Calcium poisoning mechanism on the selective catalytic reduction of NO\textsubscript{x} by ammonia over the γ-Fe\textsubscript{2}O\textsubscript{3} (001) surface

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Abstract
γ-Fe\textsubscript{2}O\textsubscript{3} has an excellent low-temperature selective catalytic reduction (SCR) deNO\textsubscript{x} performance, but its resistance to alkaline earth metal calcium (Ca) is poor. In particular, the detailed mechanism of Ca poisoning on the γ-Fe\textsubscript{2}O\textsubscript{3} catalyst at the atomic level is not clear. Hence, the density functional theory method was used in this research to investigate the influence mechanism of Ca poisoning on the NH\textsubscript{3}-SCR over the γ-Fe\textsubscript{2}O\textsubscript{3} catalyst surface. The findings reveal that NH\textsubscript{3}, NO, and O\textsubscript{2} molecules can bind to the γ-Fe\textsubscript{2}O\textsubscript{3} (001) surface to generate coordinated ammonia, monodentate nitroso, and adsorption oxygen species, respectively. The main active site is Fe\textsubscript{1-top}. For the γ-Fe\textsubscript{2}O\textsubscript{3} with Ca poisoning, the Ca atom has a high adsorption energy on the surface of γ-Fe\textsubscript{2}O\textsubscript{3} (001), which covers the catalyst surface and reduces the active sites. The presence of Ca atom decreases the adsorption performance of NH\textsubscript{3}, while slightly improving the NO and O\textsubscript{2} adsorption. In particular, the Ca atom restrains the NH\textsubscript{3} activation and NH\textsubscript{2} formation, which is detrimental to the NH\textsubscript{3}-SCR process.

Keywords NH\textsubscript{3}-SCR · DFT · Fe-based catalysts · Alkaline earth metal · Poisoning

Introduction
Nitrogen oxides (NO\textsubscript{x}) that consist chiefly of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) are one of the main substances of air pollution (Dimitriades 1972; Taylor 1993; Crutzen and Arnoldt 1986), which bring great harm to human social life. Controlling NO\textsubscript{x} emissions is one of the hot research directions of pollutant emission reduction. Selective catalytic reduction (SCR) technology is the mainstream technology to reduce NO\textsubscript{x} emissions at present, and deNO\textsubscript{x} catalysts are at the heart of it. Selective catalytic reduction of NO\textsubscript{x} by NH\textsubscript{3} (NH\textsubscript{3}-SCR) using V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} catalysts is the most mature technology to reduce NO\textsubscript{x} emissions from stationary sources (Stakheev et al. 2015). V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} catalysts with an NH\textsubscript{4}\textsuperscript{+} layer show an increased NO\textsubscript{x} removal efficiency over a wide temperature range (150–420 °C) compared with the V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} catalysts (Lee et al. 2021). However, the vanadium catalysts are toxic and easy to produce secondary pollution, so its application is limited. In addition, the high concentration of dust will lead to varying degrees of deactivation and wear of catalysts, and the SCR reactor is usually placed downstream of the dust removal and desulfurization unit (Pena et al. 2004). The flue gas temperature is low and the activity of V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2} catalysts is limited at low temperature. Therefore, the development of low-temperature SCR catalysts has been received more and more attention (Li et al. 2011). Sulfur dioxide, alkali metals, alkaline earth metals, and other hazardous chemicals are frequently found in fly ash produced from coal-fired flue gas (Kling et al. 2007; Krocher and Elsener 2008; Li et al. 2015; Li et al. 2016a; Li et al. 2016b). They often reduce the NO\textsubscript{x} removal efficiency of SCR catalysts and shorten their service life. Among them, calcium (Ca) is a typical poison with high content in the flue gas of coal-fired power plants (Strege et al. 2008), so it is vital to study the environmentally acceptable SCR deNO\textsubscript{x} catalysts adapted to low-temperature and alkaline environment.

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Iron (Fe) oxides have become the focus of research on the new deNO\textsubscript{x} catalysts because of their high selectivity, high activity, abundance of resources, low price, and environmental friendliness (Busca et al. 1998; Han et al. 2019). Shen et al. (2010) used a sol–gel approach to prepare the Fe–Mn–Ce/TiO\textsubscript{2} catalyst. The results show that adding Fe to NH\textsubscript{3}-SCR increases its activity at low temperature. Yao et al. (Yao et al. 2010a, b; Liang et al. 2016) investigated the removal characteristics of NO\textsubscript{x} from flue gas using γ-Fe\textsubscript{2}O\textsubscript{3} in fluidized bed. They found that the γ-Fe\textsubscript{2}O\textsubscript{3} exhibited a good NO\textsubscript{x} removal efficiency at 200–290 °C, and the deNO\textsubscript{x} efficiency can reach up to 90% at 250 °C. Liu et al. (2016) prepared environment-friendly Fe–Ce–Ti composite oxide catalysts via a hydrothermal method. The outcomes indicate that the addition of Fe significantly improves the NO reduction rate (more than 90% at 200 °C), N\textsubscript{2} selectivity (near 100% N\textsubscript{2} selectivity), and anti-SO\textsubscript{3} ability of the catalyst. Yang et al. (2011, 2013) discovered that γ-Fe\textsubscript{2}O\textsubscript{3} had a better deNO\textsubscript{x} efficiency than α-Fe\textsubscript{2}O\textsubscript{3}. Especially, when the temperature is higher than 300 °C, γ-Fe\textsubscript{2}O\textsubscript{3} can be transformed into α-Fe\textsubscript{2}O\textsubscript{3}, resulting in a decrease in deNO\textsubscript{x} efficiency. These studies laid a foundation for the development of iron-based deNO\textsubscript{x} catalysts at low temperature.

