Theoretical Study of the Catalytic Activity and Anti-SO₂ Poisoning of a MoO₃/V₂O₅ Selective Catalytic Reduction Catalyst

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ABSTRACT: In this paper, density functional theory has been applied to study the mechanism of anti-SO₂ poisoning and selective catalytic reduction (SCR) reaction on a MoO₃/V₂O₅ surface. According to the calculation results, the SO₂ molecule can be converted into SO₃ on V₂O₅(010) and further transformed into NH₄HSO₄, which poisons V₂O₅. If V₂O₅ and MoO₃ are combined with each other, charge separation of V₂O₅ and MoO₃, which are negatively and positively charged, respectively, occurs at the interface. In ammonium bisulfate liquid droplets on the MoO₃/V₂O₅ surface, NH₄⁺ tends to adhere to the V₂O₅(010) surface and can be removed through the SCR reaction and HSO₄⁻ tends to adhere to the MoO₃(100) surface and can be resolved into SO₃ and H₂O, which can be released into the gas phase. Thus, MoO₃/V₂O₅ materials are resistant to SO₂ poisoning. In the MoO₃/V₂O₅ material, Brønsted acid sites are easily formed on the negatively charged V₂O₅(010) surface; this reduces the energy barrier of the NH₃ dissociation step in the NH₃-SCR process and further improves the catalytic activity.

1. INTRODUCTION

NOₓ is one of the main air pollutants contributing to the formation of complex pollutants such as acid rain and town smog. Selective catalytic reduction (SCR) in which NH₃, as a reducing agent, reacts with NOₓ in the presence of O₂ to produce N₂ and H₂O is the technique most widely used to reduce NOₓ emitted from stationary and mobile sources.¹⁻⁴

At present, commercial NH₃-SCR catalysts employ V₂O₅-based catalysts supported on the anatase phase of TiO₂.¹⁻⁴ It is reported that the anatase phase of TiO₂ has poor mechanical strength and that high loading of V₂O₅ promotes the transformation of anatase to the rutile phase, which increases the material’s catalytic activity.¹ To overcome this shortcoming, SCR catalysts with high activity can be obtained by doping V₂O₅-based catalysts with other metal oxides; for example, the addition of WO₃ and MoO₃ can improve the stability and the catalytic activity of the catalysts.⁶⁻⁹ However, V₂O₅−WO₃−Ti catalysts lose their activity quickly when exposed to waste gases containing arsenic, whereas V₂O₅−MoO₃−TiO₂ catalysts can maintain their stability in the presence of arsenic.¹⁰⁻¹² Xu et al.¹³ showed that the addition of MoO₃ improved the sulfur resistance of the catalyst. The mechanism through which the addition of MoO₃ increases the activity of V₂O₅−TiO₂ has been investigated. Lietti et al.⁶,⁸,⁹ suggest that the interaction between vanadium species and the metal oxide after the addition of MoO₃ improves the catalytic activity. Qiu et al.¹⁴ consider that the introduction of MoO₃ enhances the adhesion between vanadium species and titanium dioxide.

The mechanism of the SCR reaction on vanadium-based catalysts supported by titanium dioxide has been widely studied. The first step in the commonly accepted SCR reaction pathway is the adsorption of ammonia on the catalytic surface. The adsorbed ammonia then reacts either with the adsorbed nitric oxide (Langmuir–Hinshelwood-type mechanism) or directly with the gaseous nitric oxide (Eley–Ridel-type mechanism) to form surface reaction intermediates, which are decomposed into nitrogen and hydrogen; the vanadium oxide sites are reduced. The reduced vanadium oxide surface is re-oxidized by oxygen molecules in the gas phase, returning the surface to its original state.¹⁵⁻¹⁸ However, it is still controversial whether the Lewis acid site or the Brønsted acid site is the active site of the reaction.²¹⁻²³ Topsoe et al.¹⁹,²⁰ determined the active sites on the surface of vanadium-based catalysts through in situ on-line Fourier transform infrared and found a direct relationship between the B acid site and the catalytic activity. It was considered that the catalytic activity was related to the ammonia species adsorbed on the B acid site. Vittadini et al.²⁴ studied the process of catalysis of NH₃ and NO by vanadium species on a titanium dioxide surface by density functional theory (DFT). It was found that NH₃...
participated in the SCR reaction and that the SCR reaction occurred even in the absence of a B acid site. Yao et al.22 also studied the SCR reaction process on a V2O5(001) surface using the DFT method. It is believed that NH4+ is more conducive to reducing NO than NH3. NH4+ participates directly in the formation of the active intermediate V2O5HH, but the formation of V2O5HH by V2O5H is very difficult. Zhu et al.23 investigated the reactivity of surface ammonia species at Lewis and Brønsted acid sites by time-resolved in situ infrared spectroscopy. It was found that although ammonia species at both the Brønsted and the Lewis acid sites participated in the SCR reaction and that surface NH4+ was more abundant, a small amount of NH3 showed a higher SCR catalyst specificity.

