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Catalytic synthesis of non-carbon fuel NH₃ from easily available N₂ and H₂O over FeO(100) surface: Reaction mechanism with density functional theory study

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The competitive adsorption and reaction mechanism for the catalytic synthesis of NH₃ from N₂ and H₂O over FeO surface was investigated in this work. Theoretical calculations results indicated that H₂O was more easily adsorbed on the FeO surface than N₂. FeO(100) surface was more stable for the adsorption of N₂ and H₂O. The interaction between N₂ and FeO(100) surface was attributed to N atom and O atom, and the interaction between H₂O and FeO(100) surface was attributed to O atom and Fe atom, which were caused by van der Waals forces and chemical bond effect respectively. In the synthesis process, H₂O was firstly dissociated over FeO(100) surface and N₂ dissociation process was the controlling step for NH₃ synthesis. The theoretical calculations results also indicated that –OH groups was not conducive to the formation of N–H bond and it changed the controlling step from the dissociation of N₂ to the formation of –NH₂. Furthermore, the existence of O atom or –OH groups from H₂O on the FeO(100) surface was not conducive to the dissociation of H₂O.

1. Introduction

Ammonia (NH₃) is not only an important chemical product but also an important non-carbon fuel. It is not only an end-product, but also a raw material for producing other chemical product. As the basic chemical raw material in the industrial production, such as urea industry, nitrogen fertilizer industry, synthetic fiber industry and synthetic resin industry, so there is a lot of demand for NH₃.^{1–3} So far, the most of studies were focused on the NH₃ synthesis by N₂ and H₂.^{4–7} In this synthesis process, the dissociation of N₂ is a key step.^{8–12} Meanwhile, the catalytic synthesis of NH₃ needs strict operating conditions, such as high reaction temperature, high reaction pressure and special catalyst.^{13–16} Furthermore, the use of H₂ consumes a lot of energy. Therefore, it is important to find out a new method for NH₃ synthesis. Xie et al. used H₂O and N₂ for the NH₃ synthesis over Ru/Al₂O₃ catalyst with dielectric barrier discharge.¹⁷ The result showed that N atom, H atom and –OH groups could be generated under the effect of dielectric barrier discharge. Therefore, the synthesis of NH₃ from N₂ and H₂O is feasible.^{18–20}

However, a lot of O atom or O₂ could be formed in the process of NH₃ synthesis from N₂ and H₂O. In order to improve the selectivity of NH₃, it is important to avoid the oxidation of NH₃. Several previous studies showed that FeO was a kind of good component for O atom capture.^{21–27} Therefore, FeO could be used for O capture in the NH₃ synthesis from N₂ and H₂O. As shown in Fig. S1, FeO was used in the NH₃ synthesis from N₂ and H₂O under 600 °C in our previous study. The results showed that NH₃ could generate over FeO surface and the selectivity of NH₃ approached 20%. Michalsky et al. used Mo₂N, Mn₂N and Cr₂N for NH₃ synthesis from N₂ and H₂O with thermochemical method.^{28–31} The synthesis reaction needed a temperature of 1400 °C. Compare with previous studies, FeO could reduce the reaction temperature in the thermochemical method. Although FeO has the advantage of lowering reaction temperature, the detailed reaction mechanisms are unknown. Therefore, it is important to study NH₃ synthesis from N₂ and H₂O over FeO.

Currently, little research has focused on the reaction mechanism for the NH₃ synthesis from N₂ and H₂O. Determining the detailed steps of the reaction mechanism is necessary because they can provide a theoretical foundation for the future application and development. Therefore, this work performed theoretical study to investigate the reaction mechanism and reaction routes of the NH₃ synthesis from N₂ and H₂O over FeO surface. Furthermore, this theoretical study further investigated the influence of different FeO surface for competitive adsorption of N₂ and H₂O.

2. Computational methods

All calculations in this work were performed using Dmol³ in the Material Studio software package.³² The molecular geometries

