TiO$_2$–SiO$_2$ supported MnWO$_x$ catalysts by liquid-phase deposition for low-temperature NH$_3$-SCR

Weizhe Lu, Hanfeng Lu and Zekai Zhang

Institute of Catalytic Reaction Engineering, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

NH$_3$-SCR is an environmentally important reaction for the abatement of NO$_x$ from different resources. MnO$_2$-based catalyst has attracted significant attention due to the excellent activity. In this paper, a series of MnWO$_x$/TiO$_2$–SiO$_2$ catalysts were prepared by liquid-phase deposition method. The catalysts were characterized by N$_2$ adsorption/desorption, XRD, TEM, XPS, FT-IR, H$_2$-TPR, TG and water adsorption capacity. The existence of SiO$_2$ improved the SO$_2$ and H$_2$O resistance of the MnWO$_x$/TiO$_2$–SiO$_2$ catalyst without decreasing the NH$_3$-SCR activity. Under the reaction conditions of 260°C and 60,000 ml$\text{g}_{\text{cata}}^{-1}$ h$^{-1}$ gas hourly space velocity (GHSV), the NO conversion was kept stable at about 95% for 140 min on stream. The excellent performance of MnWO$_x$/TiO$_2$–SiO$_2$ catalyst is considered to be originated from the texture properties and active species dispersion improvement by SiO$_2$ in the support and low-temperature preparation.

1. Introduction

Nitrogen oxides are one of the major pollutants that endanger the atmosphere air, which can cause severe environmental problems such as acid rain, smog and photochemical pollution. deNO$_x$ is a hot topic in the environmental fields in the past decades, and many researchers continue to be concerned till present. Comparing to the other routes, it is a desirable way to reduce NO$_x$ to harmless N$_2$. Selective catalytic reduction of NO$_x$ via NH$_3$ (NH$_3$-SCR) thereby has been widely studied and applied in the elimination of nitrogen oxides [1,2].

In general, NO$_x$ are mainly released from the combustion of fossil fuels at different stationary or mobile resources. The nature of the two types of exhaust gases is quite different. The catalysts are also evolved into two series, the transition metal oxide-based catalysts for the stationary resources, and the
zeolite-based catalysts for the mobile resources. V₂O₅-WO₃(MoO₃)/TiO₂ as the representative of the vanadium-based metal oxide catalyst has been commercialized and widely used in industry [3,4]. The working temperature window of V₂O₅-WO₃(MoO₃)/TiO₂ is mainly in the temperature range of 300–400°C, and it cannot completely remove NOₓ below 250°C. The working temperature window means a strict requirement for working conditions and high energy consumption [5]. Therefore, it attracts many researchers to find new catalyst systems that can operate at lower temperatures.

Among newly developed catalyst systems, Mn and Ce oxide-based catalysts have shown outstanding performance [6–11]. Especially, manganese-oxide-based catalysts can achieve very high NOₓ conversion even below 100°C temperature, which makes them a very competitive alternative NH₃-SCR catalysts system [12,13]. However, the main shortcoming of Mn-based catalysts is the poor resistance to the SO₂ in the exhaust gases. Therefore, Ce-based catalysts, especially Ce-W mixed oxides catalysts, attracted some more attention in the very recent years. At present, the commonly accepted catalyst for SO₂ poisoning is that a large amount of sulfate is formed, which blocks the catalyst pores and inactivates the active sites. Li’s and He’s groups have done a lot of research and made notable progress [14–17].

Meanwhile, Mn-based catalysts are still worthy to be studied as long as the sulfur resistance is improved. By investigation, it is found that tungsten may possess the ability. Tungsten has been added and helped for the V, Ce-based catalysts, and even for the NiWS catalyst in the hydrodesulfurization process [18,19]. Liu et al. first considered MnWO₄ as the main active phase and got high deNOₓ efficiency from 60 to 250°C [20]. Sun et al. then prepared a series of WₓMn₁₋ₓOᵧ catalysts via coprecipitation method [21]. W₀.₃₃Mn₀.₆₆Oₓ catalyst with amorphous or poorly crystalline Mn and W species showed the highest NH₃-SCR activity within a broad temperature range of 230–470°C. Our group also prepared the MnWTOₓ̵₂₅ catalyst with MnWO₄ crystal structure and obtained a high activity in the range of 200–400°C [22,23].

The deactivation of the NH₃-SCR catalyst mainly comes from two aspects, the poisoning caused by the reaction of SO₂ with the active components, and the coverage or blocking (coking) of the surface of the ammonium sulfate [24–26]. Owing to the viscosity of NH₄HSO₄ and (NH₄)₂SO₄, it is easy to bind to the catalyst and reduce the specific surface area. The formation of NH₄HSO₄ and (NH₄)₂SO₄ often needs water. If the surface has well-hydrophobic properties, it would be possible to reduce the water adsorption and thus decrease the formation of NH₄HSO₄ and (NH₄)₂SO₄; i.e. the sulfur resistance of the catalyst is expected to be improved by increasing the hydrophobicity of the catalyst surface [27,28].

