Polymeric vanadyl species determine the low-temperature activity of V-based catalysts for the SCR of NO\textsubscript{x} with NH\textsubscript{3}

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The structure of dispersed vanadyl species plays a crucial role in the selective catalytic reduction (SCR) of NO with NH\textsubscript{3} over vanadia-based catalysts. Here, we demonstrate that the polymeric vanadyl species have a markedly higher NH\textsubscript{3}-SCR activity than the monomeric vanadyl species. The coupling effect of the polymeric structure not only shortens the reaction pathway for the regeneration of redox sites but also substantially reduces the overall reaction barrier of the catalytic cycle. Therefore, it is the polymeric vanadyl species, rather than the monomeric vanadyl species, that determine the NH\textsubscript{3}-SCR activity of vanadia-based catalysts, especially under low-temperature conditions. The polymeric vanadia-based SCR mechanism reported here advances the understanding of the working principle of vanadia-based catalysts and paves the way toward the development of low vanadium-loading SCR catalysts with excellent low-temperature activity.

INTRODUCTION

Nitrogen oxides (NO\textsubscript{x}), as key precursor pollutants inducing the formation of acid rain, photochemical smog, and haze, are mainly emitted from power plants and mobile diesel vehicles. Selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (i.e., NH\textsubscript{3}-SCR) over vanadia-based catalysts is one of the most widely adopted techniques for the removal of NO\textsubscript{x} from stationary and mobile sources (1–4). The lower exhaust temperature of advanced combustion engines requires an in-depth understanding of the active center and the reaction mechanism (2, 7, 8).

For the commercial vanadia-based catalysts, previous studies revealed that dispersed vanadyl species, serving as the active moieties for NO\textsubscript{x} reduction, are mainly present as isolated monomeric and polymeric vanadyl species (9–12), the distributions of which are closely related to the content of V\textsubscript{2}O\textsubscript{5}. As for V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts, in situ laser Raman analysis performed by Went \textit{et al.} (12) confirmed that monomeric species predominated at low vanadia loading of 1.3 weight % (wt %) V\textsubscript{2}O\textsubscript{5}, at 80% of vanadyl species. With increasing vanadia loading from 1.3 to 3.0 wt %, the fraction of monomeric species decreased monotonically, while the percentage of polymeric species increased from 20 to 33%. Vanadia-based catalysts with 2 to 3 wt % V\textsubscript{2}O\textsubscript{5} are commonly used in industrial applications for mobile source emission control (15). Moreover, for commercial V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts, sulfate species are commonly present in the anatase TiO\textsubscript{2} used. As revealed by Nam’s group (16), sulfate can enhance the transformation of isolated vanadyl species to polymeric vanadyl species. Therefore, the polymeric vanadyl species may play an important role in the removal of NO\textsubscript{x} from mobile sources. However, currently proposed NH\textsubscript{3}-SCR schemes over vanadia-based catalysts mainly focus on the reaction process occurring on isolated monomeric vanadyl species (1, 7, 8, 17), without considering the polymerization of reactive sites and their coupling effects. The working principle of polymeric vanadyl species remains unclear.

Here, using a TiO\textsubscript{2} support pretreated with sulfate species, we successfully obtained V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts with varying proportions of polymeric and monomeric vanadyl species, which exhibited marked differences in NH\textsubscript{3}-SCR activity. By combining the results of experimental measurements with density functional theory (DFT) calculations, we found a polymeric vanadyl-based NH\textsubscript{3}-SCR mechanism, which is energetically more favorable than the reaction schemes based on monomeric vanadyl species. Therefore, it is the polymeric vanadyl species, rather than monomeric vanadyl species, that determine the activity of vanadia-based catalysts, especially under low-temperature conditions. This finding shows that the surface structure of dispersed vanadia plays a critical role in the NH\textsubscript{3}-SCR reaction. In addition, the experimental approach used here provides an efficient way to develop high-performance low vanadium-loading SCR catalysts.

