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Significant promotion effect of the rutile phase on V_2O_5/TiO_2 catalysts for NH_3 -SCR⁺

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A large amount of polymeric vanadyl species owing to higher interaction energy between vanadia and anatase than rutile and the synergistic effect of vanadium oxides, anatase and rutile TiO_2 contributes to an excellent NH₃-SCR activity of the vanadia-based catalysts with high rutile content and low specific surface area.

Nitrogen oxides (NO_x) emitted from automobile and fossil fuel combustion are one of the major air pollutants, contributing to environmental and human health hazards such as photochemical smog, acid rain and haze.^{1,2} The selective catalytic reduction of NO_x with ammonia (NH₃-SCR) over the V₂O₅–WO₃(MoO₃)/TiO₂ catalyst is one of the state-of-the-art and widely commercialized technologies for abating NO_x from mobile and stationary sources.^{3–5} However, vanadia-based catalysts show high catalytic activity only in a narrow medium-temperature range.^{6–8} Therefore, improving vanadia-based catalysts is a significant challenge, especially at low temperatures.

Anatase TiO_2 has been widely applied to support vanadia catalysts for selective catalytic reduction of NO_x with NH_3 because of its excellent properties. These include: (1) the active vanadia species can be uniformly dispersed on the surface of TiO₂, and (2) under SCR reaction conditions, the sulfation of TiO₂ is weak and reversible due to the low decomposition temperatures of Ti(SO₄)₂ or TiOSO₄.^{3,9} However, V₂O₅/TiO₂ (anatase) is unstable so that at higher temperature and pressure, metastable anatase TiO₂ converts into the thermodynamically stable rutile form. V₂O₅ favors anatase sintering,

the anatase/rutile transformation and the loss of surface area.¹⁰ MoO₃ or WO₃ can be introduced to inhibit transformation of the anatase phase to rutile. In recent years, there have been several publications reporting rutile TiO₂ as a support for NH₃-SCR catalysts, including vanadia-based¹¹⁻¹³ and nonvanadia-based^{14–16} catalysts. A Sn-doped rutile TiO₂-supported V₂O₅ catalyst exhibited higher activity for NH₃-SCR and stronger SO₂ and water resistance than the traditional V_2O_5 /anatase TiO₂ catalyst, because the addition of Sn promoted the amount of surface chemisorbed oxygen, NH₃/NO adsorption and the redox capability.¹² The order of NH₃-SCR catalytic performance over TiO₂-supported ceria-based catalysts was as follows: CeO₂/ rutile > CeO_2 /brookite > CeO_2 /anatase, owing to the reduction properties, surface adsorbed oxygen species, surface Ce³⁺ content and the amount of acid sites.¹⁴ These studies indicated that the crystal phase of the support has a significant impact on the catalytic performance. It was reported that a small amount of TiO₂ rutile phase can enhance the NH₃-SCR activity of V/TiO₂ catalysts due to the fact that the decrease of the conduction band level improved the formation of reduced V species and superoxide ions.¹³ However, it is unclear the synergistic effects of vanadium oxides, anatase TiO2, and rutile TiO2 and the aggregation state of vanadium species. The change of vanadium species and their interaction still needs to be investigated in depth, which will be beneficial for the rational design of catalysts.

In this study, two mixed-phase TiO_2 supports with different ratios of anatase and rutile phase were used to load vanadium oxides for selective catalytic reduction of NO_x with NH₃. Interestingly, the catalyst with high rutile phase content exhibited superior NH₃-SCR catalytic performance. Both experimental methods and density functional theory (DFT) calculations were employed to study the roles of rutile and anatase TiO_2 .

To investigate the crystal structure of the prepared vanadiabased catalysts, XRD patterns were firstly measured, and the results are shown in Fig. 1. All the diffraction peaks observed are ascribed to TiO_2 , including the anatase (PDF#21-1272) and rutile (PDF#21-1276) phases. The phase content can be

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Fig. 1 XRD profile of vanadia-based catalysts.

calculated from the integrated intensities of the rutile and anatase peaks. According to the literature,^{13,17} if only rutile and anatase exist on a catalyst, the weight fraction of rutile (W_R) can be calculated from:

$$W_{\rm R} = \frac{A_{\rm R}}{0.884A_{\rm A} + A_{\rm R}}$$

where $A_{\rm R}$ and $A_{\rm A}$ represent the integrated intensities of rutile (110) and anatase (101) peaks, respectively. The weight fractions of rutile phase in V/Ti-1 and V/Ti-2 were about 8% and 58%, respectively. It can be seen that, the anatase phase content of Ti-2 decreased, while the rutile phase content increased accordingly, compared with Ti-1. No diffraction peak corresponding to vanadia species was detected for the vanadia-based catalysts, demonstrating that the vanadia species were homogeneously distributed or present with a very small particle size on the support surface. The dissolution of V into the TiO₂ lattice was not observed.