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of the reactants, transition states (TS), intermediate complexes (IM), and products were calculated and optimized using the GGA/PBE method from density functional theory.^{33,34} A density functional semi-core pseudopotential method was used for the core electrons of Fe, and the all-electron method was used for the core electrons of H, N and O.^{35,36} A double-numeric quality basis set with polarization functions (i.e., DNP, version 3.5) was used.^{34,37,38} The tolerances of the SCF, energy, gradient and displacement convergence were 1.0×10^{-6} hartree (Ha), 1.0×10^{-5} Ha, 2.0×10^{-3} Ha/Å and 5.0×10^{-3} Å, respectively. All calculations using spin-polarized set were performed and the TS method for DFT-D correction was used. The k points of a (3x3x1) Monkhorst-Pack grid were used for bulk lattice optimizations. FeO(100) surface, FeO(110) surface, FeO(111) O-surface and FeO(111) Fe-surface were modelled by seven atomic layers slab with a p(3x3) supercell by 15 Å thick vacuum layer. Self-consistent field convergence was declared when at least two of the above criteria were satisfied. Electronic energies and zero point vibration energies (ZPVE) were calculated at the same level of theory. Linear synchronous transit/quadratic synchronous transit/conjugate gradient (LST/QST/CG) calculations were used to ensure that all of the transition states connected to the intended reactants and products. Transition states were identified by the presence of a single imaginary frequency, which corresponded to the reaction mode. To evaluate the reliability of calculation method and parameters, the geometries of monomers H₂O and N₂ were calculated and showed in Fig. 1. As shown in Fig. 1, the discrepancies of bond lengths and bond angles between the experimental and theoretical values are less than 0.008 Å and 0.1°, respectively.³⁹⁻⁴² It indicated that the viability of the selected methodology and the reliability of the parameters generated. Therefore, the current calculations met the requirements of reliability and assert the usefulness of the calculations to follow.

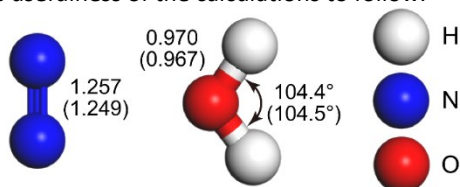


Fig. 1. Optimized geometries of H₂O and N₂ (bond length in Å and angles in °, the experimental values are in brackets)

3. Results and Discussion

3.1. Influence of surface on competitive adsorption

To determine the relative (competitive) adsorption of N₂ and H₂O over different FeO surface, their corresponding optimized geometries and adsorption energies have been calculated and showed in Fig. 2, Fig. 3, Fig. 4, Fig. 5 and Table 1. As seen in Fig. 2-5 and Table 1, the absolute values of the adsorption energy of N₂ over different FeO surface are all lower than that of H₂O. It indicated that H₂O was more easily adsorbed on the FeO surface than N₂, which suggested that H₂O adsorbed first on the catalyst and then reacted with N₂. Meanwhile, the absolute values of the adsorption energy of N₂ and H₂O over FeO(100) surface are

the highest among that over different FeO surface, which suggested that FeO(100) surface was more stable for the adsorption of N₂ and H₂O. Furthermore, compared with FeO(111) O-surface and FeO(111) Fe-surface, the absolute values of the adsorption energy of N₂ over FeO(111) O-surface was lower and the absolute values of the adsorption energy of H₂O over FeO(111) Fe-surface was lower. It indicated that N₂ was more easily adsorbed on the FeO(111) O-surface than H₂O, and H₂O was more easily adsorbed on the FeO(111) Fe-surface than N₂. According to Fig. 2 and Table 1, the interaction between N₂ and FeO(100) surface was attributed to N atom and O atom, which was caused by van der Waals forces. Meanwhile, the interaction between H₂O and FeO(100) surface was attributed to O atom and Fe atom, which was caused by chemical bond effect. Therefore, FeO(100) surface was used for investigating the synthesis of NH₃. In this work, two H₂O molecules were involved in the whole reaction of NH₃ synthesis. Therefore, it is necessary to investigate the influence of water monomer and water dimer (H₂O)₂ for adsorption process and dissociation process. The adsorption energy and dissociation energy of H₂O were -10.33 kcal/mol and 32.49 kcal/mol respectively. The adsorption energy and dissociation energy of (H₂O)₂ were -12.86 kcal/mol and 29.71 kcal/mol respectively. Compare with H₂O, the adsorption energy of (H₂O)₂ was higher and the dissociation energy of (H₂O)₂ was lower. It indicated that (H₂O)₂ adsorption process over FeO(100) was more stable and (H₂O)₂ was easier to produce H atom. This results is consistent with previous study.⁴³ When H₂O or (H₂O)₂ and N₂ simultaneously adsorbed on the FeO(100) surface, the adsorption energy of H₂O+N₂ and (H₂O)₂+N₂ were -15.47 kcal/mol and -10.69 kcal/mol. It indicated that (H₂O)₂ was not conducive to the simultaneous adsorption of H₂O and N₂. Therefore, water monomer was more suitable for NH₃ synthesis in this work.

