Exploring Trimetallic Clusters Containing Alkali and Alkaline Earth Metal Atoms with High Activity for Nitrogen Activation

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Abstract

Activation of dinitrogen (N_2) is the critical step in nitrogen reduction reaction (NRR) in ammonia synthesis. In this paper, reaction mechanisms of N_2 activation on trimetallic clusters Mo_2M ($M=Li, Na, K, Mg$, and Ca) and $Mo_{3-x}Ca_x$ ($x = 2-3$) were systematically studied by density functional theory calculations. Unlike Mo_2 which is inert to N_2 , clusters with alkali or alkaline earth metal atoms have much higher reactivity towards N_2 in terms of both thermodynamics and kinetics. Particularly, in one reaction path of N_2 with $MoCa_2$, all the intermediates and transition states are well below the energy sum of the reactants, indicating that the dissociation of N_2 on $MoCa_2$ can take place spontaneously in gas-phase reactions. N_2 transfers on clusters with different coordination modes, and the N–N bond is gradually activated. When N_2 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.

1. Introduction

Nitrogen-containing compounds are useful not only in agriculture [1] but also in new energy sources [2-6]. However, N_2 is difficult to be activated because of its strong $N\equiv N$ triple bonds, large highest occupied molecular orbital-lowest 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 up to 400 °C and high pressure 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 N_2 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 N_2 on the single metal atom is 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 Fe_3 clusters fixed on the surface of $\theta-Al_2O_3$ can be good catalysts for heterogeneous ammonia synthesis [23]. The catalytic mechanism of N_2 conversion to NH_3 on Fe_3/Al_2O_3 (010) was studied theoretically. They further studied the catalytic mechanism of N_2 to NH_3 on monodisperse Rh_1Co_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 N₂ activation by gas-phase clusters, mainly focusing on metal clusters [30-35], metal carbide clusters [36, 37], and metal nitride clusters [38, 39]. Coordination modes of N₂ on supporting atoms were found critical for N₂ activation. On bimetallic clusters, N₂ can first obtain the adsorption intermediate of side-on: end-on and then dissociate [35, 37], or it can pass through the intermediate of side-on: side-on and then dissociate [40-42]. On trimetallic clusters, N₂ is adsorbed on the center of the metal triangle in the form of end-on: side-on: side-on or end-on: end-on: side-on coordination modes before dissociation [43-46].

In the theoretical work of some bulk phases, it is predicted that trimetallic clusters can have good NRR activity [23, 47]. Some studies have shown that there are various coordination modes of N₂ on three metal atoms, which is beneficial for the dissociation of N≡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 N≡N triple bond under mild conditions [43-45, 48]. 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 N₂ activation on trimetallic clusters in this work.

Previous experimental studies have found that the doping of alkali/alkaline earth metals into the catalysts (e.g., Ru) can promote NRR sufficiently [49]. The reason is that the doped metals are easy to provide electrons so that the π* antibond orbitals of N₂ can obtain electrons to activate the N≡N triple bonds. However, there are few studies on the interaction between alkali /alkaline earth metal atoms with N₂ [50], let alone the study of trimetallic clusters. Therefore, in this work, based on Mo₂ clusters, we try to introduce alkali and alkaline earth metal atoms into systems to investigate the microscopic mechanism of the N≡N bond activation on these clusters and explore systems with high reactivity. The specific research systems include Mo₂, Mo₂M (M=Li, Na, K, Mg, and Ca), and Mo_{3-x}Ca_x (x = 2-3).

2. Calculation Methods

Density functional theory (DFT) calculations using the Gaussian 09 program package [51] were carried out to investigate the structures of Mo₂, Mo₂M (M=Li, Na, K, Mg, and Ca), and Mo_{3-x}Ca_x (x = 2-3) as well as the reaction mechanisms of Mo₂ + N₂, Mo₂M + N₂, and Mo_{3-x}Ca_x (x = 2-3) + N₂. The Mo₂ + N₂, Mo₂M + N₂, and Mo_{3-x}Ca_x (x = 2-3) + N₂ are optimized using the TPSS functional [52] and def2-TZVP basis set

[50, 53]. The adsorption energy of N₂ on the Mo₂M cluster is defined as
$$E_{ad} = E_{(Mo_2M-N_2)} - E_{(Mo_2M)} - E_{(N_2)}$$
, where E is the total electron energy corrected with zero-point vibration energy (ZPE). It is clear that E_{ad} is also the relative energy with respect to the separated reactants. 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_{N_2}) of key intermediates and transition states were calculated by the Multiwfn program [54], to measure the activation degree of N_2 during the reaction of N_2 with Mo_2M and $\text{Mo}_{3-x}\text{Ca}_x$ ($x = 2-3$).