The textural parameters of the vanadia-based catalysts derived from the N_2 physisorption results, including specific surface areas, pore volumes and average pore diameters, are given in Table S1 (ESI†). V/Ti-2 had smaller BET surface area, pore volume and pore diameter than V/Ti-1. According to the densities, weight ratios, and deduced average crystallite sizes of anatase and rutile particles, the contribution of surface areas from anatase and rutile phase is 96:4 and 50:50 for V/Ti-1 and V/Ti-2, respectively. Usually, larger specific surface area signifies more surface sites to adsorb reactant gas, presenting higher catalytic activity. Therefore, the NH₃-SCR performance of the V/Ti-1 and V/Ti-2 catalysts was tested and compared, and the results are shown in Fig. 2.

The V/Ti-1 catalyst showed low NH₃-SCR efficiency. The NO_x conversion increased with temperature, and only 80% NO_x conversion was achieved over V/Ti-1 at 354 °C. However, the V/Ti-2 catalyst with higher rutile phase content exhibited much better catalytic performance than V/Ti-1. About 32% and 94% NO_x conversions were obtained at 290 °C over V/Ti-1 and V/Ti-2, respectively. Both catalysts presented higher than 90% N₂ selectivity in the temperature range investigated. The TiO₂



Fig. 2 NH₃-SCR activity of vanadia-based catalysts. Reaction conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] = 5$ vol%, N₂ balance and GHSV = 100 000 h⁻¹.

support with 12% rutile phase was also used to synthesize a vanadia-based catalyst, denoted as V/Ti-3, and the NH₃-SCR activity is shown in Fig. S1 (ESI[†]). As we can see, the catalytic activity was promoted with the increase of rutile phase. Fig. S2 (ESI[†]) exhibits the effects of SO₂ and H₂O on the SCR activities of the catalysts. After the introduction of SO₂ + H₂O, the catalytic activity of V/Ti-1 increased gradually and the NO_x conversion first decreased sharply and then increased gradually over V/Ti-2 until reaching 100%. This indicated that the presence of SO₂ and H₂O promoted the catalytic performance possibly due to the increase of acid sites.

HR-TEM was used to investigate the morphologies of V/Ti-1 and V/Ti-2. As shown in Fig. S3(a and e) (ESI⁺), V/Ti-1 and V/Ti-2 both have a nanoparticle-like morphology with $\sim 20-50$ nm nanoparticle diameters. The lattice fringes with 0.35 nm interplanar spacings in Fig. S3(b and f) (ESI⁺) can be attributed to anatase $TiO_2(101)$. The rutile phase $TiO_2(110)$ and (101) planes, with 0.32 and 0.25 nm interplanar spacings, respectively, can also be observed in Fig. S3(c, g and h) (ESI[†]). Thus, the anatase and rutile phases of TiO₂ both existed in V/Ti-1 and V/Ti-2, consistent with the XRD results. However, no structural features of vanadium species could be observed, indicating that the vanadium species were well dispersed on the surface of TiO₂. SEM images and elemental mapping images of V/Ti-1 and V/Ti-2 are shown in Fig. S4 (ESI⁺). These two catalysts both showed irregular particles, with the particle size of V/Ti-2 being larger than that of V/Ti-1. The vanadium oxides were well dispersed on V/Ti-2 and V/Ti-1.

The XRF results of V/Ti-1 and V/Ti-2 catalysts are shown in Table S3 (ESI[†]). The loading amounts of vanadium for the two catalysts were similar to each other. Except for the vanadium and titanium oxides, there also existed several impurities, such as MgO and Al₂O₃. There was no significant difference in the chemical composition between V/Ti-1 and V/Ti-2.