After desulphurization and dust removal, there will still be a small amount of alkali metals, alkaline earth metals, heavy metals, and other substances in the flue gas (Guo et al. 2017). Some studies on the effect of alkali metals on the deNO\textsubscript{x} of the V\textsubscript{2}O\textsubscript{5}-based catalysts have been carried out (Kong et al. 2018; Qian et al. 2022). Potassium compounds are discovered to diminish the amount of chemisorption of NH\textsubscript{3} on the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts and to deactivate the Brønsted acid sites on the catalysts’ surfaces. Du et al. (2015) studied the alkali deactivation of the V\textsubscript{2}O\textsubscript{5}-based catalysts by a density functional theory calculation (DFT). The decrease of oxidation capacity and the enrichment of inactive nitrite and nitrate species on the surface of the catalyst are responsible for the low deNO\textsubscript{x} efficiency. Ca poisoning in coal-fired power plants is also common and serious because coal-fired power plants use a large number of high-calcium coal such as powder river basin for power generation (Li et al. 2016c). However, the effect mechanism of Ca on the deNO\textsubscript{x} of Fe-based catalysts is still a gray area. Wang et al. (2020) synthesized fresh and different Ca poisoned Fe–Ce/Ti catalysts to study their deNO\textsubscript{x} performance. They found that Ca doping could lead to an obvious decrease in the deNO\textsubscript{x} activity of the Fe–Ce/Ti catalysts. Gao et al. (2020) found that Ca poisoning decreased the deNO\textsubscript{x} activity of the Cu-SAPO-18 catalyst because the doping of Ca blocks parts of the micropores and reduces the amount of L and B acid sites on the catalyst surface.

Although there are some researches on the mechanism of alkali metals and alkaline earth metal poisoning, the detailed effect of Ca poisoning on the deNO\textsubscript{x} of Fe-based catalysts is rarely involved. Therefore, the purpose of this research is to look into the influence of Ca poisoning on the adsorption characteristics of NO, NH\textsubscript{3}, and O\textsubscript{2} on the γ-Fe\textsubscript{2}O\textsubscript{3} (001) surface by a DFT method to promote the application of iron-based catalysts in coal-fired power plants.

**Computational details**

The DFT calculation was performed by a Vienna ab initio software package version 5.4 (Dong et al. 1996; Kresse and Furthmüller 1996; Rohrbach et al. 2003). Perdew-Burke-Ernzerhof and generalized gradient approximation methods were adopted for spin-polarized calculation (Fiederling et al. 1999; Grimme 2006; Wu and Cohen 2006). For Fe, Mn, Ce, and other transition metals, the strong Coulomb interaction can greatly affect the description of the system because of the local characteristics of d or f orbital electrons (Dudarev et al. 1998; Bengone et al. 2000). Therefore, the Hubbard U method was used to calculate the U\textsubscript{eff} of Fe, which was set to 4.0 eV (Rohrbach et al. 2004). In the self-consistent field iteration, the convergence thresholds of force and energy were set at 0.02 eV/Å and 10\textsuperscript{−5} eV, respectively.

The bulk model of γ-Fe\textsubscript{2}O\textsubscript{3}, which possesses a cubic anti-spinel structure, is shown in Fig. 1a. The crystal cell characteristics are as follows: a = b = c = 8.405 Å; α = β = γ = 90° (Jørgensen et al. 2007). For the optimization of γ-Fe\textsubscript{2}O\textsubscript{3} bulk model, the convergence tests of the kinetic energy cutoff and K-points were performed (Monkhorst and Pack 1976). The results are shown in Fig. S1. It can be seen from Fig. S1 that they meet the convergence requirements at 500 eV and 5×5×5, respectively. Compared with the experimental data, the error of the optimized cell parameters (a = b = c = 8.527) is 1.45%, demonstrating that the calculation is reliable. For the lowest energy facet of γ-Fe\textsubscript{2}O\textsubscript{3}, the (001) surface is a relatively common and stable crystal (Yanagihara et al. 2006). Hence, we chose the γ-Fe\textsubscript{2}O\textsubscript{3} (001) surface for the further study. As shown in Fig. 1b, to reduce symmetry, 2×2 slab model and 15 Å vacuum layers were established. Five atomic layers were chosen, with the lower three layers fixed and the above two layers relaxed. Its relative energy was computed by using Monkhorst–Pack 1×1×1 grid because of the large size of the slab model. To calculate the adsorption of NH\textsubscript{3}, NO, and O\textsubscript{2} on the surface of γ-Fe\textsubscript{2}O\textsubscript{3} (001), these small molecules were optimized by putting them in a crystal lattice of 10 Å. In addition, the transition states and reaction energy barriers of NH\textsubscript{3} dehydrogenation over the catalyst surface were calculated via the climbing-image nudged elastic band (CI-NEB) method (Prabowo et al. 2019).