In this work, a series of TiO₂–SiO₂-supported MnMOₓ catalysts were prepared by a liquid-phase deposition (LPD) method. The introduction of SiO₂ increases the specific surface area of the catalyst; moreover, probably by the reaction of manganese nitrate and ammonia tungstate to form MnWO₄, the catalysts could be prepared at relatively low temperature, which greatly improves the activity and N₂ selectivity of the MnWOₓ/TiO₂–SiO₂ catalyst as well as the SO₂ and H₂O resistance.

2. Experimental procedure

2.1. Catalyst preparation

MnWOₓ/TiO₂–SiO₂ catalysts were prepared by two main procedures. The first step is to prepare TiO₂–SiO₂ support by a sol–gel method. The method used TEOS (n-ethyl silicate) and TBOT (tetrabutyl titanate) as precursors. Taking 10% SiO₂–90% TiO₂ as an example, a suitable amount of TEOS (1.0 ml) was mixed in anhydrous ethanol, then a small amount of distilled water (about 2.0 ml) and several drops of 1 mol l⁻¹ HCl were added stirring for 30 min at room temperature to adjust pH = 2 and got solution A. Meanwhile, 5.0 ml of acetic acid was mixed with 49.0 ml anhydrous ethanol, then a small amount of distilled water (about 2.0 ml) and several drops of 1 mol l⁻¹ HCl were added to adjust pH < 3 and got solution B. Solutions A and B were then uniformly mixed by stirring to get solution C. Then 13.5 ml anhydrous ethanol and 13.5 ml TBOT were uniformly mixed to get solution D. Solution D was added into solution C at a rate of 3 ml min⁻¹ under vigorous stirring at room temperature. The resulting material was dried in an oven at 80°C for 12 h to obtain the TiO₂–SiO₂ dry gel. The gel was ground into powder to obtain the support.

Considering the dispersion of active components on the hydrophobic support, a modified liquid deposition method was used to load the MnWO₄ on the TiO₂–SiO₂. Manganese nitrate solution (50% Mn(NO₃)₂) and tungaline ((NH₄)₁₀W₁₂O₄₁·xH₂O) were used as precursors; 0.845 g (NH₄)₁₀W₁₂O₄₁·xH₂O and 2.386 g Mn(NO₃)₂ solution were dissolved with the same molar oxalic acid in deionized water. TiO₂–SiO₂ powder was added to the solution and the mixture was vigorous stirred...
for 1 h. Ammonia water (0.5 mol l\(^{-1}\)) was slowly added into the mixture to adjust the pH to 10 to achieve the precipitation of active species. The mixture was filtered, washed and the precipitate in the oven was dried at 110 °C for 12 h. At last, the sample was moved into the muffle and calcined at 200 °C for 2 h to obtain the target MnWO\(_x\)/TiO\(_2\)–SiO\(_2\) catalyst. The samples were labelled as Mn\(_x\)W\(_y\)O\(_x\)/TiO\(_2\)–SiO\(_2\)(n), where \(x\) and \(y\) are the molar ratio of Mn : W and \(n\) is the percentage of SiO\(_2\) to (SiO\(_2\) + TiO\(_2\)).

### 2.2. Catalyst characterization

\(\text{N}_2\) adsorption/desorption of the catalysts were measured by a Micromeritics 3Flex physical adsorption instrument. The samples were heated to 200 °C under vacuum pressure and kept for 10 h before measurement. Specific surface area was calculated using the BET method.

Crystal structure of the catalysts were detected by an ARL SCINTAG X'TRA instrument (Shimadzu.) using Cu Ka radiation in 2θ range of 10–80° with a step size of 0.02°.

H\(_2\) temperature-programmed reduction (H\(_2\)-TPR) was conducted on a chemical adsorption apparatus (Finetec Corp.). The samples were pretreated at 400 °C in Ar for 40 min. The TPR analysis was carried out in a reducing gas mixture (30 ml min\(^{-1}\)) consisting of 5% H\(_2\) and balance Ar from 60 to 800 °C at a rate of 10 °C min\(^{-1}\). TCD detector temperature was 60 °C.

X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos AXIS Ultra DLD clutches spectrophotometer. Excitation source was the monochromatic Al Ka radiation (\(h\nu = 1486.6\) eV). The power was 45 W. The working voltage was 15 kV. Scanning area was 300 × 700 μm. The data were corrected using the C1 s 284.8 eV as the standard.

Skeleton FT-IR spectra of the catalysts were recorded using BRUKER VERTEX70 FT-IR apparatus, with the sample in KBr pellets.

Morphologies of the catalysts were disclosed by a Philips-FEI company Tecnai G2F30 S-Twin type high-resolution transmission electron microscopy. The samples were solved in ethanol solution to get the dispersed particles. The accelerating voltage was 300 kV.

