

# Adsorption-Induced Active Vanadium Species Facilitate Excellent Performance in Low-Temperature Catalytic NO<sub>x</sub> Abatement

Zhihua Lian, Jie Wei, Wenpo Shan, Yunbo Yu, Petar M. Radjenovic, Hua Zhang, Guangzhi He, Fudong Liu, Jian-Feng Li,\* Zhong-Qun Tian, and Hong He\*

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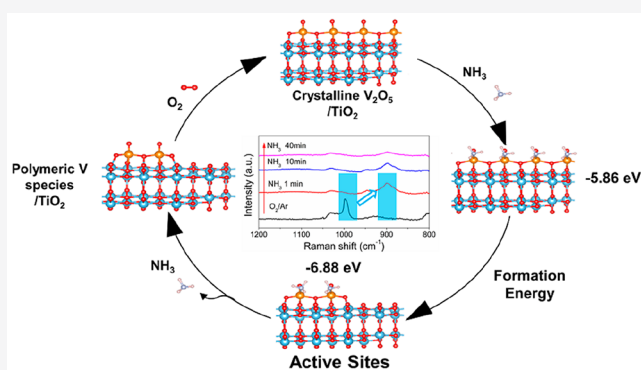
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**ABSTRACT:** Vanadia-based catalysts have been widely used for catalyzing various reactions, including their long-standing application in the deNO<sub>x</sub> process. It has been commonly considered that various vanadium species dispersed on supports with a large surface area act as the catalytically active sites. However, the role of crystalline V<sub>2</sub>O<sub>5</sub> in selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> (NH<sub>3</sub>-SCR) remains unclear. In this study, a catalyst with low vanadia loading was synthesized, in which crystalline V<sub>2</sub>O<sub>5</sub> was deposited on a TiO<sub>2</sub> support that had been pretreated at a high temperature. Surprisingly, the catalyst, which had a large amount of crystalline V<sub>2</sub>O<sub>5</sub>, showed excellent low-temperature NH<sub>3</sub>-SCR activity. For the first time, crystalline V<sub>2</sub>O<sub>5</sub> on low-vanadium-loading catalysts was found to be transformed to polymeric vanadyl species by the adsorption of NH<sub>3</sub>. The generated active polymeric vanadyl species played a crucial role in NH<sub>3</sub>-SCR, leading to remarkably enhanced catalytic performance at low temperatures. This new finding provides a fundamental understanding of the metal oxide-catalyzed chemical reaction and has important implications for the development and commercial applications of NH<sub>3</sub>-SCR catalysts.



## INTRODUCTION

Reactive sites are essential in heterogeneous and homogeneous catalysis. Identification and characterization of active species is a prerequisite for understanding any catalytic reaction mechanism and for the rational design of high-performance catalysts.<sup>1</sup> However, the species identified by common *ex situ* methods can differ from those present under realistic catalytic reaction conditions.<sup>2–4</sup> Therefore, it is crucial to accurately determine the active species under reaction conditions. In a number of cases, catalytic surfaces have been found to undergo reconstruction under reaction conditions.<sup>5,6</sup> For example, the composition and chemical state of core–shell Rh<sub>0.5</sub>Pd<sub>0.5</sub> bimetallic nanoparticles were found to change dramatically under redox conditions.<sup>7</sup> Under selective catalytic reduction reaction conditions for NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR), mobilized Cu ions were reported to travel through zeolite windows and form transient ion pairs that participated in an O<sub>2</sub>-mediated Cu<sup>I</sup> → Cu<sup>II</sup> redox step integral to the catalytic reaction.<sup>8</sup>

Vanadia-based catalysts are attracting great interest in many industrially important processes, such as the production of sulfuric acid by SO<sub>2</sub> oxidation, selective oxidation of hydrocarbons, and NH<sub>3</sub>-SCR.<sup>9,10</sup> NH<sub>3</sub>-SCR of NO<sub>x</sub> over vanadia-based catalysts is a widely used strategy for controlling NO<sub>x</sub> emissions.<sup>11–18</sup> Vanadium species act as the active sites in the

catalytic reaction. Therefore, it is important to investigate these species in depth, especially under reaction conditions.

A number of different vanadium species, such as monomeric vanadyl, polymeric vanadate, and V<sub>2</sub>O<sub>5</sub> crystallites, can exist on the surface of vanadia-based catalysts used in NH<sub>3</sub>-SCR reactions.<sup>19,20</sup> At low vanadia concentrations, monomeric vanadyl species can form on the catalyst surface, while at higher concentrations, polymeric vanadate species and crystalline V<sub>2</sub>O<sub>5</sub> can exist on the catalyst surface.<sup>21</sup> Previously, we found that monomeric vanadyl species possessed lower NH<sub>3</sub>-SCR activity than polymeric vanadyl species, especially at low temperatures.<sup>22</sup> The coupling effect of the polymeric structure shortened the reaction pathway for the regeneration of redox sites and substantially reduced the overall reaction barrier of the catalytic cycle. Thus, the concentration of polymeric vanadyl surface species can dictate the low-temperature activity of vanadia-based catalysts for NH<sub>3</sub>-SCR. Surface-dispersed vanadia species have received a lot of

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attention, while only scant attention has been paid to crystalline  $V_2O_5$ . Crystalline  $V_2O_5$  has usually been found to exist on catalysts with a low specific surface area or after high-temperature treatment. However, the role of crystalline  $V_2O_5$  in the  $NH_3$ -SCR of  $NO_x$  remains unclear. Investigating crystalline  $V_2O_5$  on catalysts in depth is beneficial to gain an understanding of the vanadia-based catalysts to enable the development of excellent  $NH_3$ -SCR catalysts.

