

Significant promotion effect of rutile phase on V₂O₅/TiO₂ catalyst for NH₃-SCR

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Experiments

Catalyst preparation and activity tests

All chemicals used in this study were analytical reagent. TiO₂ support was supplied by Alfa Aesar Company, and this sample was denoted as Ti-1. Ti-1 was treated in 10% H₂/N₂ at 700 °C for 2 h to obtain Ti-2. 1 wt.% V₂O₅/TiO₂ were prepared by impregnation method according to the previous work ¹, using two types of TiO₂ and an aqueous solution of NH₄VO₃ (H₂C₂O₄ was added to facilitate the dissolution of NH₄VO₃). After impregnation, the excess water was removed using a rotary evaporator at 60 °C. The sample was first dried at 100 °C overnight and then followed by calcination at 500 °C in air for 3 h. In addition, a catalyst with 0.7% V₂O₅ loading on Ti-2 (denoted as 0.7V/Ti-2) was prepared to ensure that the VO_x surface densities on Ti-1 and Ti-2 supports are similar with each other.

The activity tests for NH₃-SCR were performed in a fixed-bed quartz flow reactor with 0.3 mL of catalysts (40-60 mesh). The inlet gas included 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂ and N₂ balance at a total flow rate of 500 mL/min (GHSV = 100 000 h⁻¹). Analysis of inlet and outlet gases were carried out according to our previous study².

Catalyst characterization

XRD, BET, NMR and H₂-TPR were conducted according to our previous works ^{2, 3}. NMR spectra were collected under ambient conditions. High-resolution transmission electron microscopy (HR-TEM) images were obtained on FEI Tecnai G2 F20 with an

acceleration voltage of 200 kV. *In situ* DRIFTS experiments were performed on and FTIR spectrometer (Nicolet iS 50) equipped with a Smart Collector and an MCT/A detector cooled by liquid N₂. Firstly, the sample was pretreated in a 20 vol % O₂/N₂ flow at 300 °C for 0.5 h, and then cooled down to 175 °C. The background spectra were collected in flowing N₂ and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 500 ppm of NH₃, 300 mL/min total flow rate, and N₂ to balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹. The Raman spectra were obtained on a Jobin-Yvon Horiba Xplora confocal Raman system. The excitation wavelength was 638 nm, and the laser power was controlled at about 1.5 mW. Before the Raman experiments, the samples were pretreated under O₂/Ar flow at 350 °C for 0.5 h. The XPS results of the catalysts were recorded on a scanning X-ray microprobe (Axis Ultra, Kratos Analytical Ltd.) using Al K α radiation (1486.7 eV). All of the binding energies were calibrated using the C 1s peak (binding energy = 284.8 eV) as standard.

DFT calculation

Density functional theory (DFT) calculations with periodic boundary conditions (PBC) were performed using the Perdew-Burke-Ernzerhof (PBE) functional⁴ as implemented in the Vienna ab initio simulation package (VASP 5.4.4).⁵ The projector augmented wave (PAW) method was used to describe the core-valence electron interaction.⁶ All calculations were spin-polarized. The plane wave energy cutoff was set to 400 eV for all atoms. For calculating the interaction energy of monomeric, dimeric vanadia species on TiO₂ surfaces, a (2 × 4) supercell of the anatase (101)

surface and (3 × 2) and (6 × 2) supercell of rutile (110) surface for monomeric and dimeric species, respectively, were used as the substrates. Only the Γ point of the Brillouin zone was sampled. A vacuum spacing of 20 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⁻¹. 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

Table S1. N₂ physisorption results of vanadia-based catalysts.

Catalysts	S _{BET} (m ² /g)	Pore volume (cc/g)	Pore diameter (nm)
V/Ti-1	39.9	0.39	39.5
V/Ti-2	31.3	0.24	30.9

The average crystallite size of Anatase and Rutile particles were calculated according the XRD results and the Scherrer equation:

$$D = \frac{k \times \gamma}{\beta \times \cos\theta}$$

The results showed that the size of Anatase and Rutile particles of V/Ti-1 is 20.2 and 44.1 nm, respectively. The size of V/Ti-2 is 33.4 and 41.9 nm.

$$V = m/\rho$$

$$S = \pi D^2$$

$$V = \pi D^3/6$$

$$S_{\text{So}} = \frac{6m}{D\rho}$$

The weight ratio of rutile for V/Ti-1 and V/Ti-2 is 8% and 58%, respectively. Assuming the densities of rutile and anatase are 4.25 and 3.90 g/cm³, respectively, according to these above equations, it can be concluded that the surface area ratios of

anatase and rutile phase are 96 : 4 and 50 : 50 for V/Ti-1 and V/Ti-2, respectively.