The water adsorption capacity of the catalysts was determined by the saturated water adsorption experiment. A total of 0.100 g of the sample was placed in an alumina crucible and heated from room temperature to 1000 °C at a rate of 20 °C min\(^{-1}\) in a 20% O\(_2\)/80% N\(_2\) atmosphere.

### 2.3. Catalytic activity tests

NH\(_3\)-SCR activity was tested in a fixed-bed quartz tube reactor (i.d. = 8 mm). The reaction conditions were as follows: 500 ppm of NO, 500 ppm of NH\(_3\), 5.0% O\(_2\) and N\(_2\) as balance, 10 vol% H\(_2\)O (when used), 100 ppm SO\(_2\) (when used). Total gas flow rate was about 500 ml min\(^{-1}\), and calculated gas hourly space velocity (GHSV) of 60 000 ml g\(_{\text{cata}}\) h\(^{-1}\). Outlet gases were measured by an online MODEL T200H/M nitrogen analyser and Thermo trace 1300 gas chromatography.

\(\text{NO conversion (X)}(\%)\) and \(\text{N}_2\) selectivity (\(S\)) were calculated by the following equations:

\[
X(\%) = \frac{\left[\text{NO}\right]_{\text{in}} - \left[\text{NO}\right]_{\text{out}}}{\left[\text{NO}\right]_{\text{in}}} \quad (2.1)
\]

and

\[
S(\%) = \frac{\left(\left[\text{NO}\right]_{\text{in}} + \left[\text{NH}_3\right]_{\text{in}}\right) - \left[\text{NO}_2\right]_{\text{out}} - 2\left[\text{N}_2\text{O}\right]_{\text{out}}}{\left[\text{NO}\right]_{\text{in}} + \left[\text{NH}_3\right]_{\text{in}}} \quad (2.2)
\]

### 3. Results and discussions

#### 3.1. NH\(_3\)-SCR activity of MnWO\(_x\)/TiO\(_2\)–SiO\(_2\) and effect of preparation conditions

Prior to this paper, the MnWO\(_x\)/TiO\(_2\) catalysts are mainly prepared by self-propagating high-temperature synthesis method (SHS) in our group, because the as-prepared samples possess very good properties such as narrow particle distribution and uniformly distributed MnWO\(_x\) species on the TiO\(_2\) support. However, it seems that the method is not very suitable for TiO\(_2\)–SiO\(_2\) support. The
sample temperature could rise to very high (greater than 1000°C) during the preparation process and affect the pore structure of the TiO2–SiO2 support.

Figure 1 shows that the activity of Mn2WOx/TiO2–SiO2(10) is somewhat worse than that of the Mn2WOx/TiO2 with the same SHS procedure. Therefore, a modified liquid deposition method is used to prepare the Mn2WOx/TiO2–SiO2 catalysts later. LPD is a method that through the reaction of the precursors salts solution forms a precipitate and deposit on the solid support pre-placed in the solution to realize the uniform loading of active components. It has been found that Mn(NO3)2 and (NH4)10W12O41 can not only react to produce a precipitation in the solution, but also form a MnWO4 structure in the precipitation [29], which is considered to be favourable for the activity of Mn2WOx/TiO2 catalysts. Here, the method is also adopted to prepare Mn2WOx/TiO2–SiO2. The sample exhibits rather high activity in NH3-SCR reaction. The NO conversion reaches 90% from 200°C to about 400°C, which is even broader than the results of the Mn2WOx/TiO2 by SHS method.

The preparation procedure has a clear influence on the activity of Mn2WOx/TiO2–SiO2 by LPD method. If the TiO2–SiO2 gel was calcined at 500°C before the LPD, the activity of the as-prepared catalyst would decrease. That is to say, the NO conversion only keeps above 90% in a narrow range of 200–230°C. It is because, after calcination, the pore structure of TiO2–SiO2 gel is decreased to some extent and the hydrophobicity increases, which is not favourable for the dispersion and deposition of active components. Nonetheless, the LPD method can effectively load MnWOx active species on the TiO2–SiO2 support and keep the activity of Mn2WOx/TiO2–SiO2 catalyst in the right preparation procedure and conditions.

Figure 2a shows the NH3-SCR activity and figure 2b shows the N2 selectivity of the MnWyOx/TiO2–SiO2 catalysts with different Mn : W ratios synthesized by LPD. It can be seen that the Mn : W ratio influences the temperature window of the MnWOx/TiO2–SiO2 catalysts. Taking 90% NO conversion as the criterion, the working temperature window of the MnWyOx/TiO2–SiO2 catalysts varies from 120 to 200°C, 120 to 300°C, 140 to 280°C, 200 to 340°C and 200 to 370°C when the Mn : W ratio decreases from 3 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 3, respectively. Taking Mn : W ratio of 1 : 1 as a dividing line, when the manganese content is rich, the catalyst has better activity at low temperatures and worse activity at high temperatures; while when the tungsten is rich, it is just in the opposite way. In general, the Mn2WOx/TiO2–SiO2 shows the widest working temperature window.