RESULTS

Catalytic activity

It is well known that vanadia-based catalysts are widely applied because of their excellent sulfur resistance. We pretreated TiO\textsubscript{2} with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} to regulate the amount of sulfur on the surface, and we obtained a series of V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts with different amounts of sulfur, denoted as 1V/xSTi (x wt % represents the sulfate content). For comparison with these sulfur-containing samples, we also prepared samples without sulfur by treating the TiO\textsubscript{2} support with NH\textsubscript{3} [i.e., Ti-NH\textsubscript{3} and 1V/(Ti-NH\textsubscript{3}) samples]. Because of the reduction of sulfate by NH\textsubscript{3}, x-ray photoelectron spectroscopy (XPS) results showed that there was no sulfur in the Ti-NH\textsubscript{3} sample (table S1).
while a small quantity of sulfur was detected in the 1V/(Ti-NH$_3$) sample owing to the existence of traces of sulfur in the vanadia precursor (NH$_4$VO$_3$). With increasing sulfur content, the specific surface area decreased slightly (table S2). There was no change in the crystalline structure, and all these samples crystallized in the anatase structure (fig. S1).

As shown in Fig. 1A, the catalytic activity of the V$_2$O$_5$/TiO$_2$ catalysts in the SCR of NO with NH$_3$ increased with increasing sulfur content. The highest NH$_3$-SCR activity was obtained over 1V/9STi and 1V/12STi samples, which yielded 90% NO$_x$ conversion at 300°C under a high gas hourly space velocity (GHSV) of 200,000 hour$^{-1}$. The purpose of this study is to elucidate the fundamental NH$_3$-SCR principles of vanadia-based catalysts; thus, we used a simplified V$_2$O$_5$/TiO$_2$ catalytic system without introducing any promoter components. A comparison of the activity with that of previously reported catalysts (18, 19) shows that the activity of our 1V/9STi catalyst, expressed in terms of reaction rate and turnover frequency (TOF), is comparable to that of many commercial V/WTi catalysts (table S3). The selectivity toward N$_2$ was maintained at about 98% over the whole temperature range (fig. S2). Moreover, the 1V/9STi sample exhibited excellent resistance to SO$_2$ and H$_2$O (fig. S3). To confirm the effect of sulfur content on SCR activity, we treated the support with NH$_3$ to remove the sulfur, and the obtained 1V/(Ti-NH$_3$) sample showed the lowest catalytic activity.

**Reactivity of surface acid sites**

It has been well established that the occurrence of NH$_3$-SCR requires both acid and redox sites on the vanadia-based catalysts working...
together (1, 20, 21). Therefore, there are basically two possibilities, i.e., a change in the acid sites or the redox sites, to explain the enhancement of catalytic performance induced by sulfur introduction.

To elucidate whether such enhancement derives from a change in the acid sites on the catalyst, we conducted temperature-programmed desorption of NH₃ (NH₃-TPD) (Fig. 1B) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Fig. 1, C and D) studies. The adsorption of NH₃ on Brønsted acid sites would result in the formation of NH₄⁺, which is generally less thermally stable than NH₃ bound to Lewis acid sites (22–24). Therefore, the low-, middle-, and high-temperature peaks of the NH₃-TPD curves are attributed to the desorption of physisorbed NH₃, NH₃ bound to weak Brønsted acid sites, and NH₃ bound to strong Brønsted and Lewis acid sites, respectively. The NH₃-TPD result (Fig. 1B) shows that a high sulfur content on the catalysts increases the amount of Brønsted acid sites, whereas it decreases the amount of Lewis acid sites, in accordance with our DRIFTS data on NH₃ adsorption (fig. S4A) and previous literature (25).

We investigated the reactivity of adsorbed NH₃ toward NO + O₂ using in situ DRIFTS (Fig. 1, C and D). The samples were exposed to NH₃ until adsorption saturation and then flushed with N₂ for collection of the background spectrum. After NO + O₂ was introduced to the samples, the DRIFTS data were collected. The occurrence of negative infrared (IR) peaks indicates the consumption of adsorbed NH₃ species. The NH₃ adsorbed on Lewis acid sites and ad-NOₓ exhibit characteristic IR peaks in the same regions (1200 to 1300 cm⁻¹ and 1500 to 1650 cm⁻¹); hence, it is difficult to differentiate these species. For the 1V/TiO₂ sample (Fig. 1C), the negative peaks at 1430 and 1672 cm⁻¹ due to NH₄⁺ on Brønsted acid sites appeared after the flow of NO + O₂ for 5 min at 150°C and became more negative over time. This result indicates that during the first 5 min, the NH₃ coordinated to Lewis acid sites participated in the NH₃-SCR reaction, and then the NH₄⁺ on Brønsted acid sites were consumed. The low reactivity of NH₄⁺ bound on Brønsted acid sites was also observed for the 1V/9STi sample (Fig. 1D). The occurrence of the asymmetric O=S=O stretching vibration peaks of sulfate species at 1361 cm⁻¹ (26, 27) denotes the consumption of NH₃ species adsorbed on sulfate sites. Similar results were also obtained at 250°C (fig. S4, B and C). Ferri and co-workers (7) have also reported that NO reacts predominantly with NH₃ coordinated to Lewis acid sites during NH₃-SCR on the V₂O₅-WO₃-TiO₂ catalyst, while Brønsted acid sites are not involved in the catalytic cycle and mainly serve as an NH₃ pool to replenish the Lewis acid sites, which is consistent with our experimental results.