3. Results And Discussion

3.1 Activation of N_2 on Mo_2 cluster

Reaction mechanisms of 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. Fig. 1 shows the reaction path between singlet Mo_2 and N_2 . N_2 is adsorbed on a Mo atom in the end-on coordination mode to form an intermediate (I1) with small adsorption energy (E_{ad}) of -0.27 eV and a weak activation of N-N bond length of 112 pm (N-N bond length of free N_2 molecule is 110 pm). The system forms a stable I2 by overcoming a low energy barrier (TS1, 0.38 eV). In I2, N_2 is adsorbed on a Mo atom in side-on, and the N-N bond length is 113 pm. Then, by overcoming a higher energy barrier (TS2, 0.72 eV), the coordination mode of N_2 changes from side-on to end-on:side-on (I3). The energy above zero point (IS1) 0.82 eV, 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 is 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 N_2 has different adsorption configurations on Mo_2 diatoms, among which the energy of N_2 adsorption on end-on is the lowest, and the conversion of different adsorption configurations needs to overcome energy barriers. Although N_2 dissociation is an exothermic reaction (the heat release is about 0.5 eV) on Mo_2 diatom, the dissociation of the N-N bond needs to overcome high energy barriers, so it is difficult for Mo_2 to react directly with N_2 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 Mo_2 clusters to explore more reactive clusters towards N_2 activation.

3.2 Reaction of Mo_2M ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{and Ca}$) with N_2

3.2.1 Adsorption of N_2 molecules at different sites of Mo_2M

Optimized structures of Mo_2M ($\text{M}=\text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{and Ca}$) clusters are all triangles, as shown in Fig. 2. $\text{Mo}_2\text{Li}/\text{Na}/\text{K}$ are doublet electronic state and $\text{Mo}_2\text{Mg}/\text{Ca}$ are triplet state. 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 the absolute values ($|E_{\text{ad}}|$) about 0.6–0.7 eV. The other initial adsorption configuration is that N_2 is close to the doped 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 relatively small $|E_{\text{ad}}|$, (less than 0.4 eV). The $\text{N}\equiv\text{N}$ 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 two metal atoms with the coordination mode of side-on:end-on. $|E_{\text{ad}}|$ of Mo_2Mg is still small (0.43 eV) while that of Mo_2Ca is as large 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_2M ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{and Ca}$) 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 $\text{Mo}_2\text{Li}/\text{Mg}/\text{Ca}$ is more negative than on Mo_2 , and the N-N bond length of Mo_2Mg and Mo_2Ca increases obviously. 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 .

3.2.2 Dissociation reaction path of N_2 on Mo_2M

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_2M and N_2 as the reference, the relative energies of the intermediates and transition states are considered.

Fig. 3 shows the reaction paths for the initial adsorption site of N_2 on a single Mo atom, including the structure 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 $\text{Mo}_2\text{Li-N}_2$ as an example. When N_2 approaches the Mo atom of Mo_2M , 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). 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 N₂ transfer on Mo₂Li, Mo₂Na, and Mo₂K 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 reaction exotherms of the three systems are –1.86, –1.42, and –1.44 eV, respectively. Therefore, no matter from the point of view of thermodynamics or kinetics, Mo₂Li/Na/K clusters have similar reactivity towards N₂, and Mo₂Li 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 N₂ transfer process on the cluster (I7→TS6→I8), the energy barrier (1.14 eV) of Mo₂Mg cluster is higher than those of the alkali metal system, while that of the Mo₂Ca 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 N₂ dissociation (I8→TS8→I10), the energy barriers (0.56 and 0.44 eV) that Mo₂Mg and Mo₂Ca clusters need to overcome is lower than that for the complete dissociation of N–N bond in the doped alkali metal systems in step I9→TS8→I10 (> 0.6 eV). In terms of the energy relative to the reactants, the energies of the transition states of the Mo₂Ca system during N₂ transfer (TS6) and N–N bond dissociation (TS8) are 0.08 and 0.01 eV, respectively, which are much lower than those of Mo₂Li (0.20 and 0.38 eV). In addition, the exotherm of the whole reaction for Mo₂Ca system reaches 2.28 eV, which is also the largest. Therefore, Mo₂Ca has relatively highest reactivity towards N₂ among all studied clusters. However, it can also be seen that the N₂ transfer process in Mo₂Ca system has a global energy barrier of +0.08 eV, and the relative energy barrier is still quite large especially for the N₂ transfer process (0.98 eV). Therefore, the reaction processes need to be further optimized. Changing the initial adsorption site may affect N₂ transfer process. In the following study, we will explore whether we can change the N₂ transfer process by changing the initial adsorption site, to reduce the energy barrier of the reaction process.