Comparing to activity, Mn : W ratio has a more pronounced effect on N2 selectivity of the catalyst. In figure 2b, over the MnWyOx/TiO2–SiO2 and MnWyOx/TiO2–SiO2, the N2 selectivity is almost unchanged with the temperature rising; while over the other samples, the N2 selectivity is decreased from about 100% to 87%, 82% and 75% when the Mn : W ratio increases from 1 : 1 to 3 : 1, respectively. The results indicate that Mn element is favourable for the low-temperature activity and W element is favourable for the N2 selectivity. It is desirable to maintain a certain manganese tungsten ratio for the MnWOx/TiO2–SiO2 catalyst to get a satisfying activity and N2 selectivity.

The support properties often can be adjusted by the composite variation and influence the catalyst properties. TiO2–SiO2 oxides with different SiO2 contents from 5% SiO2/95% TiO2 to 20% SiO2/80%
TiO₂, which are labelled as TiO₂–SiO₂(5), TiO₂–SiO₂(10) and TiO₂–SiO₂(20), are studied. Figure 3a shows the results of the activities of the samples in the NH₃-SCR reaction. Taking 90% NO conversion as criterion, the increase of SiO₂ content in the support does not change the working temperature window of Mn₂WOₓ/TiO₂–SiO₂ too much. All the low-temperature boundaries of the working temperature windows are around 170°C. When the SiO₂ content increases from 5% to 20%, it only makes the high-temperature boundary move a slight degree to the high-temperature direction, and slightly widens the working temperature window. The working temperature windows of Mn₂WOₓ/TiO₂–SiO₂(10) and Mn₂WOₓ/TiO₂–SiO₂(20) are the same as 170–370°C.

The addition of SiO₂ also has a positive effect on the N₂ selectivity of the catalyst, as shown in figure 3b. It can be found that N₂ selectivity on the Mn₂WOₓ/TiO₂ (without SiO₂) catalyst at 50°C began to decrease rapidly with the increase of temperature. Nonetheless, the N₂ selectivity can be maintained at above 90% on all the Mn₂WOₓ/TiO₂–SiO₂ samples. Further, as the SiO₂ content increases, N₂ selectivity decreases slowly, and it decreases the slowest on the Mn₂WOₓ/TiO₂–SiO₂(20) sample.

### 3.2. The resistance of MnWOₓ/TiO₂–SiO₂ to H₂O and SO₂

As is known, the flue gas usually contains SO₂ and water vapour, which often affects the NH₃-SCR catalyst performance. It is the primary reason that the Mn₂WOₓ/TiO₂ catalyst is modified by SiO₂ in this paper. Figure 4 shows the NH₃-SCR results of Mn₂WOₓ/TiO₂–SiO₂ catalysts with different SiO₂ content in 100 ppm SO₂ at different reaction temperature. The SO₂ is introduced after 60 min of reaction time on stream.

It can be seen that SiO₂ has a significant effect on the sulfur resistance of the Mn₂WOₓ/TiO₂–SiO₂ catalyst. Taking the introduction time of SO₂ flow (60 min) as the initial point, for the Mn₂WOₓ/TiO₂ catalyst, the NO conversion begins to decrease after 90 min (total 150 min time on stream) reaction after the introduction of SO₂ flow. It decreases with a slow rate till 240 min (total 300 min), and then...
Figure 4. NH₃-SCR activity of Mn₂WO₆/TiO₂–SiO₂ in 100 ppm SO₂.

Figure 5. NH₃-SCR activity of Mn₂WO₆/TiO₂–SiO₂(5) and Mn₂WO₆/TiO₂–SiO₂(10) at 260°C in the presence of H₂O, SO₂ and SO₂ + H₂O.

...decreases with a significant rate to 55% at 420 min (total 480 min), where SO₂ is switched off. The NO conversion then rises back to about 65% in SO₂-free flow after 120 min (total 600 min on stream). The performance of Mn₂WO₆/TiO₂–SiO₂(5) was similar to that of Mn₂WO₆/TiO₂ catalyst before 240 min, but the NO conversion decreased significantly slower than the Mn₂WO₆/TiO₂ catalyst. The NO conversion is still close to 80% at 420 min, and after SO₂ switches off for 120 min, it rises back to close to 90% again. For the catalyst Mn₂WO₆/TiO₂–SiO₂(10), the NO conversion decreases with a rather slow rate after 30 min of SO₂ flow introduction in a linear style till 300 min, where the NO conversion is kept at about 80%. In the remaining time, no significant change is observed even though the SO₂ is switched off. Finally, for the catalyst Mn₂WO₆/TiO₂–SiO₂(20), the NO conversion decreases clearly in a different way from other samples. A number of stable platforms appeared on the profile, mainly in the range of 160–220 min, 260–300 min and 330–420 min total time on stream. When the SO₂ is switched off, the NO conversion can rise back to about 70% after 120 min. The results show that the appropriate amount of SiO₂ is beneficial to improve the sulfur resistance of the Mn₂WO₆/TiO₂–SiO₂ catalyst.