Herein, a high-temperature (850 °C) calcination pretreatment step was used to obtain  $TiO_2$  with a small specific surface area, on which crystalline  $V_2O_5$  was deposited (V/Ti-850). Surprisingly, V/Ti-850 had much higher  $NH_3$ -SCR activity than the untreated catalyst (V/Ti). To further investigate the effect of pretreatment, *in situ* Raman spectroscopy was performed under real  $NH_3$ -SCR conditions. The *in situ* Raman results demonstrated that crystalline  $V_2O_5$  in V/Ti-850 could transform to polymeric vanadyl species during  $NH_3$  adsorption, which remarkably enhanced the catalytic performance for low-temperature  $NH_3$ -SCR of  $NO_x$ . This novel finding provides fundamental insight into the  $NH_3$ -SCR reaction and has important implications for the development and commercial application of  $NH_3$ -SCR catalysts, especially vanadia-based catalysts with low loading.

## EXPERIMENTAL SECTION

**Catalyst Preparation.** The V/Ti catalyst was prepared by a conventional impregnation method with  $TiO_2$  (DT-51, Millennium Chemicals) as the support and ammonium metavanadate (1.0 wt %  $V_2O_5$ ) as the precursor. First, ammonium metavanadate was dissolved in oxalic acid solution followed by mixing with  $TiO_2$  powder. Then, the resulting slurry was dried in a rotary evaporator after stirring. Finally, the obtained powder was dried overnight at 100 °C and subsequently calcined at 500 °C for 4 h in static air.  $TiO_2$  was calcined at 850 °C for 2 h in static air to obtain Ti-850, and V/Ti-850 was synthesized with Ti-850 as a support by the same procedure used for V/Ti.

**Activity Test.** The activity tests were carried out in a fixed-bed quartz flow reactor with 0.3 mL of the catalyst (40–60 mesh). The reaction gas consisted of 500 ppm of  $NO$ , 500 ppm of  $NH_3$ , 5%  $O_2$ , 5%  $H_2O$  (when used), and 100 ppm of  $SO_2$  (when used), balanced with  $N_2$ . The total flow rate was 500 mL  $min^{-1}$ , with a gas hourly space velocity (GHSV) of 100 000  $h^{-1}$ . The concentrations of  $NO$ ,  $NO_2$ ,  $N_2O$ , and  $NH_3$  were continuously analyzed by a Fourier transform infrared gas analyzer (Thermo Fisher IGS) equipped with a 2 m gas cell.

**Catalyst Characterization.** Brunauer–Emmett–Teller (BET) analysis, X-ray diffraction (XRD), and  $H_2$  temperature-programmed reduction ( $H_2$ -TPR) were conducted using the procedures reported in our previous works.<sup>22,23</sup> The Raman spectra were measured on a Jobin-Yvon Horiba Xplora confocal Raman system. The excitation wavelength was 638 nm, and a 50× microscope objective with a numerical aperture of 0.55 was used in all Raman measurements. The laser power was controlled at about 1.5 mW. *In situ* experiments were performed in a customized Raman cell made in-house with atmospheric and temperature control. Before the Raman experiments, the samples were pretreated under  $O_2/Ar$  flow at 350 °C for 0.5 h. A reactant mixture (50 mL  $min^{-1}$ ) of 500 ppm of  $NH_3$  and/or 500 ppm of  $NO$  and 5%  $O_2$  balanced with Ar was subsequently introduced into the *in situ* cell, and time-dependent *in situ* Raman spectra were obtained. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F20 microscope with an acceleration voltage of 200 kV. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed on a Fourier transform infrared (FTIR) spectrometer (Nicolet iS50) equipped with a Smart Collector and a MCT/A detector cooled by liquid  $N_2$ . First, the sample was pretreated in a 20 vol %  $O_2/N_2$  flow at 300 °C for 0.5 h and then cooled to 175 °C. The background spectra were

collected in flowing  $N_2$  and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 500 ppm of  $NH_3$  or 500 ppm of  $NO$  + 5 vol %  $O_2$ , 300 mL  $min^{-1}$  total flow rate, and  $N_2$  balance. All spectra were recorded by accumulating 100 scans with a resolution of 4  $cm^{-1}$ .

**Density Functional Theory (DFT) Calculations.** DFT calculations with periodic boundary conditions (PBCs) were performed using the Perdew–Burke–Ernzerhof (PBE) functional,<sup>24</sup> as implemented in the Vienna *ab initio* simulation package (VASP 5.4.4).<sup>25</sup> The projector augmented wave (PAW) method was used to describe the core–valence electron interaction.<sup>26</sup> All calculations were spin-polarized. The DFT+U approach was applied to the V atom in  $VO_x$  and Ti atom in  $TiO_2$  with the values of  $U_{eff} = 2.0$  and 2.3 eV, respectively, to describe the on-site Coulomb interactions.<sup>27</sup> The plane wave energy cutoff was set to 400 eV for all atoms. To calculate the formation energy of monomeric, dimeric, and crystalline  $V_2O_5$  on  $TiO_2$  surfaces, a (2 × 4) supercell of the anatase (101) surface with two stoichiometric  $TiO_2$  layers was used as the substrate.<sup>22</sup> Atoms in the bottom stoichiometric  $TiO_2$  layer were kept frozen at their bulk positions, whereas all other atoms were fully relaxed. Only the  $\Gamma$  point of the Brillouin zone was sampled. A vacuum spacing of 15 Å was used to avoid the periodic image interaction normal to the surface. The conjugate gradient algorithm was used for geometric optimization until the forces on all relaxed atoms were less than 0.02 eV Å<sup>-1</sup>. The Gaussian smearing method with a smearing width of 0.05 eV was applied to accelerate the convergence of integration at the Brillouin zone.