The vanadia structures were investigated by solid state ⁵¹V NMR spectroscopy, and the results are shown in

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Fig. 3. For both V/Ti-1 and V/Ti-2, seven peaks were observed. According to the literature,^{18–20} the peaks located at -509, -528 ppm and -607 ppm could be attributed to monomeric vanadyl species and V₂O₅-like nanoparticles, respectively, while the peaks at -558, -584, -627 and -648 ppm were due to polymeric vanadyl species. The peak ratios for each peak are also shown in Fig. 3. As compared with V/Ti-1, V/Ti-2 presented a larger amount of polymeric vanadyl species.

Due to the fact that V⁴⁺ is NMR silent, XPS was used to investigate the valence distribution of V on V/Ti-1 and V/Ti-2 (as shown in Fig. S5, ESI⁺). In addition, the Raman spectra were also exhibited in Fig. S6 (ESI[†]), which is not sensitive to the oxidation state of vanadium. The state of vanadium on both catalysts mainly presented as V^{5+} and V^{4+} . The ratio of V^{5+} on V/Ti-2 was much higher than that on V/Ti-1. In the Raman spectra, the peak intensity at 925 cm⁻¹, attributed to polymeric vanadyl species,²¹ for V/Ti-2 was stronger than that for V/Ti-1. Therefore, from these results, it can be concluded that a greater amount of polymeric species existed on V/Ti-2 than on V/Ti-1. In our previous work,²¹ it was proposed that polymeric vanadyl species present a lower overall reaction barrier for the catalytic cycle and lead to markedly better catalytic performance than monomeric vanadyl species. Therefore, the more abundant polymeric vanadyl species on V/Ti-2 will contribute to the higher NH₃-SCR activity.

The increase in the amount of polymeric vanadyl species over V/Ti-2 might be due to its smaller specific surface area than V/Ti-1. The loading of V_2O_5 on Ti-2 was decreased to 0.7% to assure that the VO_x surface densities on the Ti-1 and Ti-2 supports were similar to each other, as shown in Table S2 (ESI†). The TOF was calculated at 200 and 260 °C, at which the NO_x conversion was lower than 30%. The results indicated higher TOF over 0.7V/Ti-2 than V/Ti-1. If it was the decreased specific surface area of V/Ti-2 that resulted in the polymerization of vanadia species, the TOF of V/Ti-1 and 0.7V/Ti-2 should also be similar to each other. Therefore, there must be some other reason for the increase in polymeric vanadyl species on V/Ti-2. The solid state ⁵¹V NMR spectra of the 0.7V/Ti-2 catalyst



Fig. 4 Optimized structures of (A) monomeric vanadia on anatase (101), (B) dimeric vanadia on anatase (101), (C) monomeric vanadia on rutile (110), and (D) dimeric vanadia on rutile (110).

are also shown in Fig. S7 (ESI†). The ratio of polymeric vanadyl of 0.7V/Ti-2 is a little higher than that of 1V/Ti-1, although they have similar surface vanadium densities.

To study the interaction of the support with the vanadia species, different doped structures were optimized by the DFT method. The interaction energies between VO_x and the TiO₂ support, E_{int} , were calculated as follows:^{22,23}

$$E_{\text{int}} = E_{\text{mono/diVO}_x - \text{TiO}_2} - E_{\text{TiO}_2} - E_{\text{V}} - \frac{x}{2}E_{\text{O}_2}$$

where $E_{\text{mono/divO}_x\text{-TiO}_2}$, E_{TiO_2} , E_V and E_{O_2} denote the energy of monomeric or dimeric vanadyl species supported on anatase $TiO_2(101)$ or rutile $TiO_2(110)$, the TiO_2 surface, the bulk vanadium and the gas-phase O2, respectively. A negative energy represents the stabilization of VO_x species on TiO₂ surfaces. From Fig. 4, it can be seen that the interaction energies between VO_x and the TiO₂ support are -7.42, -18.28, -6.99 and -17.97 eV for monomeric vanadia on anatase (101), dimeric vanadia on anatase (101), monomeric vanadia on rutile (110), and dimeric vanadia on rutile (110), respectively. The interaction energies for monomeric and dimeric vanadia on anatase are both larger than those on rutile. The high E_{int} reflects the stability of the complexes and describes the strong interactions between TiO2 and vanadia species. This result indicated that vanadia species tend to interact with the anatase phase more than the rutile phase.