To further evaluate the effect, the performance of Mn₂WO₆/TiO₂–SiO₂(10) is then tested under 230°C and 200°C. However, the results in figure 4b are not very good. At 230°C, NO conversion has dropped below 50% after 420 min on stream; and at 200°C, NO conversion only is left no more than 20%. It means that the effect of SiO₂ is still limited and the catalyst needs to be more improved in the future.

Next, the activity of Mn₂WO₆/TiO₂–SiO₂(5) and Mn₂WO₆/TiO₂–SiO₂(10) at 260°C in the presence of 10% H₂O and SO₂ + H₂O together are investigated in figure 5. Both of the NO conversions can maintain above 95% in the presence of 10% H₂O. After the H₂O is switched off, the activity of the catalyst can be fully restored in a short time, indicating that the catalyst has good resistance to H₂O. In the 10 vol% H₂O and 100 ppm SO₂ atmosphere, the NO conversion profile on the Mn₂WO₆/TiO₂–SiO₂(5) is similar with that in the 100 ppm SO₂ flow, while its decrease degree is a little slight. The NO conversion is kept above 80% at 480 min. When H₂O and SO₂ are stopped, NO conversion rate rises rapidly. As for the Mn₂WO₆/TiO₂–SiO₂(10), the NO conversion quickly decreases to about...
and keeps at that level till 480 min. When the H2O and SO2 is switched off, it also rises back to about 90% in a short time. That is to say, both of the samples show good resistance to the H2O and SO2.

### 3.3. Catalysts characterization

Table 1 lists some texture properties such as the specific surface area, the average pore size and pore volume of the TiO2–SiO2 supports and the Mn2WOx/TiO2–SiO2 catalysts prepared by sol–gel method and LPD. It can be found that the addition of SiO2 clearly increases the specific surface area of TiO2–SiO2 gels comparing to TiO2. With the increase of SiO2 amount, the specific surface area of TiO2–SiO2(5), TiO2–SiO2(10) and TiO2–SiO2(20) increases from 263.9 and 283.5 to 332.6 m² g⁻¹; the pore volume increases from 0.145 and 0.158 to 0.213 cm³ g⁻¹, respectively. While the average pore size is kept at about 2.2 nm, only TiO2–SiO2(20) is increased to 2.6 nm. When the active species are loaded on the TiO2–SiO2 support, all the specific surface areas and pore volumes of Mn2WOx/TiO2–SiO2 catalysts are decreased, while the average pore sizes are increased. The Mn2WOx/TiO2–SiO2(5) catalyst can be found to have the best pore structure and keep the largest specific surface area of 235.9 m² g⁻¹, the average pore diameter of 2.9 nm and pore volume of 0.170 cm³ g⁻¹.

Table 2 lists their texture properties after the NH3-SCR reaction with/without H2O and SO2 flow.

80% and keeps at that level till 480 min. When the H2O and SO2 is switched off, it also rises back to about 90% in a short time. That is to say, both of the samples show good resistance to the H2O and SO2.

### Table 1. The texture properties of different catalysts and supports before reaction.

| samples                  | BET surface area (m² g⁻¹) | average pore diameter (nm) | pore volume (cm³ g⁻¹) |
|--------------------------|---------------------------|----------------------------|----------------------|
| Mn2WOx/TiO2–SiO2(20)     | 219.5                     | 2.7                        | 0.150                |
| Mn2WOx/TiO2–SiO2(10)     | 219.6                     | 2.6                        | 0.142                |
| Mn2WOx/TiO2–SiO2(5)      | 235.9                     | 2.9                        | 0.170                |
| Mn2WOx/TiO2              | 184.1                     | 2.9                        | 0.135                |
| TiO2–SiO2(20)            | 332.6                     | 2.6                        | 0.213                |
| TiO2–SiO2(10)            | 283.5                     | 2.2                        | 0.158                |
| TiO2–SiO2(5)             | 263.9                     | 2.2                        | 0.145                |
| TiO2                     | 215.7                     | 2.2                        | 0.120                |

### Table 2. The texture properties of different catalysts after reactions.

| samples                  | BET surface area (m² g⁻¹) | average pore diameter (nm) | pore volume (cm³ g⁻¹) |
|--------------------------|---------------------------|----------------------------|----------------------|
| Mn2WOx/TiO2–SiO2(20)–SO2 | 147.7                     | 2.8                        | 0.104                |
| Mn2WOx/TiO2–SiO2(20)–H2O | 208.7                     | 2.7                        | 0.143                |
| Mn2WOx/TiO2–SiO2(20)–SO2+H2O | 140.5                      | 2.8                        | 0.099                |
| Mn2WOx/TiO2–SiO2(10)–SO2 | 177.2                     | 2.7                        | 0.120                |
| Mn2WOx/TiO2–SiO2(10)–H2O | 210.2                     | 2.6                        | 0.136                |
| Mn2WOx/TiO2–SiO2(10)–SO2+H2O | 167.8                      | 2.6                        | 0.109                |
| Mn2WOx/TiO2–SiO2(5)–SO2 | 187.9                     | 2.7                        | 0.129                |
| Mn2WOx/TiO2–SiO2(5)–H2O | 221.4                     | 2.9                        | 0.161                |
| Mn2WOx/TiO2–SiO2(5)–SO2+H2O | 168.6                      | 2.8                        | 0.118                |
| Mn2WOx/TiO2–SO2          | 125.2                     | 3.1                        | 0.096                |
| Mn2WOx/TiO2–H2O          | 174.3                     | 2.9                        | 0.124                |
| Mn2WOx/TiO2–SO2+H2O      | 116.5                     | 3.1                        | 0.087                |

