6551–6558
45. Zhou M, Jin X, Gong Y, Li J (2007) Angew Chem Int Ed 46:2911–2914
46. Gong Y, Zhao Y-Y, Zhou M-F (2007) J Phys Chem A 111:6204–6207
47. Mafune F, Tawaraya Y, Kudoh S (2016) J Phys Chem A 120:4089–4095
48. Jiang G-D, Mou L-H, Chen J-J, Li Z-Y, He S-G (2020) J Phys Chem A 124:7749–7755
49. Li Z-Y, Li Y, Mou L-H, Chen J-J, Liu Q-Y, He S-G, Chen H (2020) J Am Chem Soc 142:10747–10754
50. Mou L-H, Li Y, Li Z-Y, Liu Q-Y, Ren Y, Chen H, He S-G (2020) J Phys Chem Lett 11:9990–9994
51. Wang Y-Y, Ding X-L, Gurti J-I, Chen Y, Huang X-Q, Li W, Wang X (2022) ChemPhysChem 23:e202100771
52. Chen Z-W, Chen L-X, Jiang M, Chen D-C, Wang Z-L, Yao X, Singh C-V, Jiang Q (2020) J Mater Chem A 8:15086–15093
53. Zhao Y, Cui J-T, Wang M, Valdivielso D-Y, Fielicke A, Hu L-R, Cheng X, Liu Q-Y, Li Z-Y, He S-G, Ma J-B (2019) J Am Chem Soc 141:12592–12600
54. Zheng J, Liao F, Wu S, Jones G, Chen T, Fellowes J, Sudmeier T, McPherson I-J, Wilkinson I, Tsang S-C-E (2019) Angew Chem Int Ed 58:17335–17341
55. Bettens T, Pan S, Proft F-D, Frenking G, Geerlings P (2020) Chem Eur J 26:12785–12793
56. Frisch M-J, Trucks G-W, Schlegel H-B, Scuseria G-E, Robb M-A, Cheeseman J-R, Scalmani G, Barone V, Mennucci B, Petersson G-A, Nakatsuji H, Caricato M, Li X, Hratchian H-P, Izmaylov A-F, Bloino J, Zheng G, Sonnenberg J-L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J-A, Jr, Peralta J-E, Ogliaro F, Bearpark M, Heyd J-J, Brothers E, Kudin K-N, Staroverov V-N, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A-P, Burant J-C, Iyengar S-S, Tomasi J, Cossi M, Rega N, Millam J-M, Klene M, Knox J-E, Cross J-B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R-E, Yazyev O, Austin A-J, Cammi R, Pomelli C, Ochterski J-W, Martin R-L, Morokuma K, Zakrzewski V-G, Voth G A, Salvador P, Dannenberg J-F, Dapprich S, Daniels A-D, Farkas O, Foresman J-B, Ortiz J-V, Cioslowski J, Fox D-J (2009) Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT
57. Tao J, Perdew J-P, Staroverov V-N, Scuseria G-E (2003) Phys Rev Lett 91:146401
58. Weigend F, Ahlrichs R (2005) Phys Chem Chem Phys 7:3297–3305
59. Andrae D, Haeussermann U, Dolg M, Stoll H, Preuss H (1990) Theor Chim Acta 77:123–141
60. Lu T, Chen F-W (2012) J Comput Chem 33:580–592

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