Table S2. TOF and rate constant of vanadia-based catalysts.

Catalysts	V ₂ O ₅ loading (%)	VO _x surface density (VO _x nm ⁻²)	TOF at 200 °C (s ⁻¹)	TOF at 260 °C (s ⁻¹)	1 st order rate constant (mol·g ⁻¹ ·h ⁻¹) at 200 °C
V/Ti-1	1	1.66	4.8×10 ⁻⁴	1.3×10 ⁻³	0.4
V/Ti-2	1	2.12	16.7×10 ⁻⁴	--	4.3
0.7V/Ti-2	0.7	1.70	6.6×10 ⁻⁴	2.7×10 ⁻³	--

Table S3. XRF results of V/Ti-1 and V/Ti-2 catalysts.

Catalysts	The mass concentration from XRF results (%)								
	V ₂ O ₅	TiO ₂	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Cl	CaO	Fe ₂ O ₃
V/Ti-1	0.85	98.01	0.07	0.29	0.25	0.32	0.04	0.13	0.04
V/Ti-2	0.83	98.16	0.05	0.14	0.19	0.34	0.08	0.14	0.07

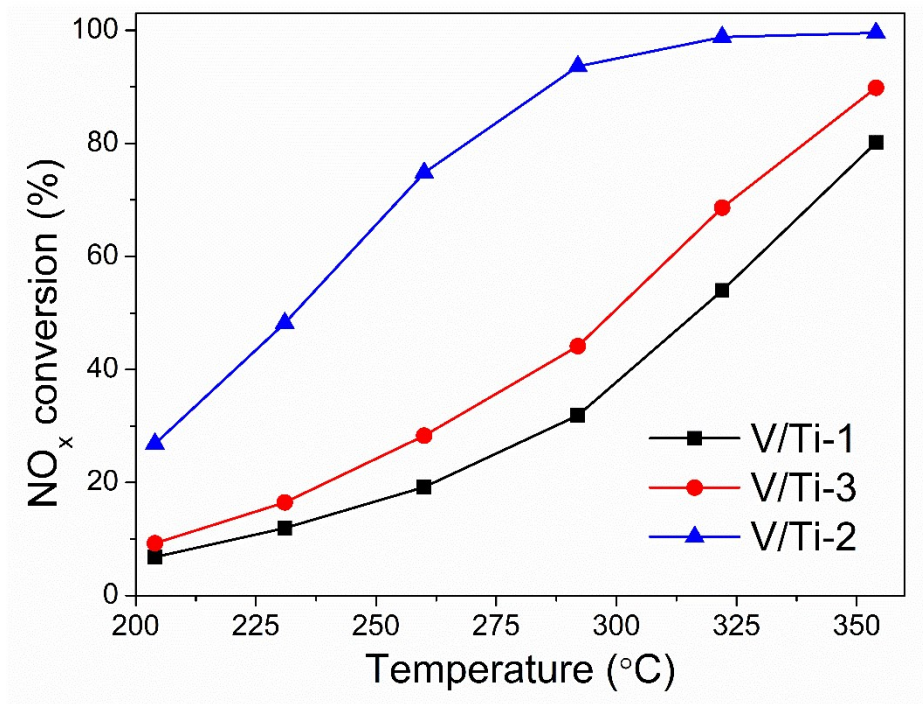


Figure S1. NH₃-SCR activity of vanadia-based catalysts with different ratios of rutile phase.

