Oxidation of NO\textsubscript{x} Using Hydrogen Peroxide Vapor over Mo/TiO\textsubscript{2}

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1. INTRODUCTION

In recent years, global air pollution has become very serious. Nitrogen oxides (NO\textsubscript{x}) produced by fuel combustion can cause acid rain, ozone depletion, and photochemical smog,\textsuperscript{1-3} causing serious harm to the human living environment. At present, the mainstream NO\textsubscript{x} emission technology is selective catalytic reduction (SCR), which uses ammonia as a reductant.\textsuperscript{4} However, SCR technology still has some disadvantages, such as harsh reaction temperature, high investment cost, and ammonia leakage problem.\textsuperscript{5} Therefore, it is urgent to develop a new environmental NO\textsubscript{x} removal technology.

As a kind of green oxidant, H\textsubscript{2}O\textsubscript{2} is of low cost and will not produce other by-products when decomposed. It can be activated into a hydroxyl radical (•OH) to promote the oxidation process.\textsuperscript{6,7} Until now, various iron-based materials have been developed to remove NO\textsubscript{x}, such as hematite,\textsuperscript{8} Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3},\textsuperscript{9} nano zero-valent iron,\textsuperscript{10} and Fe/TiO\textsubscript{2}.\textsuperscript{11} Fe\textsuperscript{2+} is recognized as the most active component in these materials. However, its poor cyclic oxidation performance limits its potential to maintain a high reactivity during long-term operation. Hao et al.\textsuperscript{12} had achieved 95% NO\textsubscript{x} removal by the co-oxidation of H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2}, but ozone leakage is still a serious problem. Guo et al.\textsuperscript{13} used ultraviolet light catalysis to treat NO and obtained a NO removal rate of 96.3%, but it is difficult to be operated in industry because of the complexity and cost of equipment. Therefore, it is urgent to develop a simple and efficient method to remove NO. Moreover, the intermediate product (NO\textsubscript{2}), which was not needed in previous studies, is usually ignored, and the intermediate product is more harmful to the environment.\textsuperscript{14}

Mo has been widely used because of its excellent water resistance and sulfur resistance. Chen\textsuperscript{15} used Fe\textsubscript{2}(MoO\textsubscript{4})\textsubscript{3} in a catalytic reaction for 100 h, but the overall removal efficiency needs to be improved. TiO\textsubscript{2} nanomaterials have many applications in water purification and the catalytic decomposition of pollutants. It has been proved that TiO\textsubscript{2} nanoparticles have a large specific surface area, good thermal stability, high catalytic activity, excellent cycling performance, and strong mechanical strength.\textsuperscript{16-19} Liu et al.\textsuperscript{20} have proved that the limited surface active sites on pure TiO\textsubscript{2} cannot efficiently activate H\textsubscript{2}O\textsubscript{2} into active groups. Mo/TiO\textsubscript{2} has excellent redox properties, which has attracted great interest in research, making it suitable for a variety of applications, such as photocatalytic activity, scarce semiconductors (diluted magnetic semiconductors), and battery-related applications.\textsuperscript{21-23} Many studies on the mechanism of action of Mo-doped TiO\textsubscript{2} and Mo-codoped impurities are performed.\textsuperscript{24-26} Therefore, the modification of TiO\textsubscript{2} in the oxidation of NO\textsubscript{x} using hydrogen peroxide is worth studying.
In this study, a Mo/TiO₂ catalyst is used to decompose gas-phase H₂O₂ and oxidize NO denitration at a low temperature range (80−160 °C) for the first time. A series of characterization techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy and energy-dispersive X-ray spectrometry (SEM−EDXS), X-ray photoelectron spectroscopy (XPS), Brunauer−Emmett−Teller (BET) measurement, and Fourier transform infrared (FTIR) spectroscopy, were used to investigate the relationship among the chemical properties, structural characteristics, and catalytic properties of the doped catalysts, and the stability of the reaction was studied.

