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Different treatment atmospheres, including oxidizing, inert and reducing conditions, all affected vanadium species and deactivated the V/TiO₂ catalyst to some extent in NH₃-SCR. The amount of active polymeric vanadyl species decreased in the following sequence: V/Ti > V/Ti-O₂ > V/Ti-N₂ > V/Ti-NH₃.

Thermal power plants and automobiles emit large amounts of nitrogen oxides (NO_x), causing ozone depletion, acid rain, photochemical smog, and haze formation.^{1–3} The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is the most effective technology for NO_x abatement, and vanadia-based catalysts (V₂O₅-WO₃/TiO₂ or V₂O₅-MoO₃/TiO₂) have been commercialized for many years due to their high catalytic activity and selectivity and superior resistance to SO₂.^{4–6} However, vanadia-based catalysts exhibit some inevitable disadvantages, such as high SO₂ oxidation activity at high temperatures and a narrow operating temperature window.^{7,8} Therefore, much attention has been paid to improving vanadia-based catalysts.

Most recently, various strategies have been employed to enhance the catalytic performance of vanadia-based NH₃-SCR catalysts.^{9–14} Different preparation methods, such as electrodeposition¹⁵ and sol-gel methods,¹⁶ have been found to influence the NH₃-SCR activity of vanadia-based catalysts. Synthesis conditions can also significantly affect the structure, physico-chemical properties and activity of these catalysts. For example, a VWTi catalyst calcined in an atmosphere

Effect of treatment atmosphere on the vanadium species of V/TiO₂ catalysts for the selective catalytic reduction of NO_x with NH₃†

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of 15% O₂ in N₂ showed higher SCR activity than catalysts calcined in pure N₂, air or pure O₂.¹⁷ V₂O₅/TNTs prepared using different vanadium precursors (NH₄VO₃ and VOSO₄) exhibited different deNO_x performances.¹⁸ However, to the best of our knowledge, the influence of aftertreatment under different atmospheres on the V₂O₅/TiO₂ catalysts has not been studied. The state of the vanadium species and NH₃-SCR activity of such catalysts as a function of preparation parameters needs to be investigated thoroughly.

In this study, V/TiO₂ catalysts were synthesized by a conventional impregnation method and then treated in different atmospheres. Although the catalysts were calcined in static air, aftertreatment in an oxidizing atmosphere (10% O₂/N₂, between the oxygen contents of air and N₂) might influence the catalyst due to the effects of the flowing atmosphere and steady oxygen concentration. Therefore, treatment in an oxidizing atmosphere was conducted in addition to inert (N₂) and reducing conditions (0.1% NH₃/N₂). The effect of treatment in different atmospheres on the vanadium species and catalytic activity was investigated.

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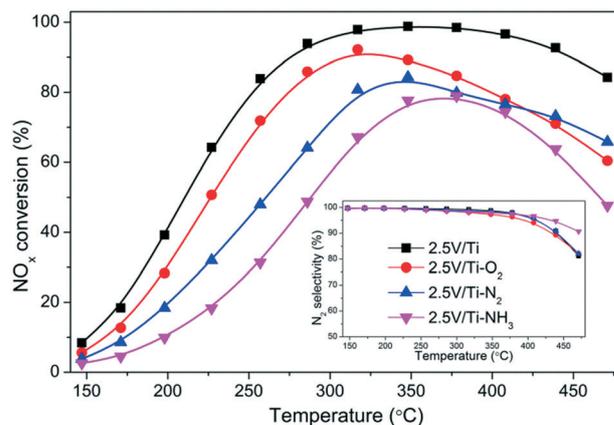


Fig. 1 NO_x conversion and N₂ selectivity (inset) over the V/TiO₂ catalysts.

The NH_3 -SCR activity over vanadia-based catalysts after different treatments is shown in Fig. 1. The fresh V/Ti catalyst presented the highest NO_x conversion, and higher than 80% NO_x conversion was obtained in the temperature range of 250–470 °C. The different aftertreatments all deactivated the catalyst to some extent. As the treatment atmosphere changed from oxidizing to reducing conditions, the catalytic activity decreased gradually, both at low and high temperatures. The N_2 selectivity over the four samples above 350 °C decreased to some degree in all cases. V/Ti- NH_3 exhibited higher N_2 selectivity than the other catalysts, with over 90% N_2 selectivity obtained in the whole temperature range investigated. V/Ti, V/Ti- O_2 and V/Ti- N_2 presented nearly 80% N_2 selectivity at 470 °C. The fresh V/Ti catalyst exhibited the highest NO_x conversion, while V/Ti- NH_3 presented the lowest NO_x conversion and the highest N_2 selectivity.