Equations (1) and (2) were used to calculate the adsorption energies of Ca atom and gas molecules on the γ-Fe\textsubscript{2}O\textsubscript{3} (001) surface of catalyst.
where $E_{\text{substrate} + \text{gas}}$ are the total energies of the adsorbed system (Ca atom/gas + substrate), $E_{\text{Ca atom}}$ and $E_{\text{gas}}$ are the energies of the isolated Ca atom and gas molecule in vacuum, and $E_{\text{substrate}}$ is the energy of the surface of $\gamma$-Fe$_2$O$_3$ (001). Note that the greater the negative adsorption energy is, the stronger the binding of molecules adsorbed on the surface is. To further explore the adsorption properties of gas molecules, the projected density of states (PDOS) and Bader charge analysis were introduced.

### Results and discussion

#### The adsorption properties of NH$_3$, NO, and O$_2$ on the $\gamma$-Fe$_2$O$_3$ (001) surface

The NH$_3$-SCR reaction is classified into Eley–Rideal (E-R) and Langmuir–Hinshelwood mechanisms. No matter which reaction mechanism is, the molecular adsorption behavior can occur on the surface of catalysts, which is the key step of SCR reaction. Therefore, the study of the adsorption process of gas molecules is helpful to understand the SCR reaction mechanism on the catalyst surface (Bengone et al. 2000). In this section, we optimized the structures of gas molecules such as NH$_3$, NO, and O$_2$ on the surface of $\gamma$-Fe$_2$O$_3$ (001) at a distance of 3 Å. Fe$_{1\text{-top}}$, Fe$_2$, O-$\text{top}$, and Hollow are the primary adsorption sites (shown in Fig. 1c).

**Adsorption configuration**

Figure 2a illustrates the optimal NH$_3$ molecule configurations on the $\gamma$-Fe$_2$O$_3$ (001) surface. Among the four adsorption models, no stable chemical bonds are formed on the Fe$_2$ sites, and both Hollow sites and O-$\text{top}$ sites are offset and adsorbed on the Fe$_{1\text{-top}}$ sites in the form of nitrogen-end. Previous research (Zhu et al. 2018) shows that NH$_3$ tends to be adsorbed on the catalyst surface by the nitrogen-end, which agrees with our findings. For Fe$_{1\text{-top}}$ site, the N-Fe$_1$ bond length is 2.193 Å, and the bond length of NH$_3$ increases from 1.006 to 1.022 Å (shown in Table 1), indicating that the N–H bond is activated by the adsorption at the Fe$_{1\text{-top}}$ site. For the Hollow and O-$\text{top}$ sites, the N–H bond lengths are 1.020 Å and 1.027 Å, respectively. The NH$_3$ molecule is deflected and the N and Fe atoms are not bonded when they are adsorbed at the Fe$_2$ site, which could be due to the weak adsorption capacity between the N terminal and the Fe$_2$ site. Figure 2b depicts the optimum configurations of NO molecule adsorbed on the $\gamma$-Fe$_2$O$_3$ (001) surface. For the
Fe₁ site and Hollow sites, NO molecules are adsorbed at a certain angle on the surface of the catalyst to form N-Fe₁ bond. The structural parameters after adsorption are listed in Table 1. The bond lengths of NO molecule adsorbed on the Fe₁-top site and the Hollow site increase from 1.168 to 1.170 Å and 1.175 Å, respectively, showing that the N–O bond is activated after adsorption. As shown in Fig. 2c, O₂ molecules are adsorbed at Fe₁ and Hollow sites on the γ-Fe₂O₃ (001) surface, whose bond lengths increase from 1.234 to 1.264 Å and 1.301 Å (shown in Table 1), respectively, showing that the O–O bond is also activated when O₂ molecules are adsorbed on the γ-Fe₂O₃ (001) surface.

Adsorption energy

To further understand the binding strength between molecules and adsorption substrate, the adsorption energies are calculated by Eq. (2), whose results are shown in Table 1. The largest value of NH₃ adsorption energy is −1.15 eV (Fe₁-top), followed by −0.58 eV (O-top site) and −0.32 eV (Fe₂ site). In general, the absolute value of adsorption energy between adsorption substrate and gas molecule is 0.5 eV as the dividing line between physical adsorption and chemical adsorption, and the absolute value of adsorption energy above 0.5 eV is chemical adsorption, on the contrary, physical adsorption (Li et al. 2018). Therefore, the adsorption at Fe₁-top and O-top sites is chemical adsorption, while the adsorption at Fe₂ site is physical adsorption. For NO molecule, as shown in Fig. 2b, NO can be placed on Fe₁-top site, O-top site, and Fe₂ site, and their adsorption energies are −0.88/−0.87, −0.72, and −0.40 eV, respectively. A large difference in the adsorption energy of NO adsorbed on the Fe₁-top site is observed compared with that on the O-top and Fe₂ sites. NO molecule is more inclined to be absorbed on Fe₁-top sites. According to Table 1, the adsorption energies of O₂ on the Fe₁-top, Fe₂, and Hollow sites are respectively −0.71, −0.09, and −1.10 eV, indicating a chemical adsorption for O₂ on the Fe₁-top site and Hollow site. Between them, Hollow site is the site with the highest adsorption energy, and its oxygen atoms bond with the Fe atoms to form more stable chemical adsorption.