Based on the BET, XRD, and HR-TEM characterization and activity test results, the V/Ti-2 catalyst with lower specific surface area and higher rutile phase content presents better NH_3 -SCR performance than V/Ti-1. The stabilities of vanadia species on different TiO₂ supports were evaluated through calculations of their interaction energies by DFT methods. Due to the stronger interaction energy of vanadyl species with anatase TiO₂ than

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rutile TiO₂, vanadia species, including monomeric and polymeric vanadyl species, tend to interact with the anatase phase more than the rutile phase. Therefore, monomeric vanadyl species would be close to each other and become polymeric vanadyl species on Ti-2 with low anatase content. Thus, more abundant polymeric vanadyl and less monomeric vanadyl are observed from the NMR and Raman results.

It was suggested that

$k = 0.6281 [V]^2$

where *k* is the rate constant, and [V] is the surface vanadium density in nm².²⁴ The reaction rate constants (mol g⁻¹ h⁻¹) of V/Ti-1 and V/Ti-2 were calculated (as shown in Table S2, ESI†). Taking the V/anatase ratios into account, the rate constant at 200 °C of V/Ti-2 with a higher rutile ratio is much larger than that of V/Ti-1. The vanadium surface densities on V/Ti-1 and V/Ti-2 are 1.66 and 2.12 VO_x per nm², respectively. Taking the surface area contributions of anatase and rutile into account and assuming that vanadium only dispersed on anatase TiO₂, the ratio of quadratic vanadium concentration of V/Ti-1 :V/Ti-2 is 1:6. However, the rate constant of V/Ti-2 is much more than six times that of V/Ti-1. Therefore, there must be a synergistic effect among vanadium oxides, anatase TiO₂ and rutile TiO₂.

Taking the surface area contribution of anatase and rutile into account, 2.5%V/Ti-1 might present similar surface vanadium density on anatase TiO₂ to 1V/Ti-2. Their catalytic activity is shown in Fig. S8 (ESI†), which showed that the catalytic activity over 2.5V/Ti-1 was close to that over V/Ti-2. Therefore, the increase of a rutile ratio is one way to increase catalytic activity and reduce vanadium loading simultaneously. As shown in Fig. S9 (ESI†), the TOF of V/Ti-2 was higher than that of 2.5V/Ti-1, indicating that the synergistic interactions among vanadium oxides, anatase and rutile TiO₂ on the V/Ti-2 catalyst promoted the NH₃-SCR activity.

Vanadia-based catalysts catalyze the NH₃-SCR reaction through the transformation of the valence state of V. Therefore, the redox capability of vanadium oxides is important to the NH₃-SCR reaction, which can be investigated by H₂-TPR (as shown in Fig. S10, ESI†). The H₂ consumptions for V/Ti-1 and V/Ti-2 were similar to each other. Compared with V/Ti-1, V/Ti-2 shows a reduction peak shifting to the lower temperature region, indicating that the interaction of V₂O₅ with TiO₂ for V/Ti-2 is stronger than that for V/Ti-1, and V/Ti-2 presents higher redox capability at low temperature. In addition, as shown in Fig. S11 and S12 (ESI†), the amount of acid sites on V/Ti-2 was larger than that on V/Ti-1. All these factors contributed to the higher catalytic activity over V/Ti-2 than V/Ti-1.

In summary, a high content of rutile phase significantly improved the NH_3 -SCR reactivity over vanadium oxides supported on mixed-phase TiO_2 at low temperatures. Due to the higher interaction energy of vanadia with anatase than rutile, vanadia species tended to disperse on anatase TiO_2 . A large amount of polymeric vanadyl species and the synergistic effect of vanadium oxides, anatase and rutile TiO_2 are beneficial for the NH_3 -SCR reaction. Therefore, high rutile content and low specific surface area contributed to excellent NH_3 -SCR activity, unexpectedly. Anatase TiO_2 has been widely used as the support of the commercial V_2O_5 - WO_3/TiO_2 catalyst for decades. Our investigation indicated that the existence of the rutile phase promoted the NH_3 -SCR activity over a vanadia-based catalyst remarkably at low temperatures. This finding also clarifies the role of the rutile phase in vanadia-based catalysts for NH_3 -SCR and provides a way to reduce vanadium loading and obtain high SCR activity at low temperature simultaneously.

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Conflicts of interest

There are no conflicts to declare.

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