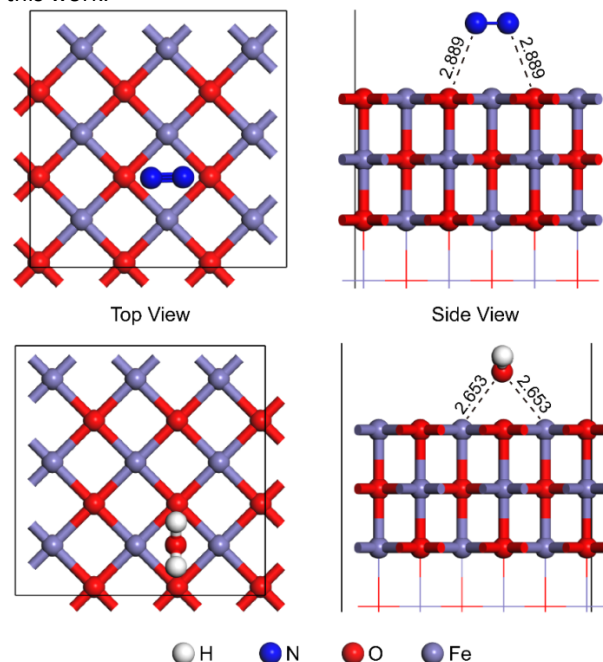


Fig. 2. Optimized geometries of N₂ and H₂O over FeO(100) surface (length in Å)

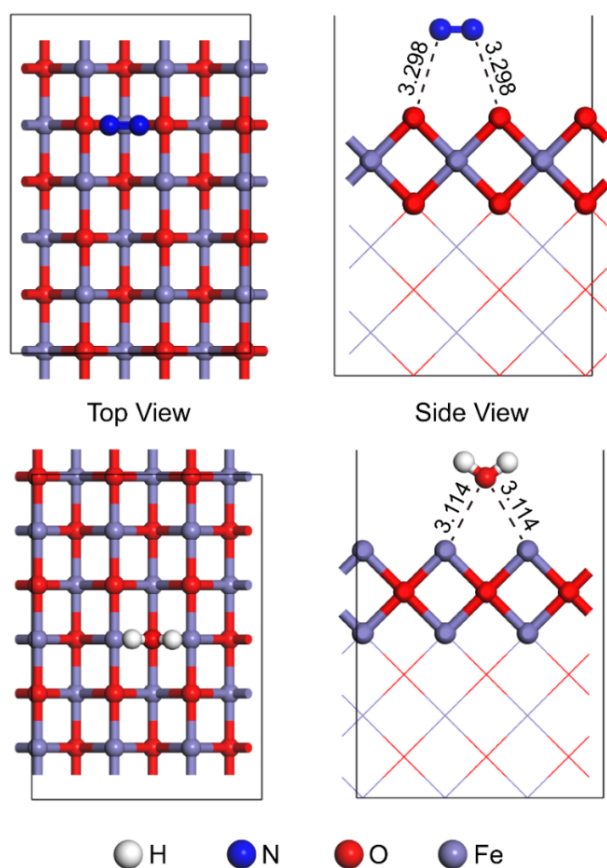


Fig. 3. Optimized geometries of N_2 and H_2O over FeO(110) surface (length in Å)

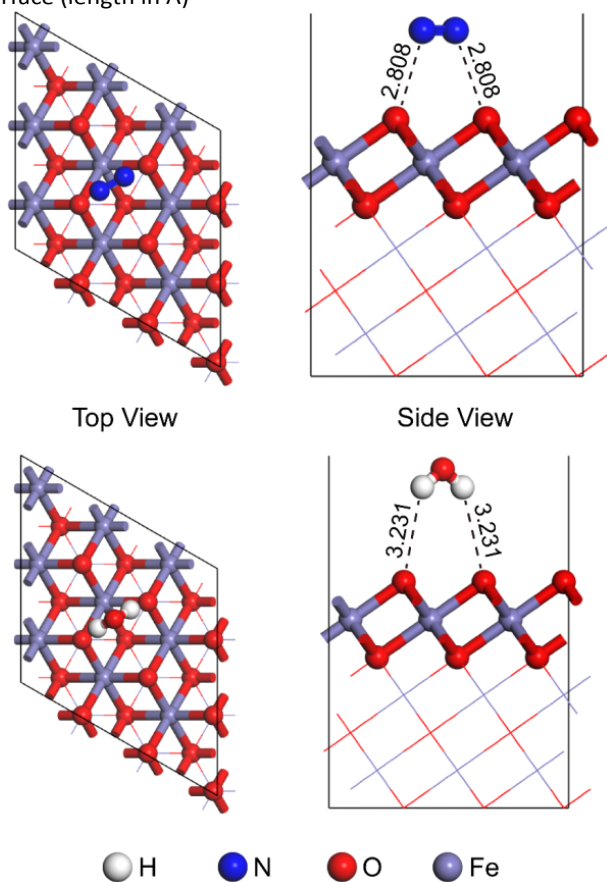


Fig. 4. Optimized geometries of N_2 and H_2O over FeO(111) O-surface (length in Å)