## RESULTS AND DISCUSSION

**Structural Properties.**  $TiO_2$  calcined at 850 °C was used to support  $V_2O_5$  (1 wt %), giving a V/Ti-850 catalyst. For comparison, a V/Ti catalyst without  $TiO_2$  pretreatment was also obtained. As shown in Table 1, the specific surface areas of

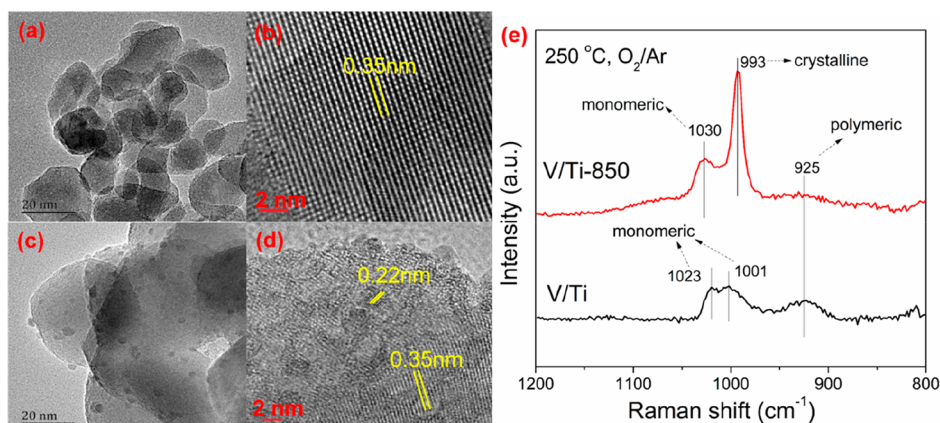
**Table 1.**  $N_2$  Physisorption Results for the Vanadia-Based Catalysts

catalyst	specific surface area (m <sup>2</sup> g <sup>-1</sup> )	average pore diameter (nm)	pore volume (mL g <sup>-1</sup> )
V/Ti	83.1	15.0	0.42
V/Ti-850	11.2	32.5	0.09

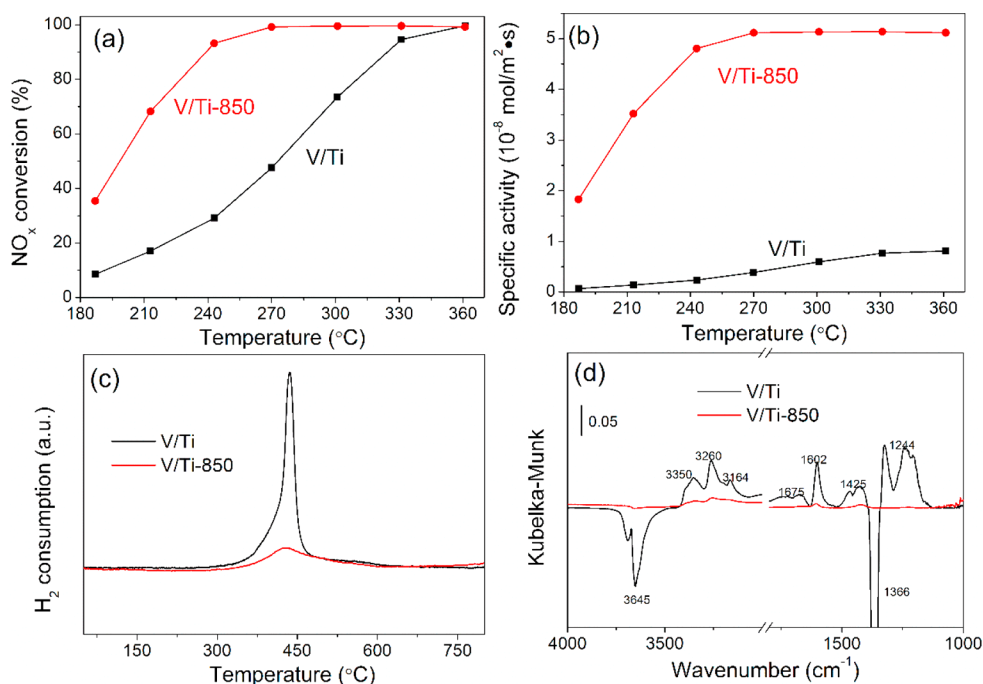
V/Ti and V/Ti-850 were 83.1 and 11.2 m<sup>2</sup> g<sup>-1</sup>, respectively.  $TiO_2$  calcination resulted in a remarkable decrease in the specific surface area and pore volume, while the average pore diameter increased. From the XRD patterns in Figure S1 of the Supporting Information, both V/Ti and V/Ti-850 possessed the crystalline anatase  $TiO_2$  structure. However, V/Ti-850 had higher  $TiO_2$  crystallinity as a result of the calcination pretreatment. Also, no diffraction peaks from vanadium species were observed for either of these catalysts.