The XRD patterns of the V/TiO₂ catalysts are shown in Fig. 2. Only peaks attributed to anatase TiO₂ were observed for all of the samples. No peaks attributed to vanadium oxide were detected, illustrating that it was present as an amorphous phase or with a very small particle size on the surface of TiO₂. The intensity of the TiO₂ diffraction peaks of the treated samples was stronger than that for the fresh V/Ti, demonstrating their higher crystallinity. Although the treatment temperature was approximately equal to the calcination temperature, differences in the atmosphere and the lengthening of the treatment time could result in diffraction peaks with stronger intensity which indicates higher crystallinity. The state of the vanadium species may also change, although this could not be observed by XRD.

The surface area and pore characterization results of the vanadia-based catalysts are shown in Table 1. As we can see, the four samples presented similar pore volumes, pore diameters and specific surface areas. The treatments in O₂, N₂ and NH₃ atmospheres did not significantly change the textural properties of the vanadia-based catalysts.

Table 1 also shows the relative surface concentrations of S for the vanadia-based catalysts based on XPS. A certain amount of sulfur existed on V/Ti, V/Ti- O_2 and V/Ti- N_2 , due to the fact that the TiO₂ support contained some sulfate ini-

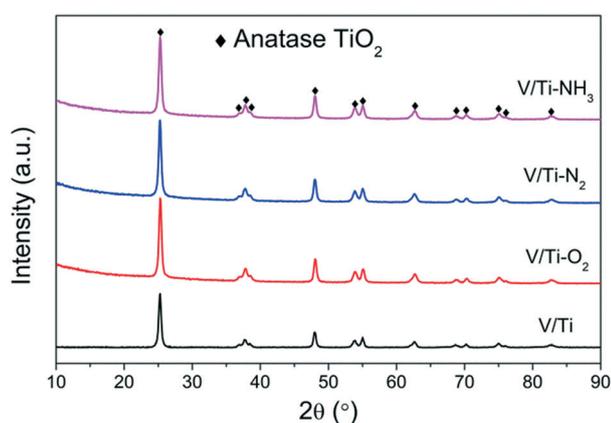


Fig. 2 XRD patterns of the V/TiO₂ catalysts.

tially. The treatments with O₂ and N₂ at high temperature both decreased the sulfate content on the catalysts, possibly due to the decomposition of some of the sulfate species. The sulfate species could be reduced to SO₂ by NH₃, and thus no sulfur was detected on V/Ti- NH_3 . The sulfate on the surface could contribute to the number of Brønsted acid sites.¹⁹ In addition, in our previous study,²⁰ the sulfur content affected the vanadium species and then the SCR activity. Therefore, the surface acidity and the state of vanadium species will be discussed later.

The XPS results of O 1s and V 2p of the V/TiO₂ catalysts are shown in Fig. S1 and S2,[†] respectively. The surface adsorbed oxygen content and high-valence V species (shown in Table S1[†]) increased after treatment in the O₂ atmosphere, while both decreased after treatment in NH₃. There was only a slight change in the vanadium valence and amount of surface oxygen species after the treatment in N₂. However, the fresh V/TiO₂ showed the highest NO_x conversion, followed by V/Ti- O_2 , N₂ and NH₃. This indicated that the adsorbed oxygen content and valence of vanadium were not the main factors affecting the catalytic activity over the V/TiO₂ samples.

The H₂-TPR results (Fig. S3[†]) showed that the samples presented similar redox capabilities, although a lower H₂ consumption was observed for V/Ti- NH_3 .