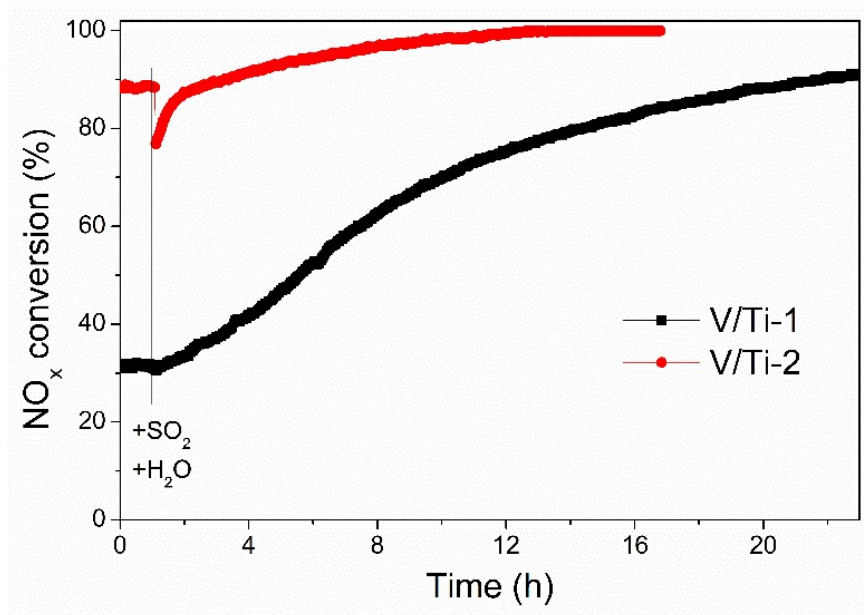


Figure S2. The effects of SO₂ and H₂O to the catalytic activity over vanadia-based catalysts. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5 vol.%, [SO₂] = 100 ppm (when used), [H₂O] = 5 vol.% (when used), N₂ balance, GHSV = 100 000 h⁻¹, and reaction temperature = 300 °C.

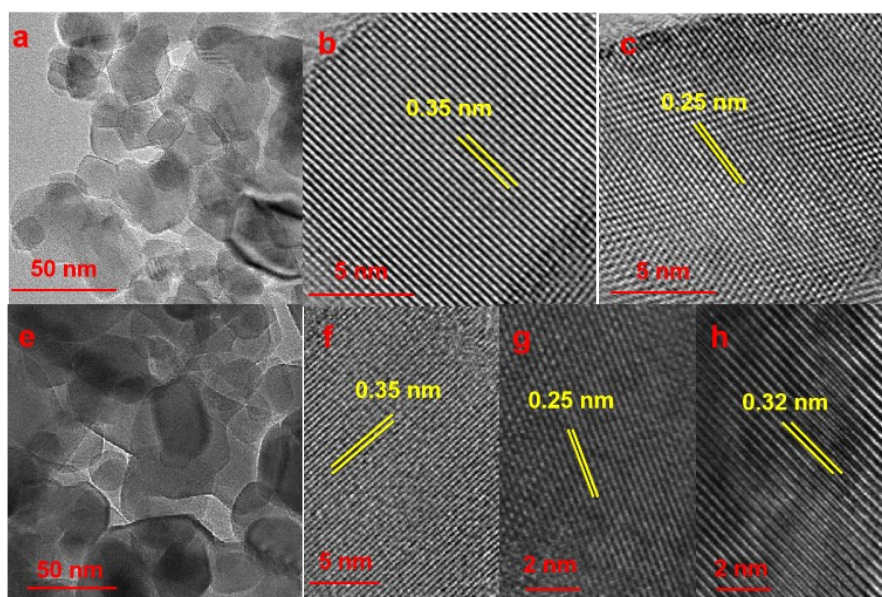


Figure S3. HR-TEM images of V/Ti-1 (a, b, c) and V/Ti-2 (e, f, g, h).