Bader charge change

Since the adsorption of gas molecules on the surface of the catalyst may be affected by a variety of factors such as the coordination of the atoms on the surface and the atomic charges of the atoms around the adsorption sites and the
sites (Zhu et al. 2018), it is not very reliable to judge whether the adsorption is chemical adsorption or physical adsorption only by adsorption energy. Therefore, it is verified by Bader charge change. The electron change was calculated by Eq. (3).

\[-Q = Q_{\text{bader}} - Z_{\text{val}}\] (3)

where \(Q_{\text{bader}}\) and \(Z_{\text{val}}\) are the Bader charge on each atom and the number of valence electrons, respectively. A positive value means that the gas molecules gain electrons, while a negative value means that they lose electrons.

Compared with free NH\(_3\) molecule, the Bader charge of each atom changes greatly after NH\(_3\) is adsorbed at the Fe\(_1\)-top, Hollow, and O-top sites. On the basis of adsorption energy, it is inferred that NH\(_3\) is adsorbed on these active sites in a stable chemisorption process. Its total charge of NH\(_3\) molecules is negative and Bader charges change from 0 e to \(-0.11/-0.13\) e and \(-0.08\) e at the Fe\(_1\)-top and O-top sites due to electron donation from the surface, indicating that NH\(_3\) loses electrons and transfers to the surface of the catalyst during the process, which strengthens the adsorption and activation of NH\(_3\). These results are in good agreement with the mechanism of reaction that NH\(_3\) binds to metal cations lacking electrons on the surface, and cations (Lewis acid sites) receive electrons from N lone pair orbitals. The results from Table 1 show that the Bader charges of NO molecule adsorbed at the Fe\(_1\)-top and O-top sites decrease from 0 e to 0.07/0.08 e and 0.05 e. These results indicate that a stable chemical adsorption occurs for NO at the Fe\(_1\)-top and Hollow sites, which is in accordance with the results of the adsorption energy measurements. NO molecules have a positive charge in both of these adsorption configurations, indicating that the whole adsorption system undergoes the charge transfer from the catalyst surface to NO molecule. This leads to the strengthening of nitrogen–oxygen bond, preventing the next activation of the adsorbed NO molecule (Fang et al. 2019). The charges on the adsorbed oxygen atom and unadsorbed oxygen atom increase significantly from 0.01 e and \(-0.01\) e to 0.08 e and 0.39 e, respectively, which suggests that the adsorption of O\(_2\) molecule on the Hollow site is chemical adsorption. The adsorption of O\(_2\) over the catalyst surface increases the number of reactive oxygen species sites, which promotes the NH\(_3\)-SCR reaction (Fang et al. 2019).

**PDOS analysis**

To further explore the bonding mechanism of gas molecules on the surface of γ-Fe\(_2\)O\(_3\) (001), the projected density of states of each component in the lowest energy configurations after adsorption (NH\(_3\) and NO at Fe\(_1\)-top site and O\(_2\) at Hollow site) were calculated. In Fig. 3a, we can see that

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Fig. 3 a–c PDOS results of NH\(_3\), NO, and O\(_2\) molecules adsorbed on the γ-Fe\(_2\)O\(_3\) (001) surface
the \( p \) orbital of \( \text{NH}_3 \) molecule and the \( d \) orbital of \( \text{Fe} \) cation show a common peak at about \(-8 \sim -6 \) and \(-5 \sim -1 \) \( \text{eV} \), respectively. These peaks can be the formant produced by the hybridization of \( \text{N} \) atom and \( \text{Fe} \) atom. Further indications show that the \( \text{N} \) atom and the \( \text{Fe} \) atom form a stable chemical bond as a result of the adsorption of the \( \text{NH}_3 \) molecule. For \( \text{NO} \) and \( \text{O}_2 \) molecules (Fig. 3b, c), the \( p \) orbital peaks of \( \text{N} \) atom (\( \text{NO} \)) and \( \text{O} \) atom (\( \text{O}_2 \)) overlap with the \( d \) orbital peaks of \( \text{Fe} \) atom due to orbital hybridization at \(-8 \sim -6 \) \( \text{eV} \) and \(-8 \sim -2 \) \( \text{eV} \), respectively, implying that there is strong chemisorption in \( \text{Fe} \sim \text{NO} \) configuration, and \( \text{O}_2 \) undergoes chemical adsorption on the surface of \( \gamma\text{-Fe}_2\text{O}_3 \) (001) to form adsorbed oxygen.

According to the results of gas adsorption configurations, adsorption energies, Bader charge changes, and PDOS analysis, it is possible to conclude that \( \text{NH}_3 \) and \( \text{NO} \) molecules can be more readily adsorbed on the \( \text{Fe}_1\text{-top} \) site, and the adsorption products are coordinated ammonia and monodenate nitroso. It is easier for \( \text{O}_2 \) molecules to form bidentate adsorbed oxygen configuration on the surface of the \( \gamma\text{-Fe}_2\text{O}_3 \) catalyst.