2. RESULTS AND DISCUSSION

2.1. Catalytic Performance. The catalytic oxidation performance of xMo/TiO₂ (x = 0, 1, 2, 3, 4%) was tested at a low temperature range (80−160 °C). The overall removal efficiency of NOₓ depends not only on the oxidation rate of NO but also on the formation rate of unwanted by-products (NO₂). As can be seen from Figure 1a, the NO oxidation rate of all Mo-modified TiO₂ samples is more than 90%. As shown in Figure 1b, the total NOₓ removal rate of 2%Mo/TiO₂ is higher than 90% in the temperature range of 80−160 °C. The results show that the addition of molybdenum to titanium dioxide can significantly improve the removal efficiency of total NOₓ. With the increase of Mo loading from 1 to 2%, the total removal rate of nitrogen oxides increases significantly, and then with the increase of Mo loading, the removal rate of total NOₓ decreases instead. It can also be seen, from Figure 1c, that an excessive loading of Mo will reduce the selectivity of NO₂. The possible reason for this phenomenon is that the overloading of Mo will cover the active sites on TiO₂, thus reducing the oxidation ability of the catalyst, which is also consistent with our previous paper. The selectivity of NO₂ decreases with increasing temperature, which may be the reason why the unstable nitrous acid, formed by oxidation, was decomposed into NO₃ and O₂ at a high temperature. Mo on the surface of TiO₂ has a strong affinity for OH, and can spontaneously decompose H₂O₂ into stable *OH (eq 1), which is determined by the reaction rate of the entire oxidation process. The stabilization of *OH leads to the accumulation of these active substances, which further triggers the continuous oxidation reaction involving OH (eqs 2−4), which leads to the complete oxidation of NO. The impact of temperature exhibited by 2% Mo on the catalyst performance is the least, and the possible reason is that most nitric acid that is produced is stable and not easy to decompose at a high temperature.

\[
\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{H}^*\text{OH} + \text{M} \quad (1)
\]

\[
\text{H}^*\text{OH} + \text{NO} \rightarrow \text{HNO}_3 \quad (2)
\]

\[
\text{H}^*\text{OH} + \text{NO} \rightarrow \text{NO}_2 + \text{H}_2\text{O} \quad (3)
\]

\[
\text{H}^*\text{OH} + \text{HNO}_2 \rightarrow \text{HNO}_3 \quad (4)
\]
where M represents the active site located at the TiO₂ surface.

2.2. Characterization of xMo/TiO₂. In order to study the structural properties of the prepared samples, XRD tests were carried out. As shown in Figure 2, the surrounding broad peaks are assigned to the (101), (004), (200), (105), (201), (116), (220), and (215) planes of pure anatase at 2θ values of 25.3, 37.9, 48.1, 54.0, 55.0, 62.8, 68.9, 70.3, and 75.2°. No sharp Mo diffraction peak was detected, which may be because of the similar ionic radii of Mo⁶⁺ (0.59 Å) and Ti⁴⁺ (0.65 Å), which caused Mo⁶⁺ to disperse well on the titanium dioxide carrier or incorporated into the matrix of titanium dioxide species in an amorphous form. As shown in Table 1, the C lattice parameters of Mo-modified TiO₂ decrease with the increase of loading, indicating that slag-doped Mo can effectively change the crystal structure. All samples have a high specific surface area, and with the increase of Mo, the specific surface area shows a downward trend, which may be attributed to the following reasons: (1) the slag, doped with excessive Mo element, will cover the surface of the carrier and partially block its pores and (2) the density of the Mo element is higher than that of Ti; so, the addition of slag to Mo will lead to an increase of the overall density, and the unit of specific surface area is m²/g.

The morphology and structure of Mo/TiO₂ were further studied by high-resolution transmission electron microscopy (HRTEM) and SEM–energy-dispersive X-ray spectrometry (EDXS). As shown in Figure 3a, we can find clear lattice stripes of Mo-modified TiO₂ particles. The good resolution plane spacing with D = 0.35 nm is well matched with the anatase (101) plane and is consistent with the XRD analysis. A lattice stripe of 0.222 nm is also found in Figure 3a, which corresponds to the lattice plane of MoO₂ (041). These results show that ultrafine Mo are uniformly mixed with the slag on the surface of TiO₂. In the SEM–EDXS characterization, Ti, O, and Mo are highly dispersed throughout the catalyst material, which is in accordance with the expectation.