**Existence of Crystalline  $V_2O_5$ .** The morphologies of the two vanadia-based catalysts were investigated with high-resolution transmission electron microscopy (HRTEM). In Figure 1a, it can be seen that the V/Ti catalyst had a nanoparticle-like morphology with ~30 nm average nanoparticle diameter. In Figure 1b, the lattice fringes with 0.35 nm interplanar spacings were attributed to  $TiO_2$  (101). No structural features of vanadium species were observed, indicating that they were highly dispersed across the V/Ti catalyst surface.

In contrast, as seen in Figure 1c, V/Ti-850 was composed of irregular particles with varying diameters between 30 and 60 nm. Besides  $TiO_2$  (101), Figure 1d also shows lattice fringes of  $V_2O_5$  (002), with 0.22 nm interplanar spacings. These spacings corresponded to the ~3–5 nm  $V_2O_5$  nanoparticles dispersed



**Figure 1.** HRTEM images of (a and b) V/Ti and (c and d) V/Ti-850 and (e) Raman spectra of vanadia-based catalysts with (red line) and without (black line) an 850 °C calcination pretreatment step, recorded under exposure to O<sub>2</sub>/Ar at 250 °C.



**Figure 2.** (a) NH<sub>3</sub>-SCR of NO<sub>x</sub> activity. (b) Specific activity normalized by the specific surface area over V/Ti and V/Ti-850. Reaction conditions: 500 ppm of NO, 500 ppm of NH<sub>3</sub>, 5 vol % O<sub>2</sub>, total gas flow rate of 500 mL min<sup>-1</sup>, and space velocity of 100 000 h<sup>-1</sup>. (c) H<sub>2</sub>-TPR results. (d) DRIFTS of NH<sub>3</sub> adsorption over V/Ti and V/Ti-850.

on the TiO<sub>2</sub> support visible in Figure 1c. Thus, the 850 °C pretreatment step produced larger and more irregular TiO<sub>2</sub> particles and decreased the specific surface area considerably, although the anatase structure was maintained. Although crystalline V<sub>2</sub>O<sub>5</sub> was observed on V/Ti-850 with HRTEM, crystalline V<sub>2</sub>O<sub>5</sub> was not detected by XRD, which is likely due to the size and concentration of V<sub>2</sub>O<sub>5</sub> particles being lower than the detection limit.

Raman spectroscopy was used to determine the structure of the surface vanadium species in both catalysts exposed to O<sub>2</sub>/Ar at 250 °C, and the results are shown in Figure 1e. According to the literature,<sup>21,28,29</sup> the Raman bands at 1023 (1030) and 993 cm<sup>-1</sup> are characteristic of monomeric vanadyl species and crystalline V<sub>2</sub>O<sub>5</sub>, respectively, while the band at 925 cm<sup>-1</sup> for V/Ti is attributed to polymeric vanadyl species.<sup>22</sup> The 1001 cm<sup>-1</sup> band was ascribed to vanadyl species in close proximity but still monomeric in nature.<sup>28</sup> In comparison to V/

Ti, V/Ti-850 contained a considerably greater amount of crystalline V<sub>2</sub>O<sub>5</sub> species. In combination of HRTEM and Raman, it can be concluded that abundant crystalline V<sub>2</sub>O<sub>5</sub> was present on V/Ti-850, while almost no crystalline V<sub>2</sub>O<sub>5</sub> was present on V/Ti. The small specific surface area of the support was the reason for the formation of crystalline V<sub>2</sub>O<sub>5</sub> on V/Ti-850.

**NH<sub>3</sub>-SCR Activity.** As shown above, both polymeric and monomeric vanadyl species were detected on V/Ti, while monomeric vanadyl and crystalline V<sub>2</sub>O<sub>5</sub> predominated on V/Ti-850. In general, it has been recognized that surface-dispersed vanadia species are the active sites for the NH<sub>3</sub>-SCR reaction; therefore, the formation of crystalline V<sub>2</sub>O<sub>5</sub> is considered undesirable. In previous work, we showed that polymeric vanadyl species had higher activity than monomeric vanadyl species in the NH<sub>3</sub>-SCR of NO<sub>x</sub>.<sup>22</sup> Also, here, the specific surface area of V/Ti was much larger than that of V/

Ti-850. Therefore, it was expected that the SCR activity over V/Ti should be higher than that over V/Ti-850.

Thus, the NH<sub>3</sub>-SCR activity over V/Ti and V/Ti-850 was investigated, and the results are shown in Figure 2a. NO<sub>x</sub> conversion over V/Ti increased with the temperature, with over 90% NO<sub>x</sub> conversion achieved above 330 °C. Surprisingly, for the V/Ti-850 catalyst, the performance was significantly enhanced, with nearly 100% NO<sub>x</sub> conversion at 243 °C and above. More remarkably, in Figure 2b, the specific activity (activity normalized by the specific surface area) of V/Ti-850 was much higher than that of V/Ti. Even in the presence of 5% H<sub>2</sub>O, V/Ti-850 still showed much higher NO<sub>x</sub> conversion than V/Ti (Figure S2 of the Supporting Information). The NO<sub>x</sub> conversion under the conditions of heating from 100 to 350 °C at the rate of 10 °C min<sup>-1</sup> (Figure S3 of the Supporting Information) also exhibited that the low-temperature activity over V/Ti-850 was better than that over V/Ti. Figure S4 of the Supporting Information shows that, like 1 V/Ti, the thermal treatment of the support also improved the SCR activity of 0.5 V/Ti. However, it decreased the NO<sub>x</sub> conversion of 3 V/Ti, indicating that the thermal treatment mainly promoted the catalytic activity of low-loaded vanadia catalysts. As a result of the existence of sulfurous compounds in fossil fuels, the effect of SO<sub>2</sub> on the catalytic activity of V/Ti-850 at 300 °C was also investigated (Figure S5 of the Supporting Information). The NO<sub>x</sub> conversion of V/Ti-850 was constant at ~90% when exposed to a gas stream with 5% H<sub>2</sub>O and 100 ppm of SO<sub>2</sub> for 12 h, indicating that the V/Ti-850 catalyst has excellent resistance to poisoning. This result, surprisingly, illustrates that V/Ti-850, containing abundant crystalline V<sub>2</sub>O<sub>5</sub>, has better catalytic performance than V/Ti, containing greater amounts of polymeric vanadyl species.