The texture properties of the heterogenous catalyst are often changed after the reaction. To investigate the properties of Mn2WOx/TiO2–SiO2 catalysts before and after the NH3-SCR reaction in the different atmospheres, table 2 lists their texture properties after the NH3-SCR reaction with/without H2O and SO2 flow.
The presence of water has little effect on the texture properties of the catalysts. All the average pore sizes do not change after reaction, and the specific surface area of the catalysts decreases about 10 m² g⁻¹. SO₂ significantly affects the nature of the catalysts. All the specific surface area and pore volumes of the catalysts after the reaction are largely reduced. The largest decrement is from Mn₂WO₄/TiO₂–SiO₂(20). The specific surface area decreases 71.8 m² g⁻¹, and the pore volume decreases 0.046 cm³ g⁻¹. The second is the Mn₂WO₄/TiO₂, 67.3 m² g⁻¹ and 0.048 cm³ g⁻¹. Mn₂WO₄/TiO₂–SiO₂(10) and Mn₂WO₄/TiO₂–SiO₂(5) show somewhat better resistance to SO₂. Their specific surface areas only decrease 42.4 and 48 m² g⁻¹. Especially, the pore volume of Mn₂WO₄/TiO₂–SiO₂(10) only decreases 0.022 cm³ g⁻¹. The average pore size of Mn₂WO₄/TiO₂–SiO₂(5) sample is the only one enlarged after the reaction. Coexistence of water and SO₂ does not show a synergistic effect on the nature of the catalysts. The change in the values is close to the sum of the influence of the two compounds.

Figure 6 shows the XRD patterns of Mn₂WO₄/TiO₂–SiO₂ catalysts.
uniform and small, but it may also mean that the resulting catalysts are predominantly the amorphous species.

Figure 7 then exhibits the morphologies of the catalysts by TEM. From the images, on the surface of the silicon-free Mn$_2$WO$_x$/TiO$_2$, there are clear crystal lattice fringes, which can be identified and attributed to the different crystal faces of the active species or the supports. The 0.345 nm lattice spacing is from (101) face of TiO$_2$; 0.240 nm and 0.366 nm spacing can be attributed with (200) and (011) face of MnWO$_4$ crystal. It is similar to our previous results obtained by SHS method [22]. The

Figure 7. TEM images of the Mn$_2$WO$_x$/TiO$_2$ – SiO$_2$ catalysts. (a,b) Mn$_2$WO$_x$/TiO$_2$, (c,d) Mn$_2$WO$_x$/TiO$_2$ – SiO$_2$(S), (e,f) Mn$_2$WO$_x$/TiO$_2$ – SiO$_2$(10), (g,h) Mn$_2$WO$_x$/TiO$_2$ – SiO$_2$(20).
results confirmed that the reaction to form manganese tungstate has occurred in the solution. The sample has well crystallinity with a uniform particles size distribution. Meanwhile, for the silicon-containing samples, the particles are also relatively small. But the lattice fringes are not very clear due to the high contents of the mixed crystal composition, which means that the SiO$_2$ affects the crystallinity of the MnWO$_x$ active species.

Figure 8 shows the H$_2$-TPR profiles of Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts.

Figure 9. O$_1$ s (a) and Mn 2p (b) XPS spectra of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts.
strength increment of the peak at the middle temperature illustrates that more TiO₂ can be reduced. The TiO₂ crystal structure might be broken and more amorphous or isolated species have been formed.  