The surface acidity is an important property for SCR catalysts. Fig. 3 shows the DRIFTS of NH₃ adsorption on the vanadia-based catalysts at 200 °C. After NH₃ was introduced, several adsorbed NH₃ species were observed. The peaks centered at 1430 and 1672 cm⁻¹ are attributed to asymmetric and symmetric bending vibrations of NH₄⁺ species on Brønsted acid sites, while the bands centered at 1248, 1600 cm⁻¹ and in the range of 3100–3400 cm⁻¹ are ascribed to symmetric and asymmetric bending vibrations and the stretching vibration of N–H bonds in NH₃ coordinatively linked to Lewis acid sites, respectively.^{21–23} The negative peaks at 3650 cm⁻¹ and 1369 cm⁻¹ were due to the consumption of surface hydroxyl and residual sulfate species through the interaction with NH₃, respectively.^{24,25} According to the IR peak intensity, the amount of acid sites, including both Brønsted and Lewis types, decreased in the following sequence: V/Ti > V/Ti- O_2 > V/Ti- N_2 > V/Ti- NH_3 , though the four samples showed similar specific surface areas. The V/Ti- NH_3 catalyst showed the weakest acidity, and only Lewis acid sites were observed. This was consistent with the sulfate content on the catalyst measured by XPS, which contributes to the number of Brønsted acid sites. The decrease in the number of Lewis acid sites could be attributed to the changes in vanadium species and increased crystallinity of TiO₂, which could act as Lewis acid sites.²⁶ During the NH₃-SCR reaction, the more abundant acid sites on the fresh V/Ti catalyst could contribute to the adsorption and activation of NH₃ and thus promote the SCR performance. From Fig. S4,[†] NH₄⁺ adsorbed on Brønsted acid sites and coordinated NH₃ on Lewis acid sites both reacted with NO_x and participated in NH₃-SCR.

In general, the surface acidity governs the NH₃-SCR activity at high temperature. The decreased surface acidity on the

Table 1 N₂ physisorption results and surface S concentrations of the V/TiO₂ catalysts

Catalyst	Specific surface area (m ² g ⁻¹)	Average pore diameter (nm)	Pore volume (ml g ⁻¹)	S atomic%
V/Ti	81.52	21.13	0.43	1.77
V/Ti-O ₂	91.36	16.91	0.39	1.22
V/Ti-N ₂	85.67	18.36	0.39	1.16
V/Ti-NH ₃	88.90	18.11	0.40	0

catalysts after the treatments, especially V/Ti-NH₃, resulted in a decrease in NO_x conversion at 350–450 °C. Strong redox capability and low acidity would lead to over-oxidation of NH₃ and lower the N₂ selectivity at high temperature. However, due to the weak redox capability, high N₂ selectivity over V/Ti-NH₃ was also obtained in the whole temperature range.

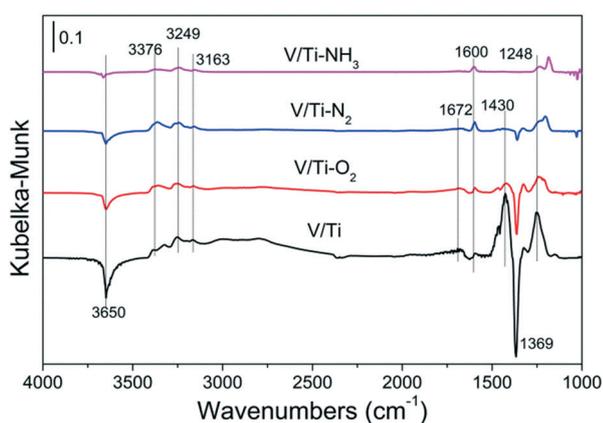
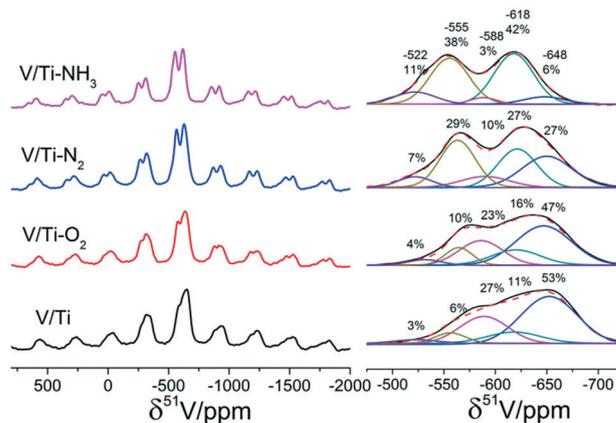
Fig. 4 shows the ⁵¹V NMR spectra of the different V/TiO₂ catalysts. For the vanadia-based catalysts, five peaks at about -522, -555, -588, -618 and -648 ppm were observed. The peak located at -522 ppm could be due to monomeric vanadyl species, while the peaks at -555, -588 and -648 ppm were related to polymeric vanadyl species.^{27,28} A peak due to V₂O₅-like nanoparticles was observed at -618 ppm.^{27,28} The ratios of monomeric species and V₂O₅-like nanoparticles increased with the change in the treatment atmosphere from oxidizing to reducing conditions, while the opposite trend was observed for polymeric species.