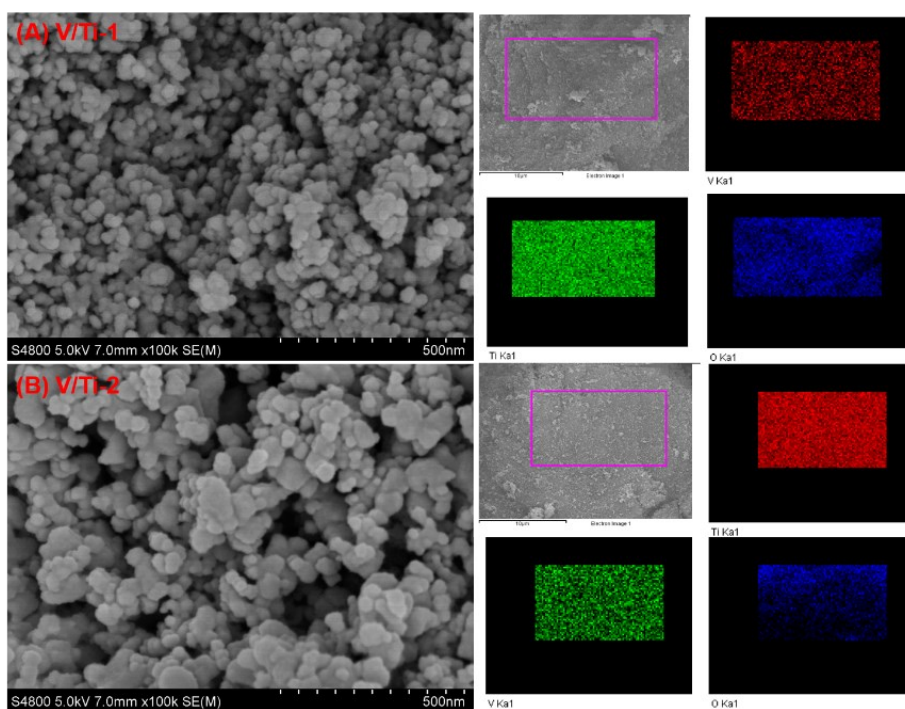


Figure S4. SEM images and elemental mapping images of V/Ti-1 and V/Ti-2.

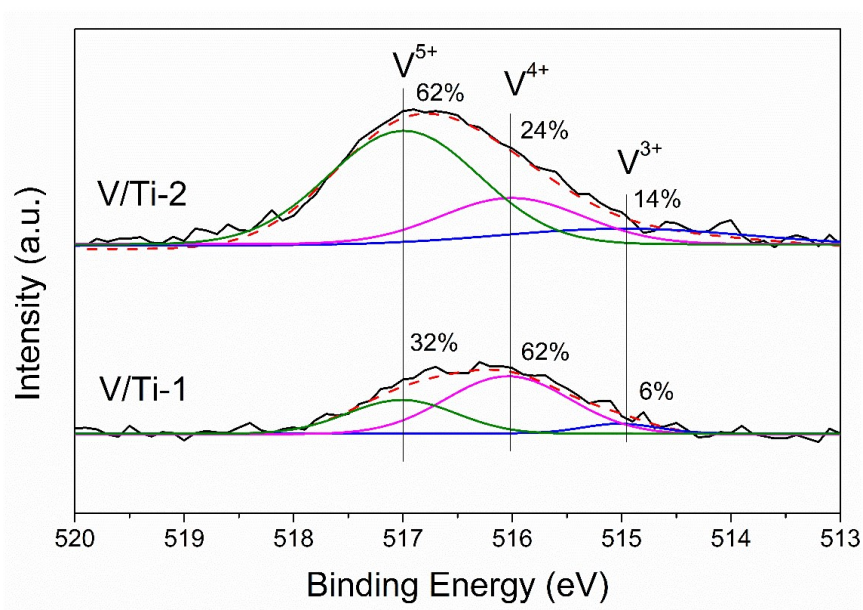


Figure S5. XPS results of V 2p on V/Ti-1 and V/Ti-2.