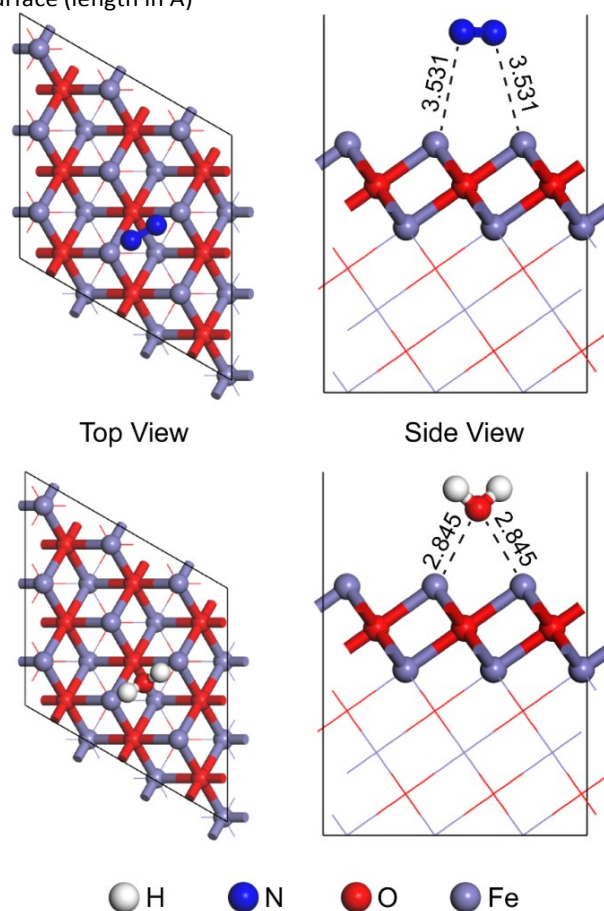


Fig. 5. Optimized geometries of N_2 and H_2O over FeO(111) Fe-surface (length in Å)

Table 1. Adsorption energies of N_2 and H_2O over different FeO surface

FeO surface	Adsorbate	Adsorption energy (kcal/mol)
FeO(100) surface	N_2	-5.28
	H_2O	-10.33
FeO(110) surface	N_2	-4.37
	H_2O	-8.84
FeO(111) O-surface	N_2	-4.71
	H_2O	-6.55
FeO(111) Fe-surface	N_2	-2.13
	H_2O	-9.14

3.2. Dissociation of H_2O , N_2 and formation of first N-H bond over FeO(100) surface

The reaction channels for the dissociation of H_2O , N_2 and formation of first N-H bond over FeO(100) surface are given in Fig. 6. Meanwhile, all related IM states in NH_3 synthesis are given in Table 2. In Fig. 6, the dissociation of H_2O was performed as $IM1 \rightarrow TS1 \rightarrow IM2$, and the dissociation of N_2 was performed as $IM2 \rightarrow TS2 \rightarrow IM3$, and the formation of first N-H bond was performed as $IM3 \rightarrow TS3 \rightarrow IM4$. In these processes, the energy barrier of N_2 dissociation (81.25 kcal/mol) over FeO(100) surface is higher than that of H_2O dissociation (49.56 kcal/mol). It suggested that H_2O dissociation occurred more easily than N_2

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dissociation. Meanwhile, the energy barrier of formation of first N-H bond (70.75 kcal/mol) over FeO(100) surface is lower than that of N₂ dissociation. It indicated that the formation of N-H bond was more easily than N₂ dissociation.