In order to clarify the surface electronic state and the interaction between the Mo and TiO₂ carriers, XPS experiments were carried out, and the results are shown in Figure 4. According to the Mo nuclear level spectrum in the diagram, there are only two oxidation state peaks at 232.5 ± 0.1 and 235.6 ± 0.1 eV, respectively, which prove the existence of Mo⁶⁺. Three different peaks are shown in the deconvolution of the O 1s XPS spectrum, which can be attributed to lattice oxygen (529.6 ± 0.1 eV, designated as O₆⁺), surface-adsorbed oxygen (531.4 ± 0.1 eV, designated as O₇⁺), and surface-adsorbed water (533.0 ± 0.1 eV). Oxygen molecules adsorbed on the surface are considered as electrophilic substances and are easy to form oxygen vacancies, which are used as active sites for absorbing and promoting the deep oxidation of NO. Therefore, in the process of catalytic oxidation, a higher O₆⁺/O₇⁺ ratio is beneficial for the removal of NO. In this study, the O₆⁺/O₇⁺ ratio of 2%Mo/TiO₂ is the highest, which proves that its surface produces the most oxygen vacancies, and its catalytic performance is the best in the experiment (Table 2).

2.3. Effect of Gas Hourly Space Velocity and Molar H₂O₂/NO. The effect of molar H₂O₂/NO on the catalytic performance was studied. The molar ratio of H₂O₂/NO is set to 2, 4, 6, 8, and 10. Figure 5 shows the relationship between the NO removal rate and molar H₂O₂/NO. As shown in Figure 5, when the molar ratio of H₂O₂ to NO increases from 2 to 8, the NO removal efficiency increases from 85.8 to 94%, and the growth rate decreases. When the H₂O₂ rate continues to increase, the total NO removal rate shows a downward trend. This can be explained by the following points: (1) the increase in the molar amount of H₂O₂ means that more H₂O₂ participates in the reaction, and H₂O₂ can promote the quenching of *OH¹¹ and (2) excessive H₂O₂ leads to an incomplete evaporation of H₂O₂ in the atomization device, which intensifies the quenching of *OH. In this study, the molar rate of H₂O₂ is 6:1 in the Mo/TiO₂/H₂O₂ system.

In practical application, the influence of gas hourly space velocity (GHSV) is the key parameter in the denitrification reactor. As shown in Figure 6, the effects of different GHSV values on NO conversion are analyzed. When GHSV decreased from 150,000 to 60,000 h⁻¹, the conversion of NO and NO₂ increased, and the selectivity of NO₂ decreased. This phenomenon can be explained by the decrease in contact time between NO and the catalyst with the increase of GHSV. Second, the growth of GHSV will reduce the contact between the catalyst and vaporized H₂O₂, resulting in a decrease in the conversion efficiency. When GHSV decreases again, the conversion rate shows a downward trend. This is because too much catalyst will accelerate the decomposition of nitrate on the catalyst surface,¹¹ and too much catalyst will also accelerate the removal of *OH. Considering the influence of

| Table 1. Lattice Parameters and Surface Area of TiO₂ Samples Modified by Mo |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| sample                    | a (Å)¹¹                      | b (Å)¹¹                      | c (Å)¹¹                      | V (Å³)¹¹                      | D (nm)¹¹                      | S_{BET} (m²/g)              |
| 1%Mo/TiO₂                  | 3.7852                      | 3.7852                      | 9.5139                      | 136.31                       | 11.6                          | 187.196                     |
| 2%Mo/TiO₂                  | 3.7845                      | 3.7845                      | 9.7143                      | 136.3                         | 14.5                          | 142.848                     |
| 3%Mo/TiO₂                  | 3.776                       | 3.776                       | 9.486                       | 135.25                       | 15.3                          | 107.604                     |
| 4%Mo/TiO₂                  | 3.785                       | 3.785                       | 9.514                       | 136.3                         | 16.9                          | 92.578                      |

¹¹The data error calculated by Jade6.0 is less than 6%.
the economy, a smaller GHSV will result in a larger reactor volume, which will increase the investment cost. Therefore, a GHSV of 60,000 h\(^{-1}\) is selected for the Mo/TiO\(_2\)/H\(_2\)O\(_2\) system.

2.4. Effect of SO\(_2\) on the Reaction. In order to observe the reaction under the actual flue gas conditions, different concentrations of SO\(_2\) were added, and their effects on the conversion of NO\(_x\) were measured. As shown in Figure 7, the effect of SO\(_2\) on NO\(_x\) oxidation is not significant.