**The poisoning property of \( \text{Ca} \) atom on the \( \gamma\text{-Fe}_2\text{O}_3 \) (001) surface**

**The adsorption of \( \text{Ca} \) atom on the \( \gamma\text{-Fe}_2\text{O}_3 \) (001) surface**

In the \( \text{deNO}_x \) process, alkaline (earth) metal poisoning is a major factor that affects the effectiveness of the catalyst. Fang et al. (2020) found that the alkali metals inhibited the activity of the \( \alpha\text{-Fe}_2\text{O}_3 \) catalyst because they were able to cover the \( \text{Fe} \) sites and prevent the adsorption of \( \text{NH}_3 \), thereby decreasing the activity of the \( \text{Fe} \) sites on the \( \alpha\text{-Fe}_2\text{O}_3 \) catalyst surface. Jiang et al. (2017) found that \( \text{Ca} \) atoms had a strong interaction with cerium and oxygen atoms, which inhibits the formation of oxygen vacancies and hydrogenation on the \( \text{CeO}_2\text{/TiO}_2 \) catalyst surface. To understand the poisoning process of \( \gamma\text{-Fe}_2\text{O}_3 \) catalysts, a \( \text{Ca} \) atom was placed on the \( \gamma\text{-Fe}_2\text{O}_3 \) (001) surface, and then its adsorption properties were studied. The optimized \( \text{Ca} \) poisoning configurations are shown in Fig. 4. The \( \text{Ca} \) atom is stably adsorbed on the \( \gamma\text{-Fe}_2\text{O}_3 \) (001) surface via combining with four \( \text{O} \) atoms. These adsorption configurations are consistent with the result of Krocher et al. (Krocher and Elsener 2008). On the \( \text{V}_2\text{O}_5 \) (010) surface, \( \text{Ca} \) was found to occupy the non-atomic hole sites. The original bond lengths of \( \text{Fe}_1\text{-top} \) and \( \text{O}_1\text{-, O}_2\text{-, O}_3\text{-, and O}_4\text{-} \) are \( 2.085 \) \( \text{Å} \) on the \( \gamma\text{-Fe}_2\text{O}_3 \) (001) surface. After the \( \text{Ca} \) atom adsorption, they become \( 2.513, 1.942, 2.350, \) and \( 1.939 \) \( \text{Å} \), respectively. Like Fig. 4(b), the lengths of the \( \text{Fe}_1\text{-O}_1\text{-, Fe}_1\text{-O}_2\text{-, Fe}_1\text{-O}_3\text{-, and Fe}_1\text{-O}_4\text{-} \) bonds become \( 1.966, 2.093, 1.963, \) and \( 1.999 \) \( \text{Å} \), and the bond lengths in Fig. 4(c) are \( 1.969, 2.261, 2.017, \) and \( 2.113 \) \( \text{Å} \), respectively. This is because \( \text{Ca} \) poisoning causes the surface distortion of the catalyst, which changes the distance between \( \text{Fe} \) and \( \text{O} \) atoms and affects the reaction performance of the catalyst (Krocher and Elsener 2008).

The energy of a single isolated \( \text{Ca} \) atom was calculated by putting four \( \text{Ca} \) atoms in a crystal lattice of \( 10 \) \( \text{Å} \). The obtained energy of each \( \text{Ca} \) atom is \( -0.58 \) \( \text{eV} \). Calculated adsorption energies of \( \text{Ca} \) atom on the \( \gamma\text{-Fe}_2\text{O}_3 \) (001) surface by Eq. (2) are \( -5.52, -5.46, \) and \( -5.55 \) \( \text{eV} \), respectively. In light of the higher adsorption energy, the covering of \( \text{Ca} \) atom on the surface of the \( \gamma\text{-Fe}_2\text{O}_3 \) catalyst may be the primary contributor to the reduction of \( \text{deNO}_x \) activity of the catalyst.
Figure 5 shows the distribution of the electron density difference (\(\rho\)) in the Ca-\(\gamma\)-Fe\(_2\)O\(_3\) (001) configurations calculated by Eq. (4).

\[
\Delta \rho = \rho [\text{Ca} - \gamma - \text{Fe}_2\text{O}_3(001)] - \rho [\text{Ca}] - \rho [\gamma - \text{Fe}_2\text{O}_3(001)]
\]

where \(\rho [\text{Ca}-\gamma-\text{Fe}_2\text{O}_3(001)]\) is the total electron density difference of Ca atom adsorbed on the \(\gamma\)-Fe\(_2\)O\(_3\) (001) surface. \(\rho [\text{Ca}]\) and \(\rho [\gamma-\text{Fe}_2\text{O}_3(001)]\) represent the electron density difference of Ca atom and surface, respectively. It can be seen from Fig. 5 that the charge is transferred between Ca atom and Fe and N atoms, meaning that even though Ca atom does not cover the site of Fe atom, the activity of Fe site is still affected.

The effect of Ca atom on gas adsorption over the \(\gamma\)-Fe\(_2\)O\(_3\) (001) surface

Figure 6 shows the adsorption structures of \(\text{NH}_3\), NO, and \(\text{O}_2\) molecules on the Ca poisoning surface. Since the absolute adsorption energy of Ca atom adsorbed on the \(\gamma\)-Fe\(_2\)O\(_3\) (001) surface shown in Fig. 4(c) is the largest, the structure is the more stable and is selected as the substrate of the molecular adsorption model. According to Fig. 6a, \(\text{NH}_3\) molecules can be adsorbed on the surface of the Ca-\(\gamma\)-Fe\(_2\)O\(_3\) (001). The N atom is bonded with Fe atom on the optimized structure. It can be found that the length of N–H is shortened from 1.022 to 1.020 Å. By comparing the N–H bond length of the \(\text{NH}_3\) molecule, it has been discovered that the poisoned catalyst has a shorter N–H bond than the fresh catalyst, which indicates that the N–H bond is not easy to break during \(\text{NH}_3\) adsorption. There is a difficulty in forming \(\equiv\text{NH}_2\), which is not favorable for the follow-up of the de\(\text{NO}_x\) reaction (Xie et al. 2020).