**Redox Capability and Acidity.** Both redox sites and acid sites are essential for the NH<sub>3</sub>-SCR reaction and can affect the catalytic performance.<sup>30</sup> Therefore, the redox capability and acidity of the vanadia-based catalysts were investigated. Figure 2c shows the H<sub>2</sub>-TPR results for the vanadia-based catalysts. Both catalysts presented a broad reduction peak centered at 430 °C, attributed to the reduction of surface vanadium or titanium species.<sup>31,32</sup> However, V/Ti-850 had a much lower H<sub>2</sub> consumption than V/Ti, indicating that it contained a lower amount of reducible species. In comparison to V/Ti-850, a stronger interaction between vanadium and titanium on V/Ti resulted in more facile reduction of titanium species, consuming a larger amount of H<sub>2</sub>.

Next, DRIFTS was used to investigate the presence of acid sites on the vanadia-based catalysts. Figure 2d shows the DRIFT spectra acquired after exposing V/Ti and V/Ti-850 to NH<sub>3</sub> and purging with N<sub>2</sub> at 200 °C. NH<sub>4</sub><sup>+</sup> adsorbed on Brønsted acid sites (1675 and 1425 cm<sup>-1</sup>) and NH<sub>3</sub> coordinated to Lewis acid sites (1602, 1244, 3350, and 3260 cm<sup>-1</sup> and  $\nu(\text{N-H})$  of 3164 cm<sup>-1</sup>) were observed.<sup>33-35</sup> From the spectra, the number of acid sites on V/Ti-850 was significantly lower than that on V/Ti, which should be related to the decreased specific surface area of V/Ti-850, in accordance with the NH<sub>3</sub>-TPD results (Figure S6 of the Supporting Information). When NO<sub>x</sub> was introduced to V/Ti and V/Ti-850 samples with pre-adsorbed NH<sub>3</sub>, the peaks attributed to adsorbed NH<sub>3</sub> species gradually diminished (Figure S7 of the Supporting Information). This indicates that the adsorbed NH<sub>3</sub> species participate in NH<sub>3</sub>-SCR of NO<sub>x</sub>.

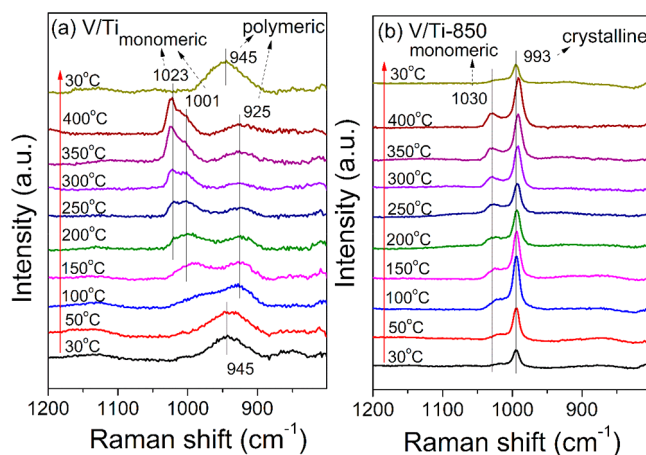
Generally, a larger specific surface area signifies more active sites, contributing to better catalytic performance. However,

V/Ti-850 had a much smaller specific surface area but higher NO<sub>x</sub> conversion than V/Ti. Surprisingly, the V/Ti-850 catalyst did not exhibit any advantages in terms of redox capability or surface acidity, of which each has been considered to be a requirement for promoting the NH<sub>3</sub>-SCR reaction. Therefore, there must be some other factor(s) to account for the excellent catalytic performance of V/Ti-850.

#### Transformation of Surface Species on Catalysts.

Previous reports have shown that bulk metal oxides can spread on the surface of oxide supports and that spreading of V<sub>2</sub>O<sub>5</sub> over the TiO<sub>2</sub> surface is favored on well-defined anatase crystal planes under oxidizing conditions.<sup>36</sup> At 230 °C under methanol oxidation conditions, crystalline V<sub>2</sub>O<sub>5</sub> completely transformed into surface vanadia species, which increased the catalytic activity.<sup>37</sup> To our knowledge, the spreading of vanadia during the NH<sub>3</sub>-SCR reaction has not been reported before. We considered whether crystalline V<sub>2</sub>O<sub>5</sub> species on V/Ti-850 could transform to surface vanadia species under heating or NH<sub>3</sub>-SCR conditions.