With the increase of the SO\(_2\) concentration, the oxidation rate of NO decreased slightly, but the total NO\(_x\) conversion remained stable, and the NO\(_2\) selectivity decreased. The possible reasons are as follows: (1) there is a competitive relationship between SO\(_2\) and NO; so, the increase of SO\(_2\) will reduce the oxidation rate of NO; and (2) proper SO\(_2\) will hydrolyze to produce sulfite and bisulfite (eq 5). Moreover, sulfite and bisulfite will further react with NO\(_2\) to promote the migration of NO\(_2\) from the catalyst surface, thus reducing the production rate of NO\(_2\) and accelerating the oxidation of NO (eqs 6 and 7).\(^{37}\)

\[
\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^- \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-} \quad (5)
\]

\[
2\text{NO}_2 + \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow 3\text{H}^+ + 2\text{NO}_2^- + \text{SO}_4^{2-} \quad (6)
\]

\[
2\text{NO}_2 + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{NO}_2^- + \text{SO}_4^{2-} \quad (7)
\]
2.5. Stability Analysis of the Catalyst. Through the mixture of SO2 and NO (SO2 = 500 ppm and NO = 500 ppm), the stability of 2%Mo/TiO2 was tested for 24 h. As shown in Figure 8, it is found that the NO conversion rate has not changed significantly after long-term operation, which proves that Mo/TiO2 has good chemical stability. The fresh and used 2%Mo/TiO2 catalysts were characterized by XRD and FTIR spectroscopy. As shown in Figure 9a, compared with the fresh XRD peak spectrum, different XRD peaks are not seen in the used catalyst, and the XRD peak spectrum is not enhanced. As shown in Figure 9b, there is no significant difference in the FTIR spectra between the fresh and old catalysts. Among them, the wide absorption peak between 3000 and 3600 cm$^{-1}$ is the tensile vibration of the basic hydroxyl group. A weak entrainment of the OH bending vibration, corresponding to the chemisorption of water molecules by the hydroxide gene, occurs between 1615 and 1635 cm$^{-1}$. SO2 oxidation generates sulfate ions, which will be adsorbed on the surface of the catalyst to cover the active sites, thus deactivating the catalyst. However, the FTIR experiment and analysis showed that no characteristic peak of sulfate ions was detected on the surface of the used catalyst, which indicates that there is no sulfate on the surface of the catalyst or that the amount covered is very small, thus proving that the catalyst has excellent sulfur resistance and stability.

3. CONCLUSIONS

In a word, a Mo-modified TiO2 catalyst was prepared by the coprecipitation method, and it was used to thermally catalyze the decomposition of H2O2 molecules to oxidize NO, showing excellent catalytic activity. The 2% Mo/TiO2 sample has the highest out-of-stock performance, a high NOx removal efficiency (92.58%), and the best effect at a low temperature range (80–120 °C). It was found that the best reaction temperature is 80 °C, the best H2O2/NO molar ratio is 6/1, and the best GHSV is 60,000 h$^{-1}$. After a long-term reaction (24 h) with the mixture of SO2 and NO, the catalytic activity remained high, and the physical properties of the catalyst showed little change. The characterization results show that Mo particles with a +6 valence are uniformly dispersed on the TiO2 surface. The loading of Mo on TiO2 in an appropriate proportion can not only promote charge transfer but also promote the adsorption of H and activate H2O2, thus producing more *OH to remove NOx.

4. EXPERIMENTAL SECTION

4.1. Materials. Ti(SO4)2 ($\geq$96%), NH3H2O·H2O (30%, w/w), (NH4)6Mo7O24·4H2O (AR), NaOH (1.5 mol/L),
CaCl₂ (99.9%), and H₂O₂ (30%, w/v) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

4.2. Catalyst Synthesis. The TiO₂ catalyst modified by Mo used in this study was prepared by a conventional coprecipitation method, according to previous literature. Under vigorous agitation via intense stirring, (NH₄)₆Mo₇O₂₄·4H₂O and Ti(SO₄)₂ in certain stoichiometric amounts were added to the aqueous solution (100 mL), and the solution was continuously vigorously stirred at an ambient temperature for 0.5 h. Slowly, the ammonia water solution was dripped until the pH was equal to 10, without aging. At a constant temperature, a water bath (80 °C) was stirred for another hour. The bath was left to stand at room temperature for 2 h, and the mother liquor was vacuum-extracted and washed with deionized water three times to complete the filtration. The obtained solid was dried at 105 °C for 12 h and then calcined at 400 °C for 6 h. Finally, all the samples were ground and screened to 40−60 mesh for an activity test. The sample is expressed as xMo/TiO₂ (x represents the loaded molar concentration of Mo).