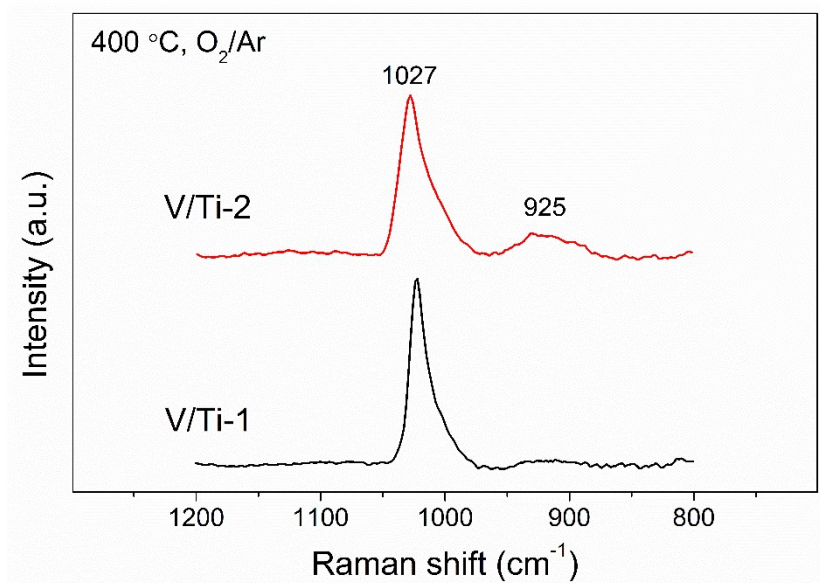


Figure S6. Raman spectra of vanadia-based catalysts.

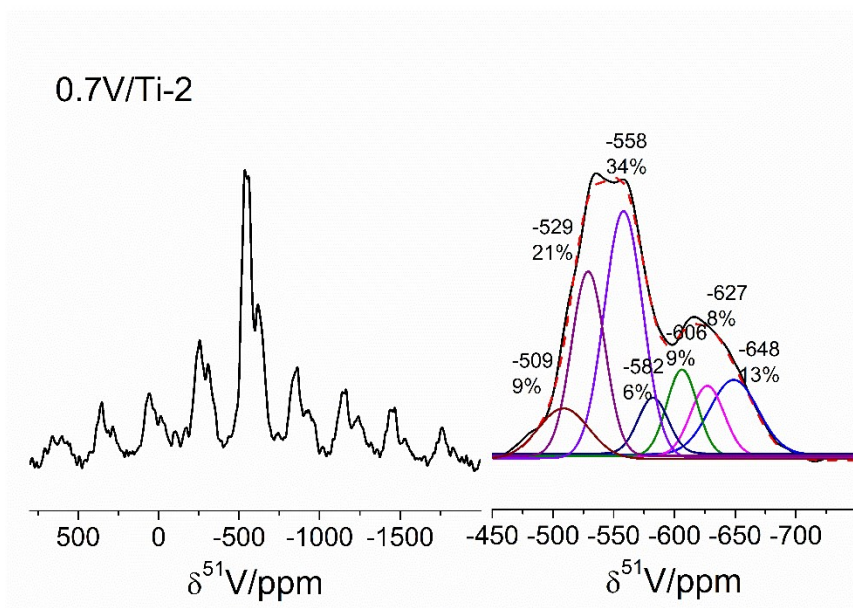


Figure S7. Solid state ⁵¹V NMR spectra of 0.7V/Ti-2.

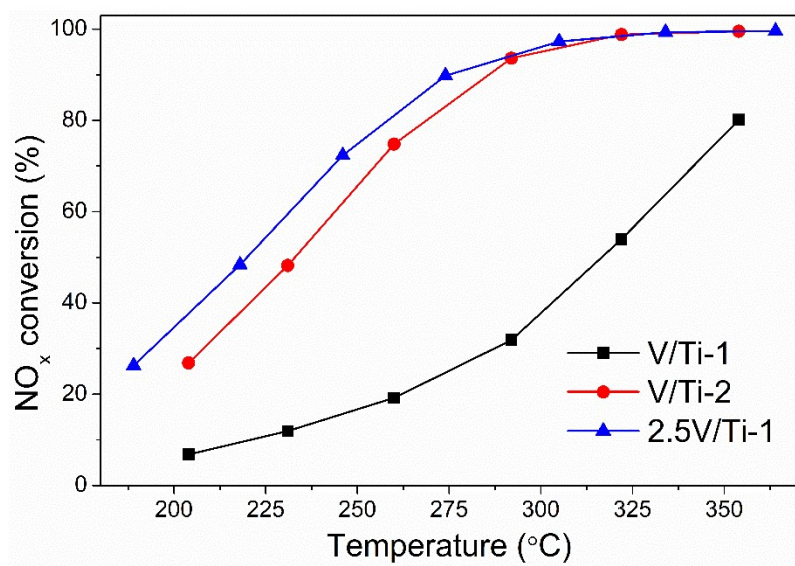


Figure S8. NH_3 -SCR activities of V/Ti-1, V/Ti-2 and 2.5V/Ti-1.