From Table 2, it can be seen that the adsorption energy of \(\text{NH}_3\) on the Fe\(_1\)-top site is \(-0.75\) eV, which is less than that on the surface of fresh catalyst \((-1.15\) eV), showing that the de\(\text{NO}_x\) activity of the Ca poisoned \(\gamma\)-Fe\(_2\)O\(_3\) catalyst decreases. And the adsorption energy of \(\text{NH}_3\) molecule on the Fe\(_1\)'-top site of the Ca-\(\gamma\)-Fe\(_2\)O\(_3\) (001) surface is \(-0.86\) eV, demonstrating that although the poisoning effect of Ca on the Fe\(_1\)'-top site of the \(\gamma\)-Fe\(_2\)O\(_3\) (001) surface decreases, it still inhibits the adsorption of \(\text{NH}_3\) molecule compared with the \(\gamma\)-Fe\(_2\)O\(_3\) (001). As a result of electron transfer, it has been determined that there is little charge transfer between \(\text{NH}_3\) molecule and Ca-\(\gamma\)-Fe\(_2\)O\(_3\) (001) surface, which indicates that alkaline earth metal makes the chemical adsorption of \(\text{NH}_3\) become weak on the \(\gamma\)-Fe\(_2\)O\(_3\) (001) surface.

In order to further analyze the bonding situation of gas molecules absorbed on the Ca-\(\gamma\)-Fe\(_2\)O\(_3\) (001) surface, the Bader charge change and the electron density difference were introduced. Figure 7b and c illustrate the distribution of electrons at the Fe\(_1\)-top site of the Ca-\(\gamma\)-Fe\(_2\)O\(_3\) (001) surface. It can be observed that vast amounts of yellow electron clouds gather towards the \(\text{NH}_3\) molecule; thus, the \(\text{NH}_3\) adsorption is further inhibited. The electron changes of \(\text{NH}_3\) increase from \(-0.22\) e to \(-0.12\) e (\(\text{NH}_3\) absorbed on Fe\(_1\)-top site) and \(-0.07\) e (\(\text{NH}_3\) absorbed on Fe\(_1\)'-top site), respectively, suggesting that the number of electrons obtained by Fe\(_1\) atom from \(\text{NH}_3\) molecule is reduced, and the interaction between Fe\(_1\) atom and \(\text{NH}_3\) is weakened (Ren et al. 2021), demonstrating that Ca atom acts as an inhibitor of \(\text{NH}_3\) molecules from adsorbing on the Fe atom of the \(\gamma\)-Fe\(_2\)O\(_3\) catalyst. The result is in good agreement with the analysis of the electron density difference.

For a deeper understanding of the adsorption mechanism of \(\text{NH}_3\) on the poisoned catalyst, the project density of state (PDOS) method was used to investigate the change in orbital configuration of the F–N pairs. The PDOS of configuration (a) in Fig. 6 is shown in Fig. 8a. As can be seen in Fig. 8a, the p orbital of N atom and the d orbital of Fe atom show a common hybridization peak at about \(-4\) eV. Compared with the result shown in Fig. 3a, the intensity of density peak of the p orbital for the N atom and the d orbital for the Fe atom decreases, suggesting that the Fe–N bond is weakening as a result of Ca poisoning, which is consistent with the results of the

![Fig. 5 a–c Electron density difference profiles of Ca atom adsorbed on the \(\gamma\)-Fe\(_2\)O\(_3\) (001) surface (cyan, lose electron; yellow, obtain electron)](image-url)
adsorption. These results show that the adsorption of NH$_3$ on Lewis acid is affected by Ca atom, and NH$_3$ molecule interacts with the Ca-γ-Fe$_2$O$_3$ (001) surface by the physical adsorption.

Figure 6c and d illustrate the adsorption configurations of NO molecule on the Ca-γ-Fe$_2$O$_3$ (001) surface. The length of N–O bond increases from 1.170 Å on the surface of γ-Fe$_2$O$_3$ (001) to 1.182 and 1.191 Å on the surface of Ca-γ-Fe$_2$O$_3$ (001), which indicates the activation of the N–O bond after Ca poisoning. The NO adsorption energies on the Fe$_{1\text{-top}}$ site and the Fe$_{1'\text{-top}}$ site are $-$1.34 eV and $-$1.22 eV, respectively, which are larger than that of on the pure surface of γ-Fe$_2$O$_3$ (001), suggesting that the Ca atom promotes the adsorption of NO molecule at the Fe$_{1\text{-top}}$ site on the Ca-γ-Fe$_2$O$_3$ (001) surface. According to electron transfer results, a larger charge transfer is observed between NO molecule and Ca-γ-Fe$_2$O$_3$ (001) surface, which indicates that the adsorption state of NO on the surface of Ca-γ-Fe$_2$O$_3$ (001) is strong chemical adsorption. In addition, according to the differential charge density diagram shown in Fig. 7d–f, the charge recombination occurs on the poisoned surface, and electron acquisition of NO molecule on the Fe site of the Ca-γ-Fe$_2$O$_3$ (001) and γ-Fe$_2$O$_3$ (001) surfaces are in the order of Ca-Fe$_{1\text{-top}}$ site (the Fe site near Ca) > Ca-Fe$_{1'\text{-top}}$ site (the Fe site far from Ca) > fresh Fe$_{1\text{-top}}$ site. The results of this analysis are in agreement with the findings of the Bader charge analysis. Additionally, the PDOS results indicated in Fig. 8b show that the density peak intensity of the $p$ orbital for the N atom of NO molecule is stronger than that of NO adsorbed