As revealed above, sulfuration increases the amount of Brønsted acid sites, whereas it decreases the amount of Lewis acid sites. Moreover, the NH₃ coordinated to Lewis acid sites preferentially participates in the NH₃-SCR reaction (7). Therefore, this result suggests that the introduction of sulfate changes not only the acid sites but also other active centers (i.e., the redox sites), and the enhancement of NH₃-SCR reactivity may result mainly from changes to the redox sites.

![Fig. 2. Energy profile of the entire NH₃-SCR process. (A) Pathways over monomeric vanadia/TiO₂ surfaces. (B) Pathways over dimeric vanadia/TiO₂ surfaces. The letters at each state correspond to the structures in Figs. 3 and 4. The barrier in the rate-determining step is marked in red font.](image-url)
**Structure of surface redox sites**

We used Raman spectroscopy to determine the structure of dispersed surface vanadyl species. According to the literature (16, 28, 29), the experimentally observed bands at 1030, 993, and 930 cm⁻¹ are characteristic of monomeric vanadyl species, crystalline V₂O₅, and polymeric vanadyl species, respectively. Therefore, the evident enhancement of the band at 930 cm⁻¹ from the 1V/Ti sample to the 1V/9STi sample indicates that the introduction of sulfate causes the polymerization of monomeric vanadyl species under low vanadium loading (Fig. 1E).

To confirm the Raman spectroscopy result, we conducted nuclear magnetic resonance (NMR) measurements. In general, the effect of ⁵¹V electronic shielding increases with the decrease of its isotropic chemical shift. The ⁵¹V NMR spectra (fig. S5) show that, with increasing sulfur content, the intensity of the central-band peak at lower chemical shifts (i.e., −655 ppm) was significantly increased, suggesting that the polymerization of vanadyl species was enhanced with sulfate introduction (30). The transformation of monomeric vanadyl to 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 (16). The XPS results (table S4 and fig. S6) show that the surface sulfate species do not have a significant effect on the valence state of the V ions; rather, they simply change the structure of dispersed vanadyl species.

**NH₃-SCR reaction pathways**

To elucidate the mechanism underlying the activity difference between monomeric and polymeric vanadyl species at the atomic scale, we carried out DFT calculations (see Figs. 2 to 4). According to the computational results, the NH₃-SCR de-NOₓ reaction over vanadia/TiO₂ catalysts proceeds via the Eley-Rideal mechanism, and both the redox sites and the acid sites are involved in the SCR process. The results of DRIFT spectra (fig. S4A) and DFT calculations (fig. S7, A and B) show that NH₃ is preferentially adsorbed on surface Ti sites (31). The adsorbed NH₃ is activated by the transfer of an H atom to the vanadyl species and subsequently reacts with NO in the gas phase, resulting in the formation of an intermediate nitrosamide (NH₂NO, denoted by the IR signals at 1505 cm⁻¹ in fig. S4D) (7) and a V-OH or V-OH₂ group (A→C, F→H, K→M, and P→R). Then, the NH₂NO intermediate is decomposed into N₂ and H₂O (C→E, H→J, M→O, and R→T). Gas-phase O₂ replenishes the consumed surface oxygen on the vanadyl species (J→K) (8). When the V=O groups are regenerated, a catalytic cycle is completed. The overall reaction barrier on the dimeric vanadyl species is predicted to be 1.34 eV, 0.21 eV lower than that on the monomeric vanadyl species (Fig. 2). According to transition state theory (32), at 493.15 K (220°C), this reduction of barriers would induce an increase in reaction rate of up to two orders of magnitude (table S5). This result indicates that the dimeric vanadyl species, rather than the monomeric vanadyl species, determine the NH₃-SCR activity of vanadia-based catalysts, which is consistent with our experimental results (Fig. 1, A and E).