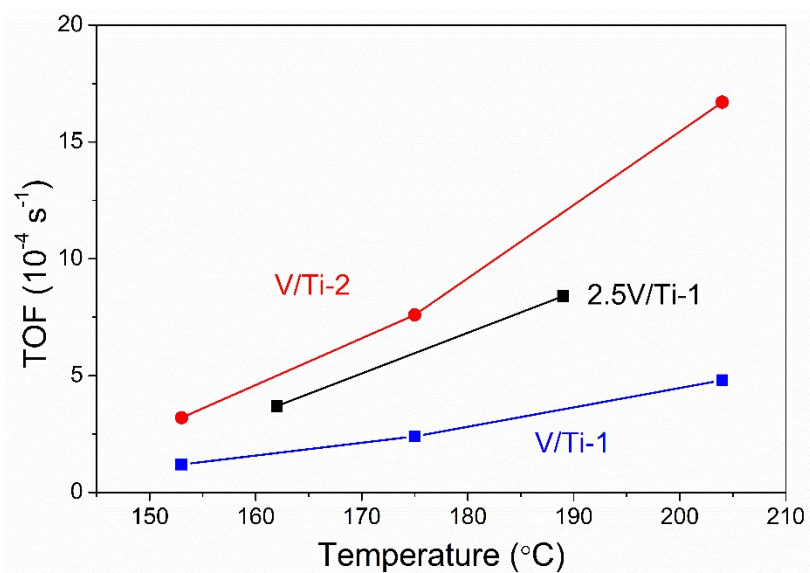


Figure S9. The TOF of V/Ti-1, V/Ti-2 and 2.5V/Ti-1.

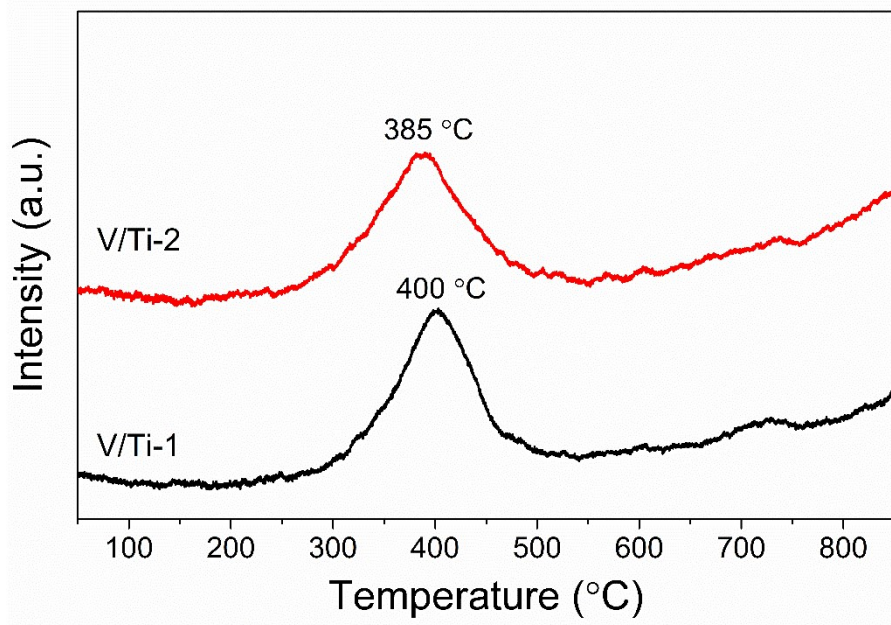


Figure S10. H₂-TPR results of vanadia-based catalysts.