Fig. 4 shows the reaction paths of N₂ with Mo₂M (M = Li, Na, K, Mg, and Ca) when the initial adsorption site of N₂ is on the doped M atoms. When N₂ is initially put near the alkali metal M (M = Li, Na, and K), it will be end-on adsorbed on M (I11). Then N₂ transfers to a more stable adsorption intermediate I12 by overcoming a small energy barrier (TS9). In I12, N₂ is adsorbed on M and Mo with the end-on:side-on coordination mode. Although N₂ 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 N₂ 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 N₂ 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 Mo₂Ca system is the same as the I8 in Fig. 3a, in which N₂ is adsorbed on the three metal atoms of Mo-Mo-Ca with the coordination mode of end-on: end-on: side-on, while in the I13 of other systems, N₂ is adsorbed on Mo-Mo-M as side-on: end-on: side-on. N₂ dissociation products can be obtained from I13 through a N-N dissociation barrier (TS11). The N₂ dissociation barrier 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 N₂ 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 Mo₂Ca. Thus, different reaction paths and lower energy barriers are obtained by changing the initial adsorption configuration of N₂. Besides, from a thermodynamic point of view, the exotherm of reaction has generally increased, from -1.86, -1.42, -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).

3.3 Dissociation paths of N₂ on MoCa₂ and Ca₃

In the above studies on Mo₂M cluster systems, N₂ transfer barriers (TS10) and dissociation barriers (TS11) in each reaction path are all higher than the initial energy of the reactants, except Mo₂Ca. Mo₂Ca has the highest reactivity towards N₂, but the energy of the transition state for N-N dissociation is still higher than the initial energy by 0.01 eV. Therefore, N₂ dissociation may not occur in all these systems because of kinetic 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 towards N₂ activation. Therefore, the reactions of N₂ with MoCa₂ and Ca₃ clusters were studied and the results are shown in Fig. 5.

After adsorption of N₂, the ground state of the MoCa₂-N₂ cluster system is triplet state, while that of the Ca₃-N₂ cluster system is singlet state. The research experience of the previous system shows that different initial adsorption configurations may lead to different reaction paths and reactivities. Therefore, for MoCa₂ system, we also consider two initial adsorption configurations of N₂.

In the MoCa₂-1 path, N₂ 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 N₂ 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 MoCa₂-1 is very stable with the adsorption energy of N₂ as -1.75 eV, which is the largest absolute value for the adsorption energy of molecular N₂ on the studied clusters in this work. For comparison, the largest value for Mo₂M clusters is -0.90 eV of I12 in Mo₂Ca 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. Although this barrier is still quite high, the relative energy of TS14

is -0.73 eV, which is well below the total energy of the reactants, indicating that this reaction can occur in gas-phase experiments. The whole MoCa_2-1 reaction path is exothermic by -1.75 eV, indicating that this reaction path is also thermodynamically feasible.

In the MoCa_2-2 path, N_2 is first adsorbed on two Ca atoms in the form of end-on:side-on (I19). Then N_2 is transferred to Mo-Ca (I20, side-on:end-on) through a relatively high energy barrier (TS15, 0.72 eV). This step 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: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 Ca_3 , N_2 first combine in 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: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 is beneficial for N-N bond activation. The whole reaction path is exothermic by -1.78 eV, just similar to the case in MoCa_2-1 path.

3.4 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 ($R_{\text{N-N}}$), Mayer bond order ($\text{MBO}_{\text{N-N}}$), N-N bond vibration frequency ($\nu_{\text{N-N}}$) and Hirshfeld charge transfer onto N_2 (Q_{N_2}). 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 $R_{\text{N-N}}$, decreased $\text{MBO}_{\text{N-N}}$ and $\nu_{\text{N-N}}$, 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_2Ca (initial N_2 adsorption on Ca, 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 are shown in Fig. 6 (data for other systems are given in the Supporting Information).