It is noteworthy that a VOOH intermediate would be formed when an H atom transfers from the adsorbed NH₃ to the adsorbed O₂ on the vanadyl species (K→O). The VOOH intermediate is converted into the O=V-OH structure instantaneously for the monomeric vanadyl species (O→P in Fig. 3). However, the existence of an adjacent vanadyl enhances the thermal stability and lifetime of the catalyst.
VOOH intermediate due to the formation of a hydrogen bond between the VOOH group and the adjacent V=O group (fig. S7C), which allows a barrierless reaction between the VOOH intermediate and NO to occur on the polymeric vanadyl species. The regeneration of redox sites, as well as the formation of a nitrous acid molecule (HNO₂), is achieved at this step (O→P in Fig. 4). Yet on the monomeric vanadyl species, the regeneration of redox sites does not occur until the P→R process (Fig. 3). In the following process, the reaction of...
adsorbed NH₃ with HNO₂ is energetically more favorable than the reaction of adsorbed NH₃ with NO (P→T in Fig. 2). Therefore, the coupling effect of the polymeric vanadyl species not only shortens the reaction pathway for the reduction of redox sites but also substantially reduces the overall reaction barrier of the catalytic cycle, which therefore greatly accelerates the NH₃-SCR reaction. On the basis of the DFT calculations and experimental evidence, the entire NH₃-SCR mechanism over the monomeric and dimeric vanadia/TiO₂ basis were deduced and is summarized in Fig. 5.

**DISCUSSION**

Our study indicates that the surface structure of dispersed vanadia significantly affects the NH₃-SCR activity of vanadia-based catalysts. Owing to the difference in elementary reaction steps, the polymeric vanadyl species exhibit markedly higher activity than the monomeric vanadyl species. The polymeric vanadia-based SCR mechanism reported here advances the understanding of the working principle of vanadia-based catalysts. In the removal of NOₓ from mobile sources, catalysts with high vanadium loading have been prepared to enhance the low-temperature activity. However, the high vanadium loading would result in a decrease of the thermal stability and an enhancement of SO₂ oxidation. Here, we successfully obtained low vanadium-loading catalysts with excellent low-temperature SCR activity, which paves the way toward solving this problem.

**MATERIALS AND METHODS**

**Catalyst synthesis and activity test**

The SO₄²⁻-pretreated TiO₂ supports were prepared by the wet impregnation method. The (NH₄)₂SO₄ was dissolved in distilled water before TiO₂ was added to the solution. The mixture was agitated for 1 hour, and then the mixture was evaporated at 60°C using a rotary vacuum evaporator before drying overnight at 100°C. The mixture was calcined in air for 3 hours at 300°C. The resulting samples were labeled as xSTi, where x is the loading amount of SO₄²⁻. 1V/xSTi catalysts were prepared by the wet impregnation method using ammonium metavanadate (1.0 wt % vanadium pentoxide) and calcined xSTi and were finally calcined in air for 3 hours at 500°C.

Before the NH₃-SCR activity tests, the catalysts were pressed, crushed, and sieved to 40 to 60 mesh. The activity tests were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH₃, 5 vol % O₂, 100 ppm SO₂ (when used), 10 vol % H₂O (when used), and N₂ balance. Under ambient conditions, the total flow rate was 500 ml/min, and the GHSV was 200,000 hour⁻¹. The effluent gas, including NO, NH₃, NO₂, and N₂O, was continuously collected in flowing N₂ and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: total flow rate (300 ml min⁻¹), 500 ppm NH₃, and/or 500 ppm NO, 5 vol % O₂, and N₂ balance. All spectra were recorded on a scanning X-ray microprobe (Axis Ultra, Kratos Analytical Ltd.) using Al Kα radiation (1486.7 eV). All the binding energies were calibrated using the C 1s peak (binding energy = 284.8 eV) as standard.

XPS spectra of the catalysts were recorded on a quadrupole mass spectrometer (HPR-20, Hiden Analytical Ltd.) to record the signal of NH₃ [mass/charge (m/z) ratio = 15 for NH₃]. Before XPS experiments, the samples (150 mg) were pretreated at 400°C in a flow of 20 vol % O₂/N₂ (50 ml min⁻¹) for 0.5 hours and cooled down to room temperature. The samples were then exposed to a flow of 1% NH₃/N₂ (50 ml min⁻¹) at 50°C for 1 hour, followed by Ar purging for 1 hour. Last, the temperature was raised to 600°C in Ar flow at a rate of 10°C min⁻¹.