Table 2 Adsorption energies, bond lengths, and Bader charge changes of NH$_3$, NO, and O$_2$ on the Ca-γ-Fe$_2$O$_3$ (001) surface

| Gas | Adsorption site | $R$ (molecule bond)/Å | Adsorption energy/eV | Bader charge change/e |
|-----|-----------------|------------------------|----------------------|----------------------|
| NH$_3$ | Fe$_{1\text{-top}}$ | 1.020 | $-$0.75 | $-$0.12 |
|       | Fe$_{1'\text{-top}}$ | 1.020 | $-$0.86 | $-$0.07 |
| NO   | Fe$_{1\text{-top}}$ | 1.182 | $-$1.34 | $+$0.40 |
|       | Fe$_{1'\text{-top}}$ | 1.191 | $-$1.22 | $+$0.22 |
| O$_2$ | Hollow | 1.318 | $-$1.79 | $+$0.49 |

Fig. 6 a–e Configurations of gas molecules adsorbed on the Ca-γ-Fe$_2$O$_3$ (001) surface; Fe, gray; O, red; Ca, green; N, blue; and H, white
on the surface of $\gamma$-Fe$_2$O$_3$ (001), suggesting that Ca poisoning enhances the adsorption of NO on the surface of $\gamma$-Fe$_2$O$_3$ (001). NO molecule is chemisorbed on the surface of the Ca-$\gamma$-Fe$_2$O$_3$ (001) and a covalent bond is formed between N and Fe atoms. The doping of Ca atoms makes the conduction band move and weakens the nonlocality of electrons. During the oxidative process, electrons are more likely to occupy high energy states, decreasing the oxidation ability (Wei et al. 2018). It is therefore difficult to transfer electrons between nitrogen oxides and the catalyst surface, and finally weakens the oxidation ability of the catalyst. The results indicate that NO reacts with $\gamma$-Fe$_2$O$_3$ catalyst to generate nitrate species when the Ca atom is added. In the presence of nitrate species, Fe active sites are occupied and further catalytic reaction is hindered, so the catalyst’s deNOx activity will be reduced.

Since the adsorption energy on the Hollow site of the $\gamma$-Fe$_2$O$_3$ (001) surface is the largest, this structure is most stable, so we studied the adsorption of O$_2$ on the Hollow site of the Ca-$\gamma$-Fe$_2$O$_3$ (001) surface. As can be seen from Table 2, the length of the O–O bond is increased to 1.318 Å on the Ca-$\gamma$-Fe$_2$O$_3$ (001) surface from the original value of 1.301 Å on the surface of $\gamma$-Fe$_2$O$_3$ (001), suggesting that the bond is activated when the O$_2$ molecule adsorbs on the surface of Ca-$\gamma$-Fe$_2$O$_3$ (001). This phenomenon is conducive to the reaction of O$_2$ and NO to generate NO$_2$, which can enhance the process of “fast SCR” (Lietti et al. 1996; Koebel et al. 2000, 2001, 2002; Madia et al. 2002; Ciardelli et al. 2004). The adsorption energy of O$_2$ molecule on the Hollow site of $\gamma$-Fe$_2$O$_3$ (001) surface is $-1.10$ eV. In addition, we can find that the adsorption energies of O$_2$ molecule on the surface of $\gamma$-Fe$_2$O$_3$ (001) are increased after Ca poisoning, which indicate that Ca has a good effect on the adsorption of O$_2$ on the surface of $\gamma$-Fe$_2$O$_3$ (001). From the electron transfer of the O$_2$ molecule shown in Table 2, it can also be seen that the electron transferred from the surface of Ca-$\gamma$-Fe$_2$O$_3$ (001) to O$_2$ is slightly larger than that transferred from the surface of $\gamma$-Fe$_2$O$_3$ (001), which is consistent with the adsorption results. As shown in Fig. 7g and h, electron density distribution of O$_2$ on the Ca-$\gamma$-Fe$_2$O$_3$ (001) surface is similar with that of O$_2$ on the $\gamma$-Fe$_2$O$_3$ (001) surface. Figure 8c shows that the density peak of $p$ orbital of O atom strongly overlaps with the $d$ orbital of Fe$_{1\text{-top}}$ atom at approximately $-8 \sim -1$ eV, supporting the statement that Fe$_{1\text{-top}}$ and O atoms undergo orbital hybridization. Furthermore, this shows that O$_2$ molecule interacts strongly with the Hollow site, which implies that the adsorption is chemisorption.