In the SCR reaction process, SO2 in flue gas is transformed into SO3, which can react with NH3 to generate ammonium bisulfate adhering to the surface of the catalyst, resulting in poisoning of the catalyst. The addition of MoO3 to the V2O5/TiO2 catalyst not only improves its catalytic activity but also delays the conversion of SO2 to SO3 and improves the sulfur resistance of the catalyst.8,9,24 For the SO2 oxidation process, Dunn et al.25 concluded that the conversion of SO2 was independent of the coverage of titanium dioxide by vanadium species. A subsequent study by Ji et al.26 showed that the Ti−O−V and V−O−V bonds in the catalyst did not play a key role in the oxidation of SO2. It was speculated that only one surface vanadium site was needed for SO2 oxidation and that the terminal V=O bond participated in SO2 oxidation.

The following uncertainties about the V2O5−MoO3/TiO2 catalyst remain: (1) although it is known that the addition of MoO3 to the V2O5/TiO2 catalyst improves its catalytic activity, the mechanism of this effect is not completely clear; (2) the involvement of Bronsted and Lewis acid sites in the SCR reaction is still controversial; (3) the idea that the oxidation process of SO2 to SO3 is related only to the terminal V=O bond of the V2O5 surface still lacks supporting evidence; and (4) the mechanism that results in sulfur resistance of the V−MoO3/TiO2 catalyst has not been thoroughly studied. In the current work, we studied the mechanism through which the addition of MoO3 improves the catalytic activity and sulfur resistance of V/Ti catalysts using the DFT method.
2. RESULTS AND DISCUSSION

2.1. Formation of NH₄HSO₄ - 2.1.1. SO₂ is Oxidized to SO₃ on the Surface of V₂O₅(010). The adsorption of SO₂ on three different sites of V₂O₅(010) (O_I, O_II, and O_III), as shown in Figure 1, was theoretically explored. The three oxygen sites on the surface of V₂O₅(010) can be classified into three types according to the number of connections with vanadium atoms: (1) O_I connected to a vanadium atom; (2) O_II with two vanadium atoms; and (3) O_III with three vanadium atoms.

The oxidation of SO₂ to SO₃ at the three oxygen sites was simulated. At the beginning, SO₂ is adsorbed by an oxygen atom on the V₂O₅(010) surface. The SO₂ then combines with the oxygen atom and is transformed into SO₃. SO₃ is desorbed according to the number of connections with vanadium atoms: (1) O_I connected to a vanadium atom; (2) O_II with two vanadium atoms; and (3) O_III with three vanadium atoms.

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2.1.2. Formation of NH₄HSO₄ on the V₂O₅(010) Surface. The process through which ammonium bisulfate is formed on the V₂O₅(010) surface is shown in Figure 4. The H₂O and NH₃ in the gas phase are first adsorbed on the surface of the catalyst. The H₂O is adsorbed on the Lewis site (on the top of the V site), and the NH₃ is adsorbed on the O_III site. The energy change in this process is ~9.69 eV. Subsequently, the adsorbed *OH₂ dissociates on the surface of V₂O₅ to form *NH₃ and *OH groups. The energy barrier of the above-mentioned process is ~1.49 eV. When SO₂ exists in the gas phase, the NH₃–O and VOH groups can further combine with SO₃ to form ammonium bisulfate.

2.2. Charge Transfer at the Interface between MoO₃ and V₂O₅. Work function is an important physical quantity reflecting the energy of electron transmission. In solid-state physics, it is defined as the minimum energy needed to transfer an electron from the interior of a solid to the surface of the object. The specific value of the work function is the difference between the vacuum level and the Fermi level on a solid surface. It is calculated as follows:

\[ \text{work function} = \text{vacuum level} - \text{Fermi level} \]  

We calculated the work functions of V₂O₅(010) and MoO₃(100) surfaces, as shown in Figure 5.

The work function of the V₂O₅(010) surface is 7.81 eV and that of the MoO₃(100) surface is 6.40 eV. The value of the surface work function of V₂O₅(010) is 1.14 eV larger than that of MoO₃(100). When V₂O₅ is in contact with MoO₃, the electrons on the MoO₃ surface spill over and flow from the MoO₃ surface to the V₂O₅ surface, resulting in the presence of negative charges on V₂O₅ and positive charges on MoO₃ close to the interface. Combining the charge separation, an internal electric field is set up at the same time.