Raman spectra were measured on a LabRAM HR 800 Raman spectrometer using a 532-nm laser as the excitation source. The spectrometer was equipped with an in situ reaction cell (PIKE Technologies), in which samples can be heated to 500°C in a gas flow. In our experiments, all catalysts were heated from room temperature to 400°C under an oxygen flow and then the Raman spectra were acquired.

The ⁵¹V solid-state NMR experiments were performed at 11.7 T on a Bruker Avance III 500 spectrometer with a resonance frequency of 131.6 MHz, using a 1.9-mm HX double-resonance probe at a spinning rate of 40 kHz. The NMR spectra of ⁵¹V were acquired using a Hahn-echo pulse sequence with a π/2 pulse width of 1.5 μs. For our samples with 1 wt % V₂O₅ loading, 60,000 scans with a 0.3-s recycle delay were used. The ⁵¹V chemical shift was referenced to V₂O₅ at ~610 ppm.

**In situ DRIFTS measurements**

In situ DRIFTS experiments were performed on a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 670) equipped with a Smart Collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Before each experiment, the sample was pretreated at 300°C for 0.5 hours in a flow of 20 vol % O₂/N₂ and then cooled down to 150 or 250°C. The background spectra were collected in flowing N₂ and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: total flow rate (300 ml min⁻¹), 500 ppm NH₃ and/or 500 ppm NO, 5 vol % O₂, and N₂ balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

**Computational details**

Geometries and energies were calculated using the Perdew-Burke-Ernzerhof functional (33) with van der Waals correction proposed by Grimme (i.e., DFT-D2 method) (34), as implemented in the Vienna ab initio simulation package (VASP 5.4.1) (35). The projector augmented wave method was used to describe the interaction between the ions and the electrons (36). The energy cutoff of the plane wave was set to 400 eV. A (2 × 4) supercell of the anatase (101) surface with two stoichiometric TiO₂ layers (about 11 Å × 15 Å × 6 Å; see fig. S7, D and E) was used as the substrate. A vacuum gap of 12 Å was used to avoid the periodic image interaction normal to the surface. During the geometrical optimization, the bottom TiO₂ layer was fixed at its bulk position, while all other atoms were allowed to relax, until the forces on each atom were smaller than 0.02 eV Å⁻¹. Only the Γ point of the Brillouin zone was sampled. The Gaussian smearing method with a smearing width of 0.2 eV was used to accelerate the convergence of integration at the Brillouin zone. The reaction
pathways and transition states were traced by the climbing image nudged elastic band method with a spring constant of 5.0 eV Å⁻² (37, 38). No obvious differences in the structural properties (<0.002 Å) and energy barriers (<0.002 eV) were observed when k points were increased from the Γ point only to a 2 x 1 x 1 k-point mesh and the energy cutoff from 400 to 600 eV (table S6), indicating that the calculations had converged, and the computational settings used here were reliable for describing the studied reactions. The coupling effect between two adjacent vanadyl species was generally applicable in dimeric and higher-order polymeric vanadia structures. During the NH₃-SCR of NO over the polymeric vanadyl species, the coupling effect between the two adjacent vanadyl species (i.e., within a dimer unit of vanadia) at the reaction site accelerated the whole catalytic cycle, and hence, it could be expected that dimeric and higher-order polymeric vanadia would have similar effects on the SCR reaction. The dimeric vanadyl species is the basic structural unit of various polymeric vanadia structures and can reasonably represent the coupling effect in polymeric vanadia structures; hence, it was used as the model in our DFT calculations.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/11/eaau4637/DC1
Fig. S1. XRD patterns of vanadia/TiO₂ samples.
Fig. S2. N₂ selectivity as a function of temperature in the feed gas of 500 ppm NO/500 ppm NH₃/5.0 vol % O₂/N₂ (200,000 hour⁻¹).
Fig. S3. Effect of H₂O and SO₂ on NO conversion over the 1V/95Ti catalyst at 350°C in the feed gas of 500 ppm NO/500 ppm NH₃/5.0 vol % O₂/N₂ (200,000 hour⁻¹).
Fig. S4. DRIFT spectra of NH₃ and NO + O₂ adsorption on the vanadia/TiO₂ catalysts.
Fig. S5. NH₃ spectra of vanadia/TiO₂ samples.
Fig. S6. V 2p XPS spectra of vanadia/TiO₂ samples.
Fig. S7. Models used in DFT calculations.