**The effect of Ca atom on NH$_3$ activation over the $\gamma$-Fe$_2$O$_3$ (001) surface**

According to previous studies (Fang et al. 2019), the dehydrogenation of NH$_3$ adsorbed on the surface of catalysts is the first step of the reaction process. In other words, the adsorbed NH$_3$ cannot react directly with other gases at the Fe$_{1\text{-top}}$ site due to the saturation of the bond. It is very necessary to study the dissociation of NH$_3$. Therefore, the dehydrogenation reaction paths of NH$_3$ before and after poisoning were explored based on the adsorption of Fe$_{1\text{-top}}$ site in Fig. 2a and Fig. 6a. In this section, a climbing-image nudged elastic band (CI-NEB) method...
is used to produce the reaction routes and transition states of NH₃ activation (Li et al. 2016d; Lin et al. 2019). Figure 9a shows that the adsorbed NH₃ undergoes a process of dehydrogenation to form NH₂, and the reaction energy barrier is 1.54 eV. On the transition state structure, it appears that a hydrogen atom leaves the N–H bond to combine with an oxygen atom on the surface of the γ-Fe₂O₃ (001) system to form an OH group. In addition, it is evident from Fig. 9b that the dehydrogenation of the adsorbed NH₃ on the Ca-γ-Fe₂O₃ (001) surface needs to overcome a larger energy barrier (3.50 eV) to form OH groups, implying that Ca doping inhibits the dehydrogenation of NH₃ to produce –NH₂ and OH groups, which is in agreement with the results of adsorption energies and PDOS. NO molecule can combine with the NH₂ after dehydrogenation of NH₃ to form NH₂NO. In the E-R reaction mechanism, NH₂NO is considered to be the intermediate product to form H₂O and N₂ (Chen et al. 2010; Liu et al. 2017; Wang et al. 2017). Therefore, the Fe-based catalyst poisoned by Ca is not conducive to the deNOₓ reaction.

**Fig. 9 a, b** Energy and configuration distribution of NH₃ dehydrogenation pathway on the γ-Fe₂O₃ (001) and Ca-γ-Fe₂O₃ (001) surfaces; Fe, gray; O, red; N, blue; H, white.
Discussion

With the results discussed above, we can conclude the detailed effects of Ca poisoning on the deNO_x performance of the \( \gamma\)-Fe_2O_3 catalyst. The schematic diagram is shown in Fig. 10. When Ca is adsorbed on the surface of \( \gamma\)-Fe_2O_3 (001), it can bind with the \( \gamma\)-Fe_2O_3 (001) surface with four oxygen atoms, which may result in the decrease of reactivity of Fe–O groups on the \( \gamma\)-Fe_2O_3 (001) surface because of the binding of alkaline earth metal atoms and surface active oxygen. According to our calculation, Ca atoms can not only be easily adsorbed on the surface of \( \gamma\)-Fe_2O_3 (001), but also reduce the activity of Fe sites on the surface. Additionally, Ca atom weakens the adsorption of NH_3 molecule, while promotes the adsorption of NO and O_2 molecules. The decrease of NH_3 adsorption energy on the surface of the poisoned catalyst means that less NH_3 molecules are adsorbed on the surface. NO molecule can react with the \( \gamma\)-Fe_2O_3 catalyst and generates nitrate by adding Ca atom, which is deposited on the catalyst surface and causes the catalyst poisoning. This result is in agreement with the analyses of the adsorption of gas molecules on the Mn/TiO_2 catalyst with alkali metal (Wei et al. 2018). Ca poisoning greatly increases the energy barrier of dehydrogenation reaction of NH_3, which is not conducive to the formation of NH_2 precursor and the subsequent deNO_x reaction. In conclusion, the adsorption of Ca on the surface of \( \gamma\)-Fe_2O_3 catalyst and the inhibition of NH_3 adsorption and dehydrogenation by Ca atom are the main reasons for the decrease of the deNO_x activity of the \( \gamma\)-Fe_2O_3 catalyst. The selection of suitable dopants will be our subsequent attempt to reduce the toxicity of Ca to Fe-based catalysts.

Conclusions

In this study, we used a density functional theory (DFT) method to determine how Ca poisoning affects the deNO_x performance of the \( \gamma\)-Fe_2O_3 catalyst. For the \( \gamma\)-Fe_2O_3 (001) surface, NH_3 and NO molecules tend to be adsorbed on the Fe_1-top site by the N terminal. The adsorption products are coordinated ammonia and monodentate nitroso. O_2 molecule is easier to form monodentate adsorbed oxygen configuration on the surface of \( \gamma\)-Fe_2O_3 (001). The detailed effects of Ca poisoning on the \( \gamma\)-Fe_2O_3 catalyst surface are mainly three points: (1) Ca atom can be easily adsorbed on the surface of \( \gamma\)-Fe_2O_3 (001) and reduces the active sites on its surface. (2) Ca atom decreases the adsorption performance of NH_3 on the surface of \( \gamma\)-Fe_2O_3 (001), while slightly improving the NO and O_2 adsorption. In addition, Ca atom reacts with NO_x to form nitrate deposited on the surface of the catalyst. (3) Ca atom restrains the NH_3 activation and NH_2 formation, which is detrimental to the NH_3-SCR process.

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Data availability All data, models, and code generated or used during the study appear in the submitted article.

Declarations

Ethics approval and consent to participate All authors have given their consent to participate in the manuscript.

Consent to publish All authors have consented to publish the manuscript in the Journal of Environmental Science and Pollution Research.

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