**Table 1. Adsorption and Desorption Energies of Each Step in the Oxidation of SO₂ to SO₃ at Three Different Oxygen Sites (O_I, O_II, and O_III) on the V₂O₅(010) Surface**

| sites | \( \Delta E \) | \( \Delta E \) | \( \Delta E \) | \( \Delta E \) |
|-------|----------------|----------------|----------------|----------------|
|       | SO₂ads(1)    | SO₂ads(1)    | O₂ads         | SO₂ads(2)    | SO₂ads(2)    |
| 1V–O | −0.194        | −0.045        | 0.064         | −2.183        | 0.326         |
| 2V–O | 1.181         | 0.363         | −0.843        | −2.981        | 0.248         |
| 3V–O | 0.306         | 1.523         | −1.793        | −2.500        | 0.432         |

\( \text{SO₂ads}(1) \) and \( \text{SO₂ads}(1) \) are the initial processes of SO₂ adsorption and SO₂ desorption, respectively. \( \text{SO₂ads}(2) \) and \( \text{SO₂ads}(2) \) are the second SO₂ adsorption process and the second SO₂ desorption process, respectively.

The oxidation of SO₂ in the gas phase was also simulated; the barrier to the SO₂ reaction with oxygen in the gas phase is 2.99 eV (see Figure 3). The rate-controlling step barrier of SO₂ oxidation to SO₃ on the V₂O₅(010) surface is 0.54 eV. It can be concluded that SO₃, which participates in the formation of NH₄HSO₄ and causes catalyst poisoning, is produced on the surface of V₂O₅.

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When an NH4HSO4 liquid droplet covers the MoO3/V2O5 catalyst, NH4+ ions preferably move to the negatively charged V2O5 surface and HSO4− moves to the positively charged MoO3 surface under the internal electric field.

2.3. SCR Reaction from NH4+ on the V2O5(010) Surface.

The energy profile and optimized geometries for all elementary steps of the SCR process from NH4+ are shown in Figure 6. When the adsorbed NH4+ occupies the OI site of the charged V2O5(010) surface, it dissociates to adsorbed NH3 and a H atom (ii−iii). In this step, NH3 is adsorbed on the Lewis acid site and H is at an OI site. The adsorbed NH3 is activated to form NH2 intermediates, releasing a hydrogen atom, and the released H atom is combined with the OH group at the OI site to form adsorbed *OH (iii−iv); the energy change in this step is 1.17 eV. The energy barrier from ii to iv is 1.49 eV. The intermediate NH2 binds to NO in the gas phase to form a nitrosamine (NH2NO) intermediate (iv−v). Subsequently, NH2NO is decomposed into N2 and H2O (iii−vi). When a V−OH group is formed, the energy of NH3 dissociation to form NH2 and H at the Lewis site changes to −1.09 eV. However, the adsorption energy of NH3 at the Lewis acid site changes to 1.80 eV (vi−vii); this represents a great change compared with the energy required during the initial NH3 adsorption process (i−ii), and this step can thus be regarded as another rate-determining process. The H atom derived from the decomposition of NH3 can then combine with VOH to form VOH2. Hydrogen dioxide is desorbed into the gas phase (viii−ix). The remaining surfaces with oxygen vacancies can be oxidized, restoring the surface to its original state (vii−i). This completes a catalytic cycle.

For comparison, the energy profile and the optimized geometries for all elementary steps of the SCR process from NH3 on the pure V2O5(010) surface, the energy barrier of the reaction-controlling step is 2.27 eV. For NH4+ on the charged V2O5(010) surface (composited with MoO3), the energy barrier is 1.49 eV. The latter value is obviously smaller than the former, suggesting that the NH4+ ions could be eliminated.

NH4+ and protons also prefer to occupy the OI site, which is the catalytic site for oxidizing SO2 on the V2O5 surface. These two processes hinder the transformation of SO2 to SO3 and reduce SO2 poisoning.

The results of the calculation also show that the energy barrier of the SCR reaction is greatly reduced when the V4+=OH group is present. According to transition state theory, the reduction of the energy barrier will increase the reaction rate.28 The presence of NH4+ and V4+=O groups enhanced the reaction activity, making it equivalent to the activity that occurs on the SCR catalyst.
2.4. Decomposition of HSO$_4^-$ on the MoO$_3$(100) Surface. The perfect MoO$_3$(100) surface does not easily adsorb HSO$_4^-$ ions. However, oxygen vacancies can be produced on the surface, and the energy increment is approximately 0.99 eV. If oxygen vacancies exist, HSO$_4^-$ can easily be adsorbed on the MoO$_3$ surface. When HSO$_4^-$ is adsorbed on the oxygen vacancy positions of MoO$_3$, it can be further decomposed into SO$_3$ and an adsorbed OH$^*$ group on the surface (iii–iv). The proton in the OH$^*$ group migrates on the surface with an energy barrier of 0.98 eV; when an oxygen atom combines with two protons, H$_2$O with an oxygen vacancy forms on the surface (vi–vii). Through this process, which is shown in Figure 8, HSO$_4^-$ ions on the MoO$_3$(100) surface can be eliminated.