REFERENCES AND NOTES
1. N. Y. Topsoe, Mechanism of the selective catalytic reduction of nitric oxide by ammonia elucidated by in situ online Fourier transform infrared spectroscopy. Science 265, 1217–1219 (1994).
2. M. Zhu, J. K. Lai, U. Turnuluri, Z. Wu, I. E. Wachs, Nature of active sites and surface intermediates during SCR of NO with NH₃ at 200°C. Table S4. Vanadium valence distribution in vanadia/TiO₂ samples obtained from XPS.
Table S5. NH₃-SCR de-NO reaction rate constants (k) at 493.15 K (220°C) over the monomeric and dimeric vanadia/TiO₂ surfaces.
Table S6. DFT-calculated structural parameters and energy barriers (ΔE) for the formation of the first NH₃/NO intermediate over the monomeric vanadia/TiO₂ surfaces (i.e., the A→C process in Figs. 2A and 3) with different computational settings. References (39–47).

8. M. Zhu, J. H. Lai, U. Turnuluri, M. E. Ford, Z. Wu, I. E. Wachs, Reaction pathways and kinetics for selective catalytic reduction (SCR) of acidic NOx emissions from power plants with NH₃. ACS Catal. 7, 8358–8361 (2017).
9. D. W. Kwon, K. H. Park, S. C. Hong, Influence of V₂O₃ surface density and vanadyl species on the selective catalytic reduction of NO by NH₃ over V₂O₃/TiO₂ for superior catalytic activity. Appl. Catal. A 499, 1–12 (2015).
10. S. Youn, S. Jeong, D. H. Kim, Effect of oxidation states of vanadium precursor solution in V₂O₃/TiO₂ catalysts for low temperature NH₃ selective catalytic reduction. Catal. Today 232, 185–191 (2014).
11. D. Yun, J. E. Herrera, A novel methodology for in situ redox active site titration of TiO₂-supported vanadia during ethanol partial oxidation catalysis. J. Catal. 350, 72–85 (2017).
12. G. T. Went, L.-J. Leu, A. T. Bell, Quantitative structural analysis of dispersed vanadia species in TiO₂ (anatase)-supported V₂O₅. J. Catal. 134, 479–491 (1992).
13. C. Li, Identifying the isolated transition metal ions/oxides in molecular sieves and on oxide supports by UV resonance Raman spectroscopy. J. Catal. 216, 203–212 (2003).
14. G. T. Went, S. T. Oyama, A. T. Bell, Laser Raman spectroscopy of supported vanadium oxide catalysts. J. Phys. Chem. 94, 4240–4246 (1990).
15. A. Marberger, M. Elsener, D. Ferri, O. Kröcher, VO₃ surface coverage optimization of V₂O₅/WO₃/TiO₂ SCR catalysts by variation of the V loading and by aging. Catalysts 5, 1704–1720 (2015).
16. S. Ch, Y. G. Lee, I.-S. Nam, S.-W. Ham, J.-B. Lee, Characteristics of V₂O₅ supported on sulfated TiO₂ for selective catalytic reduction of NO by NH₃. Appl. Catal. A 200, 177–188 (2000).
17. L. Amaranth, F. Falsig, S. B. Rasmussen, J. V. Lauritsen, P. G. Moses, A complete reaction mechanism for standard and fast selective catalytic reduction of nitrogen oxides on low coverage VO₃/TiO₂(001) catalysts. J. Catal. 346, 188–197 (2017).
18. W. S. Hu, X. Gao, Y. W. Deng, R. Qu, C. H. Zhang, X. B. Zhu, K. F. Cen, Deactivation mechanism of arsenic and resistance effect of SO₄²⁻ on commercial catalysts for selective catalytic reduction of NO with NH₃. Chem. Eng. J. 293, 118–128 (2016).
19. M. H. Kim, S.-W. Ham, Determination of N₂O emissions levels in the selective reduction of NO by NH₃ over an on-site-used commercial V₂O₅–WO₃/TiO₂ catalyst using a modified gas cell. Top. Catal. 53, 597–607 (2010).
20. N. Y. Topsoe, J. A. Dumesic, H. Topsoe, Vanadia/Titania catalysts for selective catalytic reduction of nitric oxide by ammonia: II studies of active sites and formulation of catalytic cycles. J. Catal. 151, 241–252 (1995).