In our previous investigation,¹⁹ different vanadium species on V₂O₅/TiO₂ catalysts were obtained by treatment of TiO₂ with sulfate species. The polymeric vanadyl species, rather than the monomeric vanadyl species, determine the NH₃-SCR activity, especially under low-temperature conditions.¹⁹ The transformation of monomeric vanadyl into polymeric vanadyl species caused by sulfate introduction may be due to the surface sites of TiO₂ being partially occupied by sulfate, which enables the vanadyl species to be close to each other. In this study, after treatment at high temperature, polymeric vanadyl species tended to aggregate and crystallize. Therefore, the ratio of polymeric species decreased and the ratio of V₂O₅-like nanoparticles increased. At the same time, after the treatment, the content of surface sulfur species decreased, due to the decomposition and reduction of sulfate. Thus, more Ti

sites became available and the ratio of monomeric vanadyl species increased slightly.

Fig. 5 shows the correlation between the catalytic activity and different vanadium species. There is a clear positive correlation of NO_x conversion at low temperature with the polymeric vanadyl species. According to the ⁵¹V MAS NMR analysis, the polymeric vanadyl species account for 86% of the total vanadium species in the V/Ti catalyst, while there was a significant reduction of such surface polymeric species on the V/Ti-NH₃ catalyst, only accounting for 47% of the total vanadium. It must be noted that, among the three peaks attributed to polymeric vanadyl, the concentrations of vanadium species at ca. -588 and -648 ppm both decreased while that at ca. -555 ppm increased in the following sequence: V/Ti → V/Ti-O₂ → V/Ti-N₂ → V/Ti-NH₃. This suggests that different polymeric species exhibited different catalytic activities.

In summary, the influence of different treatment atmospheres on the catalytic activity and structure of V/TiO₂ catalysts was investigated. The catalyst treated under an oxidizing atmosphere (10% O₂) showed better catalytic performance than that treated under an inert atmosphere (N₂), while that treated under a reducing atmosphere (0.1% NH₃) exhibited the lowest catalytic activity for the selective catalytic reduction of NO with NH₃. Due to decomposition or reduction at high temperature, the surface sulfur content decreased on V/Ti-O₂, V/Ti-N₂ and V/Ti-NH₃. The amount of acid sites was also reduced, consistent with the lower sulfur content and higher crystallinity. Therefore, the catalytic activity at high temperature decreased after the treatment. The aftertreatment also resulted in changes in the vanadium species, especially a decrease in the amount of active polymeric vanadyl species. Therefore, the treatments with O₂, N₂ and

**Fig. 3** DRIFTS of NH₃ adsorption on the V/TiO₂ catalysts at 200 °C.**Fig. 4** Solid state ⁵¹V NMR spectra of the different V/TiO₂ catalysts.

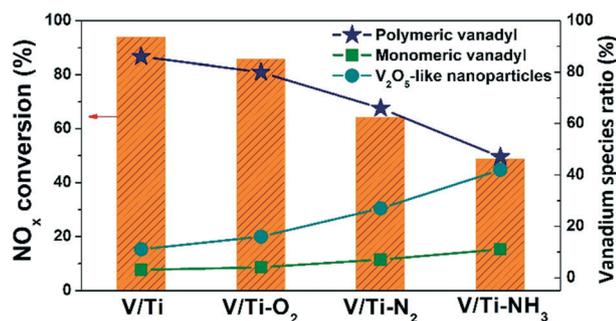


Fig. 5 Correlation of NO_x conversion at 285 °C with different vanadium species.

NH₃ all deactivated V/TiO₂ to some extent. The different polymeric vanadium species corresponding to different NMR peaks and the corresponding NH₃-SCR mechanism will be studied further in the future.

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Conflicts of interest

There are no conflicts to declare.

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