In Fig. 6, I3 (also I13, I17, and I25) is the last intermediate just before N-N bond dissociation. Before the position of I3 is the transfer process of N₂ on these clusters, while after I3 the N₂ dissociates. Generally, the N-N on Mo₂ clusters has shorter $R_{\text{N-N}}$, larger $\text{MBO}_{\text{N-N}}$ and $\nu_{\text{N-N}}$, and less Q_{N_2} than those on the other clusters, especially for I3 and TS3. This indicates that the clusters containing Ca atoms have a higher ability to activate N₂ bonds than Mo₂ clusters. Taking MoCa₂ as an example, the activation process of N₂ is as follows (see also Fig. 5). When N₂ is adsorbed on MoCa₂ cluster in the form of end-on:side-on, the corresponding $R_{\text{N-N}}$, $\text{MBO}_{\text{N-N}}$, $\nu_{\text{N-N}}$, and Q_{N_2} are changed from free N₂ (1.10 Å, 2.82, 2373 cm⁻¹, and 0 |e|) to I15 (1.14 Å, 2.29, 1971 cm⁻¹, and -0.23 |e|), indicating that activation of N₂ is not very evident. After I15 is TS12, which has a similar structure to I15 and the activation of N₂ in TS12 (1.15 Å, 2.22, 1932 cm⁻¹, and -0.27 |e|) is also similar to that in I15. This is just corresponding to the tiny energy barrier from I15 to TS12. After TS12, I16 is obtained in which N₂ 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. N₂ further changes the adsorption mode on MoCa₂ to get I17 through TS13. TS13 is similar to I16, just as the previous case of TS12 to I15. I17 is the last intermediate before N-N dissociation, in which N₂ is end-on:side-on:side-on adsorbed on Mo-Ca-Ca three atoms. The interaction between N₂ 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.

4. Conclusions

In this work, we explored clusters with high activity for nitrogen activation by using DFT calculations on the reactions of N₂ with well-designed metal clusters. The reaction of N₂ on Mo₂ cluster was calculated at first, and the results show that Mo₂ is inert to N₂. Then, the reactions of N₂ with Mo₂M (M=Li, Na, K, Mg, and Ca) were calculated. Two initial adsorption sites for N₂ 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 N₂ and reducing the energy barriers for both transfer and dissociation of N₂ on clusters. Among them, Mo₂Ca cluster has the highest ability to activate N₂, 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 MoCa₂ and Ca₃ were tested. In one reaction path, all the intermediates and transition states N₂ on MoCa₂ are well below the energy sum of the reactants, indicating the dissociation of N₂ on MoCa₂ 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 N₂). On the clusters, N₂ is gradually activated by changing the adsorption mode, and the adsorption mode of N₂ 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 towards N₂ activation, which may be used as a guide to design the active sites of single-cluster catalysts for nitrogen activation and conversion.

Declarations

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Conflict of interest The authors declare no competing interests.

Author contributions Xue-Qian Huang: Writing – original draft, Investigation. Xun-Lei Ding: Supervision, Project administration, Writing – review & editing. Jian Wang: Data curation, visualization. Ya-Ya Wang: Conceptualization, review. Joseph Israel Gurti: Data curation, review. Yan Chen: Data curation, Validation. Meng-Meng Wang: Validation, review. Wei Li: Conceptualization, Project administration. Xin Wang: Methodology, Validation.

Availability of and 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

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Figures

Figure 1

The reaction path of Mo₂ and N₂ calculated by TPSS functional. N-N bond lengths (pm), the adsorption energy (eV) of N₂ for intermediates, transition states, and products are given.

Figure 2

TPSS functional calculated adsorption of N_2 at different sites of trimetallic clusters Mo_2M ($M = Li, Na, K, Mg, \text{ and } Ca$). One is adsorbed on the Mo atom (a), and the other is adsorbed on the M atom (or M-Mo) (b). The N-N bond length (pm) and the adsorption energy (eV) of N_2 are given.

Figure 3

Reaction path of Mo₂M (M = Li, Na, K, Mg, and Ca) with N₂ when the initial adsorption site is on a single Mo atom. a) The structure of intermediates and transition states, and the N-N bond length (pm) in intermediates. b) Relative energy with respect to the reactants.

Figure 4

Reaction path of Mo₂M (M = Li, Na, K, Mg, and Ca) with N₂ when the initial adsorption site is on M. a) The structure of intermediates and transition states, and the N-N bond length (pm) in intermediates. b) Relative energy with respect to the reactants.

Figure 5

Reaction paths of MoCa₂ and Ca₃ with N₂. MoCa₂-1 and MoCa₂-2 represent the initial adsorption of N₂ on Mo and Ca atoms, respectively. a) The structure of intermediates and transition states, and the N-N bond length (pm) in intermediates. b) Relative energy with respect to the reactants.

Figure 6

Four properties of the transition states and intermediates indicate the activation of N-N bonds in the reactions of Mo_2 , Mo_2Ca , MoCa_2 , and Ca_3 with N_2 . a) N-N bond lengths ($R_{\text{N-N}}$), b) Mayer bond order ($\text{MBO}_{\text{N-N}}$), c) N-N bond vibration frequencies ($\nu_{\text{N-N}}$), and d) Hirshfeld charge (Q_{N_2}). As a reference, the horizontal line in each figure indicates the specific property of the triple N-N bond in free N_2 .

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