21. C. Wang, S. Yang, H. Chang, Y. Peng, J. Li, Dispersion of tungsten oxide on SCR performance of V₂O₅–WO₃/TiO₂. Acidity, surface species and catalytic activity. Chem. Eng. J. 235, 520–527 (2013).
22. Z. Lian, F. Liu, H. He, K. Liu, Nb-doped VO₃/CoO₃ catalyst for NH₃-SCR of NO at low temperatures. RSC Adv. 5, 37675–37681 (2015).
23. S. Roy, B. Biswanath, M. S. Hegde, G. Madras, Low-temperature selective catalytic reduction of NO with NH₃ over T₄ₓ₇–Mₐ₃Oₓ₂ catalysts. J. Phys. Chem. C 112, 6002–6012 (2008).
24. R. Jin, Y. Liu, Z. Wu, H. Wang, T. Gu, Low-temperature selective catalytic reduction of NO with NH₃ over MnCe oxides supported on TiO₂ and Al₂O₃: A comparative study. Chemosphere 78, 1160–1166 (2010).
25. H. Zhao, S. Bennici, J. Shen, A. Auroux, Nature of surface sites of V₂O₅–TiO₂/2− catalysts and reactivity in selective oxidation of methanol to dimethoxymethane. J. Catal. 272, 176–189 (2010).
26. R. Q. Long, R. T. Yang, Selective catalytic reduction of nitrogen oxides by ammonia over Fe₆⁺-exchanged TiO₂-pillared clay catalysts. J. Catal. 186, 254–268 (1999).
27. F. Liu, K. Asakura, H. He, W. Shan, X. Shi, C. Zhang, Influence of sulfation on iron titanate catalyst for the selective catalytic reduction of NO for NH₃, Appl. Catal. B 103, 369–377 (2011).
28. S. Besselmehl, E. Löffler, M. Mühler, On the role of monomeric vanadyl species in toluene adsorption and oxidation on V₂O₅/TiO₂ catalysts: A Raman and in situ DRIFTS study. J. Mol. Catal. A Chem. 162, 401–411 (2000).
29. A. Christodoulakis, M. Machi, A. A. Lemenoudis, S. Boghossian, Molecular structure and reactivity of vanadia-based catalysts for propane oxidative dehydrogenation studied by in situ Raman spectroscopy and catalytic activity measurements. J. Catal. 222, 293–306 (2004).
30. J. Z. Hu, S. Xu, W.-Z. Li, M. Y. Hu, X. Deng, D. A. Dixon, M. Vasiliu, R. Craciun, Y. Wang, X. Bao, C. H. F. Peden, Investigation of the structure and active sites of TiO₂ nanorod supported VO₃ catalysts by high-field and fast-spinning ⁵¹V MAS NMR. ACS Catal. 5, 3945–3952 (2015).
31. F. Giraud, C. Geantet, N. Guilhame, S. Gros, L. Porcheron, M. Kanniache, D. Bianchi, Experimental microkinetic approach of de-NOx by NH₃ over V₂O₃/WO₃/TiO₂ catalysts. 1. Individual heats of adsorption of adsorbed NH₃ species on a sulfated-free TiO₂ support using adsorption isobars. J. Phys. Chem. C 118, 15664–15676 (2014).
32. S. Canneaux, F. Bohr, E. Henon, KiSThelP: A program to predict thermodynamic properties and rate constants from quantum chemistry results. J. Comput. Chem. 35, 82–93 (2014).

33. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

34. S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 27, 1787–1799 (2006).

35. G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

36. G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999).

37. G. Henkelman, B. P. Uberuaga, H. Jönsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 113, 9901–9904 (2000).

38. G. He, J. Ma, H. He, Role of carbonaceous aerosols in catalyzing sulfate formation. ACS Catal. 8, 3825–3832 (2018).

39. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-Garcia, A. J. Cohen, W. Yang, Revealing noncovalent interactions. J. Am. Chem. Soc. 132, 6498–6506 (2010).

40. T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 33, 580–592 (2012).

41. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01 (Gaussian Inc., 2013).

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