Figure 5 shows the Raman spectra of V/Ti and V/Ti-850 under an O<sub>2</sub>/Ar atmosphere at different temperatures. At relatively low temperatures of 30–50 °C, Raman bands at 940 cm<sup>-1</sup>, attributed to polymeric vanadyl species, were observed on V/Ti (Figure 3a). With an increasing temperature, the



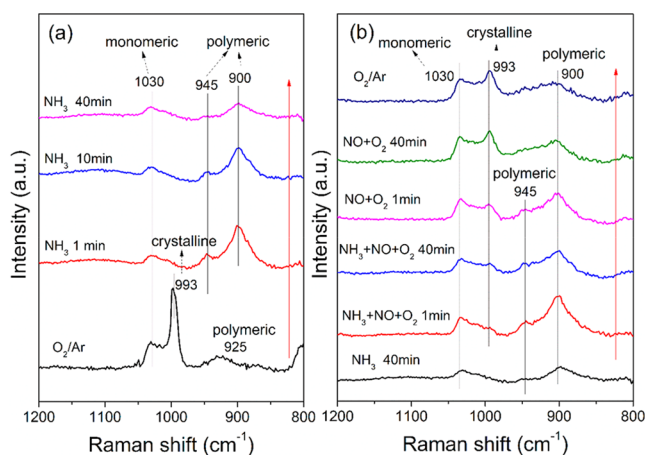
**Figure 3.** Raman spectra of (a) V/Ti and (b) V/Ti-850 under an O<sub>2</sub>/Ar atmosphere at different temperatures.

bands at 1001 and 1023 cm<sup>-1</sup> ascribed to surface monomeric vanadyl species appeared, and their intensity increased with a concomitant decrease in the intensity of the 940 cm<sup>-1</sup> band, which also red shifted to 925 cm<sup>-1</sup>. This red shift might be due to a change in the degree of polymerization of the vanadyl species.<sup>21,29</sup> At 400 °C, the intensity of the 940 cm<sup>-1</sup> band was much weaker than at 30 °C, while the 1023 cm<sup>-1</sup> band became dominant, indicating that most of the polymeric vanadyl species were transformed into surface monomeric vanadyl species. This might be the main reason for the low catalytic activity over V/Ti. It has been reported that surface migration or diffusion of vanadium species on TiO<sub>2</sub> occurs at temperatures high enough to overcome the intrinsic resistance.<sup>37</sup> Decreasing the temperature back to 30 °C caused polymerization of monomeric vanadyl species, and thus, the band corresponding to polymeric species reappeared at 940 cm<sup>-1</sup>. Therefore, the vanadium species on the V/Ti catalyst can be reversibly transformed by altering the temperature.

In contrast, the vanadium species observed on V/Ti-850 behaved differently at an elevated temperature from those on V/Ti (Figure 3b). At 30 °C, two bands at 993 and 1030  $\text{cm}^{-1}$ , attributed to crystalline  $\text{V}_2\text{O}_5$  and monomeric vanadyl species, respectively, were observed for V/Ti-850. With an increasing temperature, the intensities of bands at 1030 and 993  $\text{cm}^{-1}$  became stronger as a result of the higher crystallinity at a higher temperature, and no polymeric species were observed during the whole process. This phenomenon was different from the studies<sup>36,37</sup> that reported the thermal spreading of crystalline  $\text{V}_2\text{O}_5$  on an oxide support surface. Decreasing the temperature back to 30 °C caused the Raman spectrum to recover to its original profile.

*In situ* Raman experiments were conducted to further investigate the effects of  $\text{NH}_3$  and/or  $\text{NO} + \text{O}_2$  on the surface structure of V/Ti and V/Ti-850. Figure S8 of the Supporting Information shows *in situ* Raman spectra of V/Ti exposed to  $\text{NH}_3$ ,  $\text{NH}_3 + \text{NO} + \text{O}_2$ , and  $\text{NO} + \text{O}_2$  atmospheres in sequence at 250 °C. The bands at 1023, 1001, and 925  $\text{cm}^{-1}$  were visible under  $\text{O}_2/\text{Ar}$ . Upon exposure to  $\text{NH}_3$ , the bands associated with vanadium species all gradually diminished. After  $\text{NO} + \text{O}_2$  was also introduced, the weak bands at 1001 and 925  $\text{cm}^{-1}$  reappeared. After shutting off  $\text{NH}_3$ , the band at 1023  $\text{cm}^{-1}$  was also observed. For the V/Ti catalyst, these results suggest that  $\text{NH}_3$  adsorbs on monomeric and polymeric vanadyl species and then reacts with  $\text{NO} + \text{O}_2$ .

For V/Ti-850 under  $\text{O}_2/\text{Ar}$  conditions (Figure 4a), crystalline  $\text{V}_2\text{O}_5$  (993  $\text{cm}^{-1}$ ) and monomeric vanadyl species



**Figure 4.** *In situ* Raman spectra of V/Ti-850 (a) at different  $\text{NH}_3$  exposure times and (b) under different reaction conditions at 250 °C.