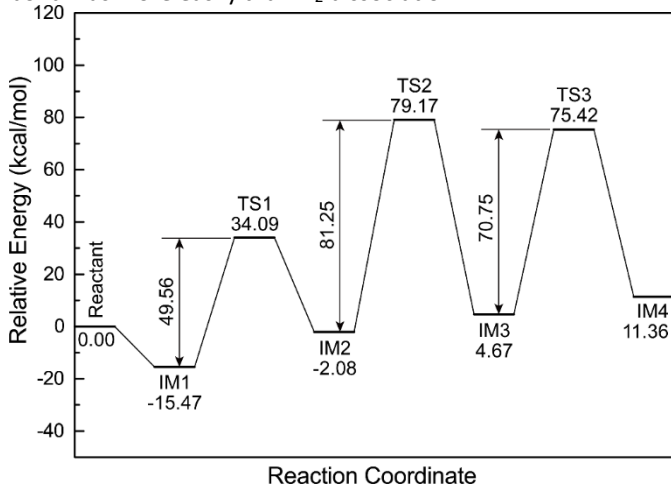


Fig. 6. Potential energy surface for dissociation of H₂O, N₂ and formation of first N-H bond over FeO(100) surface

Table 2. All related IM states in NH₃ synthesis

IMs	State
IM1	H ₂ O + FeO + N ₂
IM2	HO-FeO-H + N ₂
IM3	HO-FeO-H + FeO-N
IM4	HO-FeO-NH
IM5	O-FeO-NH ₂
IM6	O-FeO-NH ₂ + H ₂ O + FeO
IM7	O-FeO-NH ₂ + HO-FeO-H
IM8	HO-FeO-NH + H ₂ O + FeO
IM9	HO-FeO-NH + HO-FeO-H
IM10	HO-FeO-NH ₂ + HO-FeO
Product	O-FeO + NH ₃ + HO-FeO

The optimized geometries for the dissociation of H₂O, N₂ and formation of first N-H bond over FeO(100) surface are presented in Fig. 7. The imaginary frequencies of the transition states are given in Table 3.

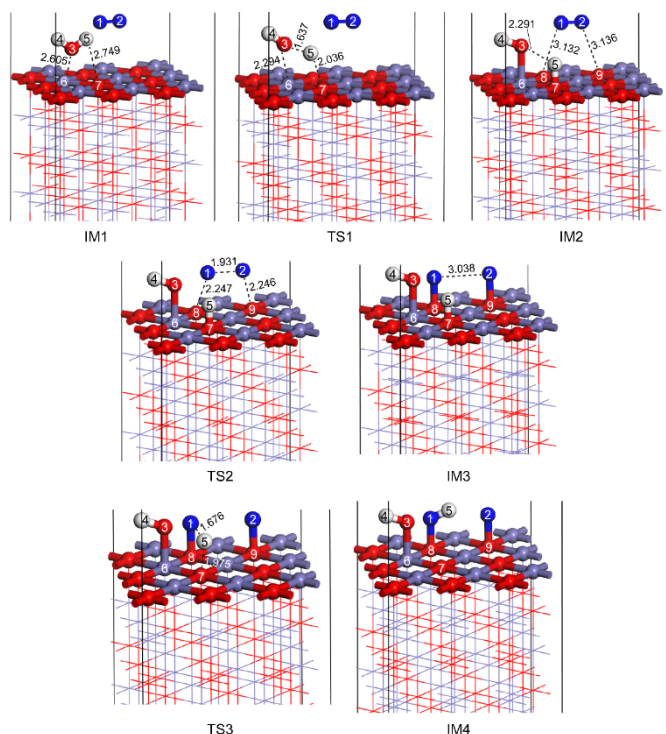


Fig. 7. Optimized geometries (of IM and TS) for dissociation of H₂O, N₂ and formation of first N-H bond over FeO(100) surface (length in Å)

Table 3. Imaginary frequencies of the transition states and bonds corresponding to relative normal vibrations for NH₃ synthesis

Transition States	Imaginary frequency (cm ⁻¹)	Bonds corresponding to relative normal vibrations
TS1	-895.42	H5-O3
TS2	-1123.37	N1-N2
TS3	-1041.59	H5-O7
TS4	-966.83	H4-O3
TS5	-1127.25	H11-O10
TS6	-862.71	H11-O7
TS7	-1093.68	H11-O10
TS8	-1316.04	H11-O7
TS9	-1208.47	H4-O3

(1) Dissociation of H₂O over FeO(100) surface

In the process (i.e., Reactant → IM1 → TS1 → IM2 → TS2 → IM3 → TS3 → IM4), H₂O first adsorbed on FeO(100) surface and then N₂ adsorbed on FeO(100) surface, forming IM1. IM1 had lower relative energy (-15.47 kcal/mol) than Reactant, which was attributed to the chemical bond effect. The distance of H5...O7 and Fe6...O3 decreased and the H5-O3 bond length increased. At the same time, the H5-O7 and Fe6-O3 bonds were formed with the break of H5-O3 bond to generate IM2 via TS1 (with just one imaginary frequency of -895.42 cm⁻¹). As seen in Fig. 7 and Table 3, H5 moved from H5-O3 in IM1 to O7 in IM2 with an energy barrier of 49.56 kcal/mol. In effect, H5 and H4-O3 in H₂O attack the O7 and Fe6 atoms in FeO(100) surface, respectively. As a result, H₂O was dissociated into -H and -OH groups over FeO(100) surface.