In order to investigate the valence state of the Mn species and O species, XPS characterization was performed for the samples. Figure 9a shows the O₁ s spectra of Mn₂WOₓ/TiO₂, Mn₂WOₓ/TiO₂–SiO₂(5), Mn₂WOₓ/TiO₂–SiO₂(10) and Mn₂WOₓ/TiO₂–SiO₂(20), and table 3 lists the quantitative results via Gauss deconvolution method. After deconvolution, three sub-bands can be found on the spectra. As previous reports, the sub-bands around 529.7 eV can be attributed to the lattice oxygen (denoted as O_b); the sub-bands around 531.1 eV to surface absorbed oxygen (denoted as O_a) such as O₂ and O₂⁻, and the sub-band around 533.2 eV can be assigned to chemisorbed water (denoted as O_a') [17,33]. With the SiO₂ introduction increases, the peak of O_b decreases and the peak of O_a and O_a' increases gradually. As the O_a is usually regarded as more reactive in redox reactions due to its higher mobility than lattice oxygen, the percentages of O_a, O_b and O_a' are often viewed as an indicator for the redox ability of the catalyst. From table 3, the O_a' per cent increases gradually from 18.32% of the Mn₂WOₓ/TiO₂ to 22.20% of Mn₂WOₓ/TiO₂–SiO₂(20). Combining the results of XRD and TEM, it may infer that the addition of SiO₂ decreases the crystallinity of the active species, increases the dispersion, and forms more surface active sites. Some reports mentioned that the sub-band around 529.7 eV could be attributed to Ti–O–Ti bonds; the sub-band around 532.1 eV to Si–O–Ti cross-linking bonds, and the sub-band around 533.2 eV to Si–O–Si bonds [34,35]. When the SiO₂ introduction increases, the peak of Ti–O–Ti bonds decreases and the peak of Si–O–Ti cross-linking bonds and Si–O–Si bonds increases gradually.

Figure 9b then shows the Mn 2p XPS spectra of the four samples and table 4 lists the quantitative results. Similarly, three sub-bands belonging to Mn³⁺ at 640.6–641.4 eV, Mn⁴⁺ at 641.9–642.3 eV and Mn²⁺ at 643.4–644.5 eV can be found on the spectra. According to the quantitative analysis, the Mn species with different valence states does not change clearly, and the average valence state does not change, which may indicate that the SiO₂ only improves the dispersion of the active species, and has not much interaction effect with the active species after loading.

At the same time, O_a' increment means that the introduction of SiO₂ increases the adsorption of water on the Mn₂WOₓ/TiO₂–SiO₂. Thus, it seems that the hydrophobicity of Mn₂WOₓ/TiO₂–SiO₂ is decreased, which shall be not favourable for the water resistance and the activity. While the above activity experiments have demonstrated that the water resistance of the catalyst is enhanced, to explain the phenomenon, the water adsorption ability of the catalysts are measured under different temperatures. The results are listed in table 5. From the results, the water adsorption capacity of the Mn₂WOₓ/TiO₂–SiO₂ samples are lower than the Mn₂WOₓ/TiO₂ at room temperature (RT) and decreased with the SiO₂ content. Further, the difference is more pronounced at high temperature (100°C).

| samples                  | O_b (BE eV) | O_b Per. (%) | O_a (BE eV) | O_a Per. (%) | O_a' (BE eV) | O_a' Per. (%) |
|--------------------------|-------------|--------------|-------------|--------------|--------------|---------------|
| Mn₂WOₓ/TiO₂              | 529.7       | 81.67        | 531.0       | 18.32        | 532.6        | 0             |
| Mn₂WOₓ/TiO₂–SiO₂(5)      | 529.7       | 78.40        | 531.0       | 19.47        | 532.6        | 2.13          |
| Mn₂WOₓ/TiO₂–SiO₂(10)     | 529.7       | 74.82        | 531.1       | 21.84        | 532.6        | 3.34          |
| Mn₂WOₓ/TiO₂–SiO₂(20)     | 529.9       | 72.60        | 531.1       | 22.20        | 532.4        | 5.21          |

| samples                  | Mn⁴⁺ (BE eV) | Mn⁴⁺ Per. (%) | Mn³⁺ (BE eV) | Mn³⁺ Per. (%) | Mn²⁺ (BE eV) | Mn²⁺ Per. (%) | Average valence |
|--------------------------|-------------|--------------|-------------|--------------|--------------|--------------|----------------|
| Mn₂WOₓ/TiO₂              | 642.2       | 13.33        | 640.8       | 30.55        | 643.4        | 56.11        | 2.6            |
| Mn₂WOₓ/TiO₂–SiO₂(5)      | 642.3       | 15.86        | 640.8       | 30.24        | 644.5        | 53.89        | 2.6            |
| Mn₂WOₓ/TiO₂–SiO₂(10)     | 642.5       | 14.68        | 641.0       | 31.42        | 644.5        | 53.89        | 2.6            |
| Mn₂WOₓ/TiO₂–SiO₂(20)     | 642.6       | 15.08        | 640.9       | 32.89        | 643.5        | 51.93        | 2.6            |
The weak water adsorption capacity of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts may come from the formation of silicon hydroxyl. The skeleton FT-IR of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts is then recorded and the results are shown in figure 10. It can be found that the hydroxyl vibration peaks at 1502 cm$^{-1}$ are significantly changed after introduction of SiO$_2$. For the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(20), it has changed from the shoulder peak to the independent peak, corresponding to its higher water adsorption. Meanwhile, the peak is weakened for the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(5) and the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(10) and their water adsorption content are somewhat lower too. Thus, the appropriate SiO$_2$ content can reduce the amount of hydroxyl groups on the catalyst surface, and the excessive SiO$_2$ increases the amount of hydroxyl groups on the catalyst surface.