4.3. Experimental Apparatus and Procedure. The experiment on the catalytic oxidative absorption of NO was carried out in a fixed bed flue gas denitration reaction experimental system, as shown in Figure 10. The experiment consisted of four parts: a gas distribution section, a reaction section, an absorption section, and a measurement section. The gas distribution section consisted of three compressed gas cylinders [N₂, NO (2%), and SO₂ (2%)], three mass flow controllers, and an injection pump (Baoding Shenchen SPLab01). The compressed steel cylinder provided a certain concentration of NO and SO₂ and used N₂ as a carrier gas to the reaction area. The injector pump provided H₂O₂ (30%, w/v) solution, and the H₂O₂ solution was heated to 140 °C through a heating belt and temperature control device for evaporation. The reaction section consisted of a quartz tube reactor with a catalyst and a controllable electric heating furnace. The absorption section consisted of three washing cylinders, two of which were filled with NaOH solution (0.3 mol/L, 0.25 L), which was used to absorb the high valence nitrogen oxides after the reaction and, finally, connected to the drying device filled with anhydrous CaCl₂. The measurement section consisted of a flue gas analyzer (testo 340, Germany). The evaporated H₂O₂ solution (30 wt %) mixed with flue gas at a constant feed rate flowed into the catalytic zone (d = 10 mm, h = 1000 mm). The reacted gas was scrubbed in a bubbling reactor, equipped with NaOH solution (d = 10 mm, h = 500 mm), and then dried by CaCl₂ solid particles. Finally, the NO and NO₂ concentrations of the outlet gas were measured by the flue gas analyzer. The NO oxidation reactions were performed over a temperature range of 80−160 °C. Unless otherwise stated, the total gas flow of the reaction gas mixture in this experiment was kept at 2 L/min, and the NO concentration was calibrated at 500 ppm. Using a catalyst with
a bulk density of 2 mL, the corresponding reaction space velocity was 60,000 h⁻¹.

4.4. Characterization and Analytical Methods. The crystal phase and cell size of the samples were determined by a high-efficiency conventional powder X-ray diffractometer (PANalytical X’Pert Powder). The specific surface area and pore volume of the specified sample were analyzed by a specified surface area and pore size analyzer (Quadrasorb 2MP). A field emission transmission electron microscope (FEI Tecnai G2 F20) was used to observe and analyze the high-resolution surface topography at 200 kV, and elemental mapping was carried out on selected areas of the sample on an energy-dispersive X-ray spectrometer (Oxford Inca), attached to a scanning electron microscope. XPS measurements were recorded by an X-ray fluorescence spectrometer (ARL Perform’X). The spectra of the catalyst, before and after the reaction, were obtained by FTIR spectroscopy. In order to measure the accuracy, all samples were degassed in a vacuum at 150 °C for more than 12 h, before analysis.

4.5. Data Process. Three aspects of catalytic oxidation performance can be evaluated: nitric oxide oxidation, nitrogen dioxide selectivity, and total nitrogen oxide removal rate. The nitrogen removal index used is the average concentration of NO (ppm).

\[ \eta_{\text{NO}} = \frac{\int_{0}^{t_1} (\text{NO}_\text{in} - \text{NO}_\text{out}) \, dt}{\text{NO}_\text{in} \cdot T} \]  
\[ \eta_{\text{NO}_2} = \frac{\int_{0}^{t_1} \text{NO}_2 \text{out} \, dt}{\int_{0}^{t_1} (\text{NO}_\text{in} - \text{NO}_\text{out}) \, dt} \]  
\[ \eta_{\text{NO}} = \frac{\int_{0}^{t_1} (\text{NO}_\text{in} - \text{NO}_\text{out} - \text{NO}_2 \text{out}) \, dt}{\text{NO}_\text{in} \cdot T} \] 

where \( T \) is the reaction temperature, \( \eta_{\text{NO}} \) is the nitric oxide oxidation, \( \eta_{\text{NO}_2} \) is the nitrogen dioxide selectivity, \( \eta_{\text{NO}} \) is the total nitrogen oxide removal rate, \( \text{NO}_\text{in} \) is the inlet concentration of NO (ppm), and \( \text{NO}_\text{out} \) is the outlet concentration of NO (ppm).

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All authors contributed to the writing of the manuscript. All authors have approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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