Figure 6. Mechanism of the SCR process from NH$_4^+$. (a) Mechanism of the standard NH$_3$-SCR reaction from NH$_4^+$ and (b) structures present at each state; the purple, red, pink, and blue circles represent V, O, H, and N atoms, respectively. (c) Energy profile of each step in the standard NH$_3$-SCR reaction (the energy barrier in the rate-determining step is marked in red).

Figure 7. Mechanism of the SCR process from NH$_3$. (a) Mechanism of the standard NH$_3$-SCR reaction from NH$_3$ and (b) structures present at each state; the purple, red, pink, and blue circles represent V, O, H, and N atoms, respectively. (c) Energy profile of each step in the standard NH$_3$-SCR reaction (the energy barrier at the rate-determining step is shown in red).

Figure 9 presents the catalytic process for SCR and the mechanism of anti-SO$_2$ poisoning. First, charge separation occurs on the MoO$_3$/V$_2$O$_5$ interface because of the difference in work functions; V$_2$O$_5$ is negatively charged and MoO$_3$ is positively charged around the interface. Second, NH$_4^+$ from ammonium bisulfate is preferably adsorbed on charged V$_2$O$_5$ and HSO$_4^-$ is preferably adsorbed on MoO$_3$. Third, in the SCR catalytic reaction, NH$_4^+$ and NO are transformed into H$_2$O and N$_2$ and HSO$_4^-$ is decomposed into SO$_3$ and H$_2$O.

3. CONCLUSIONS

Through DFT calculations, it has been clearly shown that SO$_2$ molecules can be catalyzed into SO$_3$ and, in the presence of NH$_3$ and H$_2$O, further transformed into NH$_4$HSO$_4$, which is
the cause of SO2 poisoning. When V2O5 is combined with MoO3, some electrons transfer from MoO3 to V2O5, creating a negatively charged V2O5 surface and positively charged MoO3. If an ammonium bisulfate liquid droplet adsorbs on the MoO3/V2O5 surface, NH4+ adheres to the terminal oxygen position on the V2O5(010) surface and can be eliminated in the subsequent SCR reaction. HSO4− adheres to the MoO3(100) surface and can be transformed into SO3 and H2O, which can be released from the MoO3 surface. In this way, NH4HSO4 on the MoO3/V2O5 surface can be continuously decomposed. In the MoO3/V2O5 material, the negatively charged V2O5(010) surface promotes the formation of Bronsted acid sites. The presence of Bronsted acid sites reduces the energy barrier of the NH3 dissociation step in the NH3-SCR process and thus improves the catalytic activity.

4. COMPUTATIONAL METHODOLOGY

The theoretical calculations are performed using the Vienna Ab initio Simulation Package (VASP). The projector augmented wave method was used to treat the ion–electron interaction. The electron exchange–correlation function of Perdew–Burke–Ernzerhof was adopted. For the V-3d states and Mo-4d states, the strong correlation energy was calculated with the LDA + U method, and the values of effective interactions (U−J) were set as 4.0 and 6.3 eV, respectively.

The V2O5(010) surface is the most thermodynamically stable single-crystal surface of V2O5, and its electronic properties are very similar to those of the bulk material. The V2O5(010) surface was constructed on the bulk crystal with Pmn21 symmetry, a 2 × 1 two-dimensional supercell (a = 7.188 Å, b = 11.468 Å) containing five layers was constructed, and the width of the vacuum layer was more than 20.0 Å. k-Point sampling used in the V2O5(010) model was 2 × 1 × 1.

The adsorption energy, E_ads, was calculated according to the expression

\[
E_{\text{ads}} = E_{\text{adsorbed species + surface}} - (E_{\text{adsorbed species}} + E_{\text{surface}})
\]

where E_ads is the adsorption energy, E_adsorbed species + surface is the energy of the given geometry containing the V2O5 surface and the adsorbing molecule, E_adsorbed species is the energy of the gas-

Figure 8. Reaction mechanism of HSO4− decomposition into SO3 on the MoO3(100) surface. (a) Optimized geometries of the reactants, transition states, intermediates, and products for all elementary steps in the reaction mechanism of HSO4− decomposition into SO3 on the MoO3(100) surface; the red, gray, pink, and yellow circles represent O, Mo, H, and S atoms, respectively. (b) Energy profile of each step in the reaction process.

Figure 9. Sketch showing the SCR catalytic process and the mechanism of anti-SO2 poisoning. (a) Charge separation process on the MoO3/V2O5 interface; (b) ionization process of ammonium bisulfate; and (c) SCR catalytic process.
phase mercury-containing species, and $E_{\text{surface}}$ is the energy of the V$_2$O$_5$ surface or the MoO$_3$ surface.

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Notes
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