### 3.4. Discussions

As mentioned earlier, this paper is intended to indirectly improve the SO$_2$ resistance of the MnWO$_x$/TiO$_2$ catalyst by increasing its hydrophobicity. According to the activity tests, the SO$_2$ and water resistance of the MnWO$_x$/TiO$_2$–SiO$_2$ catalyst can be really improved under the premise that the NH$_3$-SCR activity is maintained. The NO conversion is no longer decreased as soon as the catalyst contacts SO$_2$, but it is maintained for some time on stream and then decreased slowly. Meanwhile, the water adsorption test shows that the water capacity of the catalyst decreases after SiO$_2$ introduction.

However, it is a little hasty to make this assertion, as SiO$_2$ introduction also changes some other properties of the catalyst. The specific surface area and pore volume of the MnWO$_x$/TiO$_2$–SiO$_2$ catalysts is clearly larger than the MnWO$_x$/TiO$_2$. The decreasing degree of the specific surface area and pore volume of the MnWO$_x$/TiO$_2$–SiO$_2$ catalysts after reaction is also lighter than the MnWO$_x$/TiO$_2$. Therefore, TG analysis has been performed after reaction and the results are displayed in Table 5.

#### Table 5. The hydrophobicity of catalysts under different temperature.

| samples           | dry basis (g) | saturated with water at RT (g) | saturated with water at 100°C (g) | water adsorption capacity at RT (g g$^{-1}$) | water adsorption capacity at 100°C (g g$^{-1}$) |
|-------------------|---------------|-------------------------------|----------------------------------|---------------------------------------------|---------------------------------------------|
| Mn$_2$WO$_x$/TiO$_2$ | 0.5408        | 0.6081                        | 0.5772                           | 0.1244                                      | 0.0673                                      |
| Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(5) | 0.5129        | 0.5755                        | 0.5426                           | 0.1221                                      | 0.0579                                      |
| Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(10) | 0.4928        | 0.5450                        | 0.5143                           | 0.1059                                      | 0.0436                                      |
| Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(20) | 0.6055        | 0.6650                        | 0.6262                           | 0.0983                                      | 0.0342                                      |

The weak water adsorption capacity of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts may come from the formation of silicon hydroxyl. The skeleton FT-IR of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts is then recorded and the results are shown in figure 10. It can be found that the hydroxyl vibration peaks at 1502 cm$^{-1}$ are significantly changed after introduction of SiO$_2$. For the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(20), it has changed from the shoulder peak to the independent peak, corresponding to its higher water adsorption. Meanwhile, the peak is weakened for the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(5) and the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(10) and their water adsorption content are somewhat lower too. Thus, the appropriate SiO$_2$ content can reduce the amount of hydroxyl groups on the catalyst surface, and the excessive SiO$_2$ increases the amount of hydroxyl groups on the catalyst surface.
From the TG results, the water adsorption capacity of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$ catalysts is clearly lower than that of the Mn$_2$WO$_x$/TiO$_2$. The weight loss of the Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(5) and Mn$_2$WO$_x$/TiO$_2$–SiO$_2$(10) catalysts in higher temperature are also significantly lower than that of the Mn$_2$WO$_x$/TiO$_2$. It may be helpful to prove that both the coke behaviour and hydrophobicity are restrained after SiO$_2$ doping.

4. Conclusion

A series of TiO$_2$–SiO$_2$ mixed oxides supports were prepared by sol–gel method, and the MnWO$_x$ active components were loaded on the supports by liquid deposition method to form a series of MnWO$_x$/TiO$_2$–SiO$_2$ catalysts. Owing to the reaction of manganese nitrate and ammonia tungstate to form MnWO$_4$, the catalysts could be prepared at low temperature. The introduction of SiO$_2$ in the TiO$_2$ support increases the N$_2$ selectivity of the MnWO$_x$/TiO$_2$ catalyst without decreasing the NH$_3$-SCR activity. Meanwhile, with appropriate SiO$_2$ (5% and 10% percentage of TiO$_2$), the sulfur resistance of MnWO$_x$/TiO$_2$–SiO$_2$ is clearly improved, the decreasing rate and degree of NO conversion are both slowed down and retarded. By a series of BET, XRD and TEM characterization, it can be inferred that the texture properties of MnWO$_x$/TiO$_2$–SiO$_2$ are modified and the dispersion of MnWO$_x$ species is improved, which is beneficial for the NH$_3$-SCR activity. Skeleton FT-IR, water adsorption capacity and XPS show that SiO$_2$ introduction decreases the water adsorption capacity especially at the high temperatures, which might be favourable for the water and sulfur resistance of the catalyst.

Data accessibility. Our data are available from Dryad Digital Repository: doi:10.5061/dryad.74pj317 [36].

Authors’ contributions. W.Z.L. carried out the molecular laboratory work, participated in data analysis, carried out sequence alignments; Z.K.Z. participated in the design of the study and drafted the manuscript; H.F.L. conceived of the study, designed the study, coordinated the study and helped draft the manuscript. All authors gave final approval for publication.

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