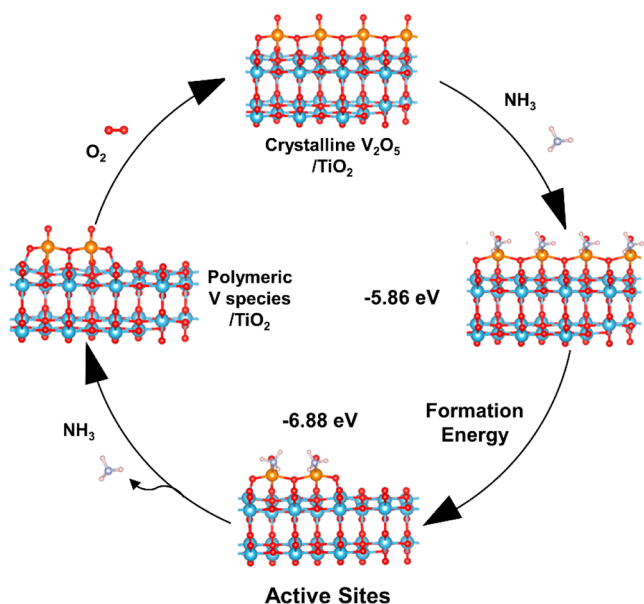
(1030  $\text{cm}^{-1}$ ) were present. Notably, upon exposure to  $\text{NH}_3$ , the band at 993  $\text{cm}^{-1}$  disappeared and two new bands at 900 and 945  $\text{cm}^{-1}$ , assigned to polymeric vanadyl species,<sup>29</sup> instantly appeared. This demonstrates that crystalline  $\text{V}_2\text{O}_5$  completely transformed to surface polymeric vanadyl species during  $\text{NH}_3$  adsorption. According to DFT calculations (Table S1 and Figure S9 of the Supporting Information), the formation energy was  $-6.00$ ,  $-6.88$ , and  $-5.86$  eV for  $\text{NH}_3$ -adsorbed monomeric, polymeric, and crystalline  $\text{V}_2\text{O}_5$  on  $\text{TiO}_2$ , respectively, indicating that adsorption of  $\text{NH}_3$  was beneficial to the formation of polymeric vanadia on  $\text{TiO}_2$ . Thus, when  $\text{NH}_3$  was introduced, crystalline  $\text{V}_2\text{O}_5$  transformed into polymeric vanadyl species, and these surface-dispersed vanadia species could act as active sites in the  $\text{NH}_3$ -SCR reaction, with polymeric vanadyl species being more active

than monomeric vanadyl species.<sup>19,22</sup> Therefore, the spreading of crystalline  $\text{V}_2\text{O}_5$  on the catalyst surface could facilitate the  $\text{NH}_3$ -SCR reaction and explains why V/Ti-850 exhibits excellent catalytic performance at low temperatures. Introducing  $\text{NH}_3$  also caused the band at 1030  $\text{cm}^{-1}$  to decrease, indicating that  $\text{NH}_3$  was also adsorbed on monomeric vanadyl species.

In addition to panels a and b of Figure 4, the changes in various vanadium species on V/Ti-850 under different atmospheres, as reflected by changes in the integrated area of their Raman peaks (1030, 900, and 993  $\text{cm}^{-1}$  for monomeric, polymeric vanadyl, and crystalline  $\text{V}_2\text{O}_5$  species, respectively), are shown in Figure S10 of the Supporting Information. When  $\text{NH}_3$  was introduced, the peak intensities of monomeric vanadyl and crystalline  $\text{V}_2\text{O}_5$  both decreased, while that of polymeric vanadyl species increased immediately. With increasing the  $\text{NH}_3$  exposure time, the intensity of the 900  $\text{cm}^{-1}$  band decreased as a result of  $\text{NH}_3$  interacting with polymeric vanadyl species. Following this, introduction of a  $\text{NO} + \text{O}_2$  atmosphere to the system caused the intensity of the 900  $\text{cm}^{-1}$  band to increase, suggesting that  $\text{NH}_3$  interacting with polymeric vanadyl species reacted with  $\text{NO} + \text{O}_2$ , allowing for more polymeric vanadyl species to be detected. Although our previous study<sup>22</sup> showed that  $\text{NH}_3$  preferentially adsorbs on Ti surface sites on V/Ti catalysts, V sites can also act as acid sites capable of adsorbing  $\text{NH}_3$  molecules. The intensities of the band associated with polymeric species (900  $\text{cm}^{-1}$ ) and those for crystalline  $\text{V}_2\text{O}_5$  decreased and increased, respectively, with increasing  $\text{NH}_3 + \text{NO} + \text{O}_2$  exposure before stabilizing, indicating that some of the polymeric vanadyl species reversibly transformed into crystalline  $\text{V}_2\text{O}_5$ . When only  $\text{NO} + \text{O}_2$  was present (i.e., shutting off  $\text{NH}_3$ ), the intensity of the band at 900  $\text{cm}^{-1}$  gradually weakened with increasing exposure time, while the bands at 993 and 1030  $\text{cm}^{-1}$  both gradually strengthened. Further oxidation of the sample at 250 °C (under  $\text{O}_2/\text{Ar}$ ) again resulted in the appearance of crystalline  $\text{V}_2\text{O}_5$  and a decrease in polymeric species. Conversion of crystalline  $\text{V}_2\text{O}_5$  to polymeric species was partly reversible, although it did not recover its original state. After the reaction progressed, crystalline  $\text{V}_2\text{O}_5$  and monomeric and polymeric vanadyl species were all present on the catalyst surface.