(2) Dissociation of N₂ over FeO(100) surface

The N1≡N2 bond length became longer as the distance of N1...O8 and N2...O9 became shorter. Meanwhile, the N1≡N2 bond broke and the N1-O8, N2-O9 bonds formed. Consequently, IM3 was generated via TS2 (with just one imaginary frequency of -1123.37 cm^{-1}) with an energy barrier of 81.25 kcal/mol through the migration of N1 and N2 from the N1≡N2 bond in IM2 to the N1-O8 and N2-O9 bonds in IM3 respectively. As a result, N₂ was dissociated into -N groups over FeO(100) surface.

(3) Formation of first N-H bond over FeO(100) surface

The bond lengths of H5-O7 became longer and the distance of H5...N1 became shorter. Additionally, the H5-O7 bond became broken and the H5-N1 bond formed. Subsequently, IM4 was formed via TS3 (with just one imaginary frequency of -1041.59 cm^{-1}) with an energy barrier of 70.75 kcal/mol through the migration of H5 from the H5-O7 bond in IM3 to the H5-N1 bond in IM4. As a result, the first N-H bond was formed over FeO(100) surface.

On the basis of these results, it is clear that H₂O was firstly dissociated over FeO(100) surface and N₂ dissociation process was the controlling step for NH₃ synthesis.

3.3. Catalytic synthesis of NH₃ over FeO(100) surface

The reaction channels and mechanisms of catalytic synthesis of NH₃ over FeO(100) surface are presented in Fig. 8, and the imaginary frequencies of the transition states are given in Table 3. For IM6 and IM8, new H₂O molecule was introduced and the following relative energies were based on IM6 and IM8 respectively. According to Fig. 8, the catalytic synthesis of NH₃ over FeO(100) could be divided into two reaction processes: 1) H migration without -OH groups; 2) H migration with -OH groups. As the difference, the reaction routes in the catalytic synthesis of NH₃ over FeO(100) could be divided into the following two routes.

Route I: IM3 → TS3 → IM4 → TS4 → IM5 → IM6 → TS5 → IM7 → TS6 → Product

Route II: IM3 → TS3 → IM4 → IM8 → TS7 → IM9 → TS8 → IM10 → TS9 → Product

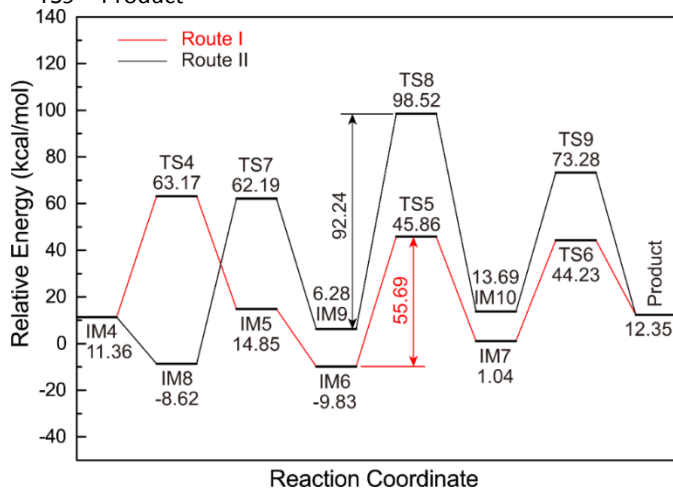


Fig. 8. Reaction channel and potential energy surface for catalytic synthesis of NH₃ over FeO(100) surface

(1) H migration without -OH groups

The optimized geometries for the catalytic synthesis of NH₃ over FeO(100) surface under H migration without -OH groups

(Route I) are presented in Fig. 9, and the imaginary frequencies of the transition states for Route I are given in Table 3. As shown in Route I, IM4 was formed from IM3 via TS3, which was same as the formation of first N-H bond in Fig. 7.