Figure 5 schematically shows the structural transformation of crystalline  $\text{V}_2\text{O}_5$  on V/Ti-850 inferred from the experimental results. In the presence of  $\text{NH}_3$ , crystalline  $\text{V}_2\text{O}_5$  on V/Ti-850 transformed into a polymeric vanadyl species as a result of the lower formation energy for  $\text{NH}_3$  adsorbed on polymeric vanadyl species than that on crystalline  $\text{V}_2\text{O}_5$ . In our previous study,<sup>22</sup> polymeric vanadyl species were found to determine the  $\text{NH}_3$ -SCR activity at low temperatures. Therefore, the active sites were generated under  $\text{NH}_3$  conditions, and V/Ti-850 exhibited excellent catalytic performance for  $\text{NH}_3$ -SCR at a low temperature. When the sample was exposed to  $\text{O}_2$  again, a part of polymeric vanadyl species reverted to crystalline  $\text{V}_2\text{O}_5$ .

It was reported that bulk vanadium oxide catalysts and W-substituted vanadium oxide catalysts show excellent  $\text{NH}_3$ -SCR activity, even at low temperatures below 150 °C.<sup>38,39</sup> In our work, *in situ* Raman results showed that the presence of  $\text{NH}_3$  induces the transformation of crystalline  $\text{V}_2\text{O}_5$  to polymeric vanadyl species, leading to remarkably enhanced catalytic performance at low temperatures. This illustrates exactly the mechanism for the high activity of the bulk  $\text{V}_2\text{O}_5$  catalyst.



**Figure 5.** Schematic of the structural transformation of  $V_2O_5$  on the V/Ti-850 catalyst.

However, the tendency of  $V_2O_5$  to spread on  $TiO_2$  might also be influenced by the preparation conditions, including the vanadium loading. Further research into conditions causing the spreading of crystalline  $V_2O_5$  is ongoing.

## CONCLUSION

High-temperature (850 °C) calcination of the  $TiO_2$  support in advance of loading with vanadia resulted in a decrease in the specific surface area, an enhancement in anatase crystallinity, and the formation of crystalline  $V_2O_5$  on the surface of the V/Ti-850 catalysts. In addition, the calcined V/Ti-850 catalyst did not have any advantages in terms of redox capability or surface acidity, which were both traditionally considered to be required in the  $NH_3$ -SCR of  $NO_x$ . However, V/Ti-850 showed significantly higher catalytic activity at low temperatures than untreated V/Ti. For the first time, we find that crystalline  $V_2O_5$  on low-vanadium-loading catalysts can transform to a polymeric vanadyl species under  $NH_3$ -SCR reaction conditions, thereby generating active sites, which remarkably enhance the catalytic performance of the vanadia-based catalyst at a low temperature. The active sites generated under reaction conditions played an important role in the  $NH_3$ -SCR reaction. This work offers an effective new approach that can guide the preparation of catalysts for commercial applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c05354>.

XRD profiles,  $NH_3$ -SCR activity, effect of  $SO_2$  on  $NO_x$  conversion,  $NH_3$ -TPD results, *in situ* DRIFTS, *in situ* Raman spectra, DFT calculation, and plot of the change in integral area of various Raman peaks (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Jian-Feng Li – State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry

for Energy Materials (iChEM), College of Chemistry and Chemical Engineering, College of Materials, College of Energy, Xiamen University, Xiamen, Fujian 361005, People's Republic of China; [orcid.org/0000-0003-1598-6856](https://orcid.org/0000-0003-1598-6856); Email: [li@xmu.edu.cn](mailto:li@xmu.edu.cn)

Hong He – Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, People's Republic of China; State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China; Email: [hhe@iue.ac.cn](mailto:hhe@iue.ac.cn), [honghe@rcees.ac.cn](mailto:honghe@rcees.ac.cn)

## Authors

Zhijia Lian – Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, People's Republic of China; [orcid.org/0000-0002-7413-180X](https://orcid.org/0000-0002-7413-180X)

Jie Wei – State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), College of Chemistry and Chemical Engineering, College of Materials, College of Energy, Xiamen University, Xiamen, Fujian 361005, People's Republic of China

Wenpo Shan – Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, People's Republic of China; [orcid.org/0000-0003-2818-5708](https://orcid.org/0000-0003-2818-5708)

Yunbo Yu – Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, People's Republic of China; State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China; University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China; [orcid.org/0000-0003-2935-0955](https://orcid.org/0000-0003-2935-0955)

Petar M. Radjenovic – State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), College of Chemistry and Chemical Engineering, College of Materials, College of Energy, Xiamen University, Xiamen, Fujian 361005, People's Republic of China

Hua Zhang – State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), College of Chemistry and Chemical Engineering, College of Materials, College of Energy, Xiamen University, Xiamen, Fujian 361005, People's Republic of China; [orcid.org/0000-0001-9588-9030](https://orcid.org/0000-0001-9588-9030)

Guangzhi He – State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China; [orcid.org/0000-0003-1770-3522](https://orcid.org/0000-0003-1770-3522)

Fudong Liu – Department of Civil, Environmental, and Construction Engineering, Catalysis Cluster for Renewable Energy and Chemical Transformations (REACT), NanoScience Technology Center (NSTC), University of Central Florida, Orlando, Florida 32816, United States; [orcid.org/0000-0001-8771-5938](https://orcid.org/0000-0001-8771-5938)

Zhong-Qun Tian – State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), College of Chemistry and Chemical Engineering, College of Materials, College of Energy, Xiamen University, Xiamen, Fujian 361005, People's Republic of China; [orcid.org/0000-0002-9775-8189](https://orcid.org/0000-0002-9775-8189)

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.1c05354>

## Notes

The authors declare no competing financial interest.

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