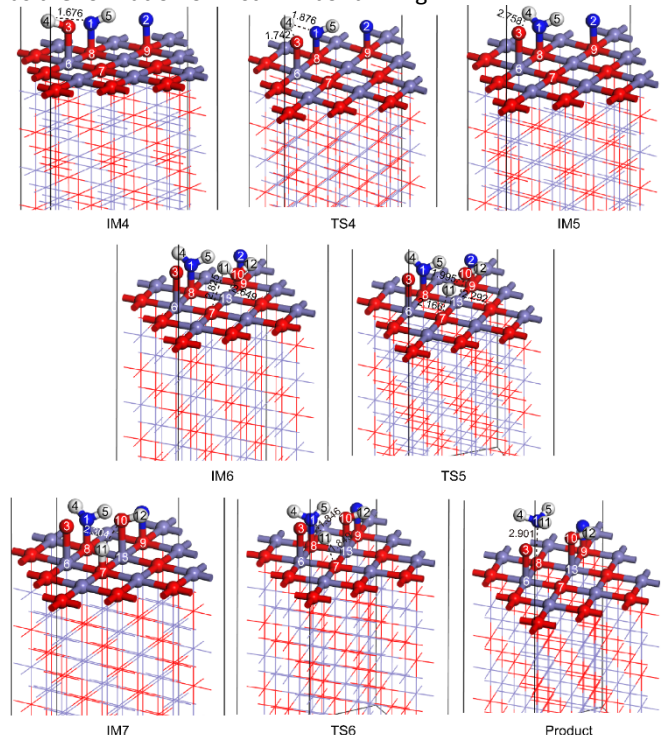


Fig. 9. Optimized geometries (of IM and TS) for catalytic synthesis of NH₃ over FeO(100) surface (Route I) (length in Å)

Next, the distance of H4...N1 decreased and the H4-O3 bond length increased. As a result, the H4-N1 bond was formed with the break of H4-O3 bond to generate IM5 via TS4, which has only one imaginary frequency of -966.83 cm^{-1} . As seen in Fig. 8 and Table 3, H4 moves from H4-O3 in IM4 to N1 in IM5 with an energy barrier of 51.81 kcal/mol.

Consequently, a new H₂O molecule approached IM5 and then IM6 was formed. The H11-O10 bond length became longer and the distance of H11...O7 became smaller. Meanwhile, the H11-O7 and Fe13-O10 bonds were formed with the break of H11-O10 bond. As a result, IM7 is generated via TS5 (with just one imaginary frequency of -1127.25 cm^{-1}) with an energy barrier of 55.69 kcal/mol through the migration of H11 from the H11-O10 bond in IM6 to the H11-O7 bond in IM7.

Concomitantly, the H11-O7 bond length became longer while the distance of H11...N1 became smaller. Additionally, the H11-O7 and N1-O8 bonds broke, and the H11-N1 bond was generated. Subsequently, Product was formed via TS6 (with just one imaginary frequency of -862.71 cm^{-1}) with an energy barrier of 43.19 kcal/mol through the migration of H11 from the H11-O7 bond in IM7 to H11-N1 bond in Product. Meanwhile, O atom from H₂O was captured on the FeO(100) surface.

Comparing with the formation of -NH, -NH₂ and NH₃, the energy barrier decreased with increasing N-H bond formation. It indicated that the N-H bond was more easily to form with the existence of N-H bond. As shown in the dissociation + Route I processes, the dissociation of N₂ was the controlling step for NH₃ synthesis.

(2) H migration with –OH groups

The optimized geometries for the catalytic synthesis of NH₃ over FeO(100) surface under H migration with –OH groups (Route II) are presented in Fig. 10, and the imaginary frequencies of the transition states for Route II are given in Table 3. As shown in Route II, IM4 was formed from IM3 via TS3, which was same as the formation of first N-H bond in Fig. 7.

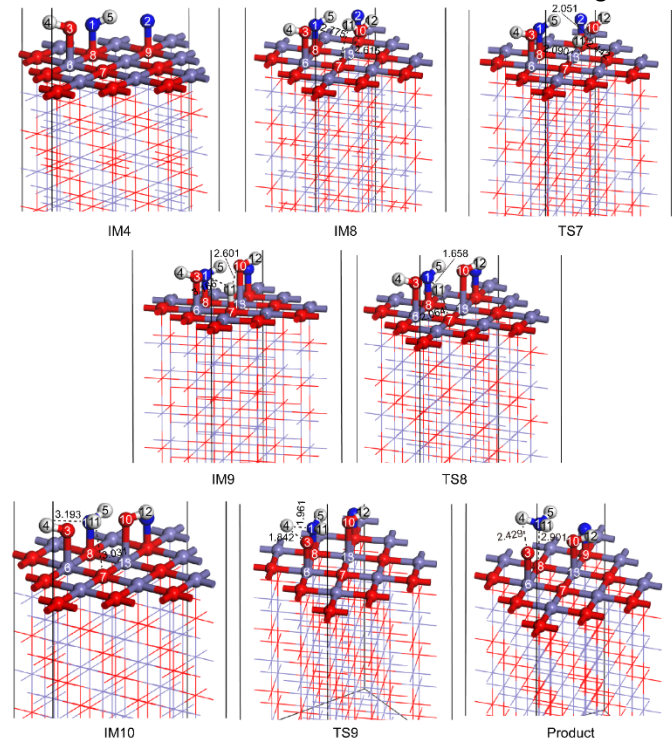


Fig. 10. Optimized geometries (of IM and TS) for catalytic synthesis of NH₃ over FeO(100) surface (Route II) (length in Å)

A new H₂O molecule approached IM4 and then IM8 was formed. The H11–O10 bond length became longer and the distance of H11...O7 became smaller. At the same time, the H11–O7, Fe13–O10 bonds were formed and H11–O10 bond broke, forming IM9 via TS7 (with just one imaginary frequency of –1093.68 cm⁻¹). As seen in Fig. 10 and Table 3, H11 moved from H11–O10 in IM8 to O7 in IM9 with an energy barrier of 70.81 kcal/mol, and H11 and H12–O10 in H₂O attack the O7 and Fe13 atoms in FeO(100) surface, respectively.

Next, the H11–O7 bond length became longer while the distance of H11...N1 became shorter. Meanwhile, the H11–O7 bond broke and the H11–N1 bond formed. Consequently, IM10 is generated via TS8 (with just one imaginary frequency of –1316.04 cm⁻¹) with an energy barrier of 92.24 kcal/mol through the migration of H11 from the H11–O7 bond in IM9 to the H11–N1 bond in IM10.

Concomitantly, the H4–O3 and N1–O8 bond lengths became longer while the distance of H4...N1 became shorter. Additionally, the H4–O3 and N1–O8 bonds broke, the H4–N1 bond formed. Subsequently, Product was formed via TS9 (with just one imaginary frequency of –1208.47 cm⁻¹) with an energy barrier of 59.59 kcal/mol through the migration of H4 from the H4–O3 bond in IM10 to the H4–N1 bond in the Product.

Comparing with Route I, the energy barrier for the formation of –NH₂ and NH₃ in Route II were higher, which

indicated that the existence of –OH groups was not conducive to the formation of N-H bond. Meanwhile, the energy barrier of TS8 (92.24 kcal/mol) was higher than TS5 (55.69 kcal/mol). It suggested that the H migration was affected by –OH groups. Furthermore, the existence of –OH groups changed the controlling step from the dissociation of N₂ to the formation of –NH₂. Meanwhile, the energy barrier of TS5 (55.69 kcal/mol) and TS7 (70.81 kcal/mol) were higher than TS1 (49.56 kcal/mol), which indicated that the existence of O atom or –OH groups from H₂O on the FeO(100) surface increased the difficult for the dissociation of H₂O. It was attributed to the occupying effect of O atom or –OH groups, which decreased the amount of surface Fe atom. This phenomenon is consistent with the literature.²⁸

4. Conclusions

The competitive adsorption and reaction mechanism for the catalytic synthesis reaction mechanism of NH₃ from N₂ and H₂O over FeO surface was investigated in this work. On the basis of the theoretical calculation results, H₂O was more easily adsorbed on the FeO surface than N₂. FeO(100) surface was more stable for the adsorption of N₂ and H₂O. Meanwhile, the interaction between N₂ and FeO(100) surface was attributed to N atom and O atom, which was caused by van der Waals forces. The interaction between H₂O and FeO(100) surface was attributed to O atom and Fe atom, which was caused by chemical bond effect. In the synthesis process, H₂O was firstly dissociated over FeO(100) surface and N₂ dissociation process was the controlling step for NH₃ synthesis. The existence of –OH groups was not conducive to the formation of N-H bond and it changed the controlling step from the dissociation of N₂ to the formation of –NH₂. Meanwhile, the existence of O atom or –OH groups from H₂O on the FeO(100) surface increased the difficult for the dissociation of H₂O.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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TOC

The existence of $-OH$ groups changed the controlling step from the dissociation of N_2 to the formation of $-NH_2$.