To investigate the redox capabilities of the vanadia-based catalysts, H₂-TPR experiments were carried out, and the results are shown in Figure S10. The H₂ reduction peak at about 400 °C could be ascribed to the reduction of V⁵⁺ to V³⁺.⁷⁻⁹ Compared with V/Ti-1, V/Ti-2 showed a reduction peak shifting to the lower temperature region. It indicates that the redox capability of V/Ti-2 was higher than V/Ti-1, which could enhance the NH₃-SCR performance. The H₂ consumption for V/Ti-1 and V/Ti-2 were similar (about 102 μmol/g) to each other.

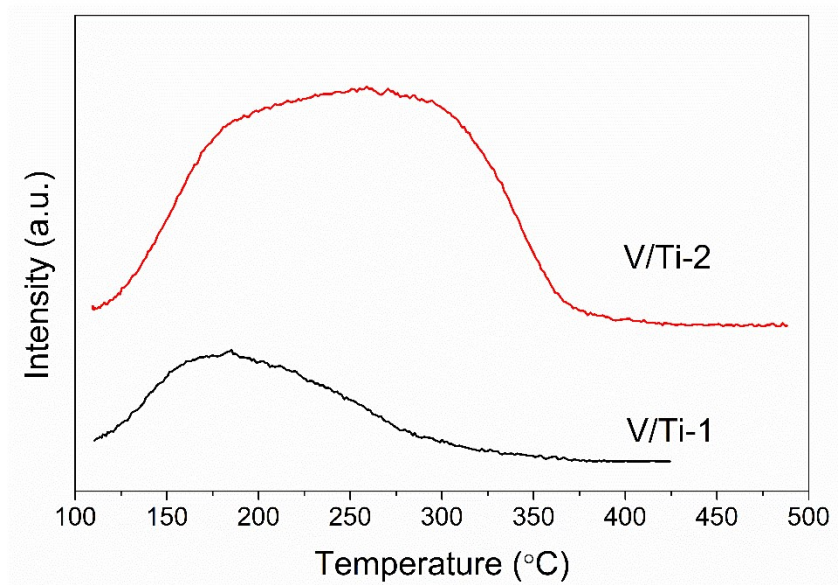


Figure S11. NH₃-TPD of V/Ti-1 and V/Ti-2.

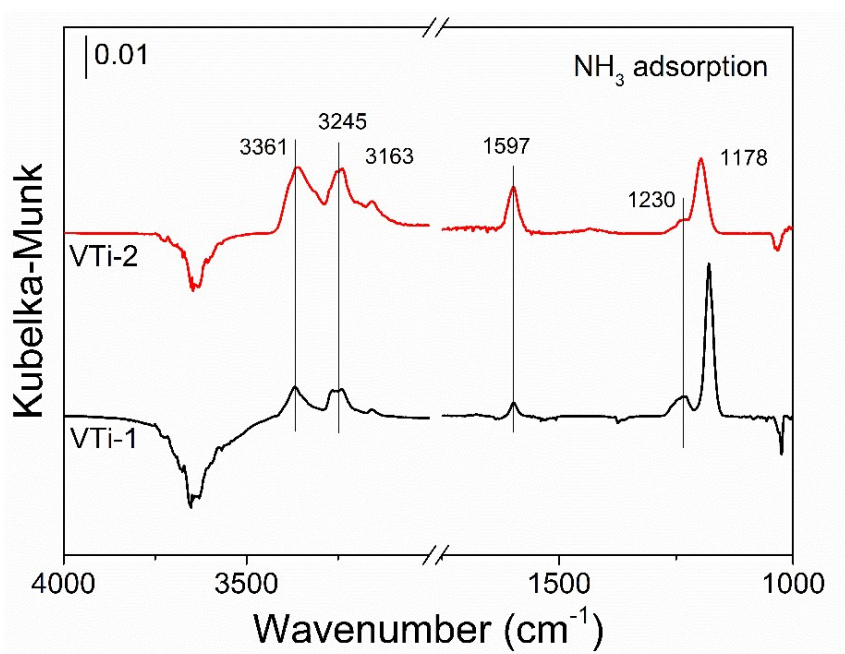


Figure S12. DRIFTS of NH₃ adsorption on vanadia-based catalysts.

Surface acidity is also an important property of the catalyst for NH₃-SCR reaction. DRIFTS of NH₃ adsorption on vanadia-based catalysts at 200 °C are shown in Figure S12. After NH₃ was introduced, several bands due to NH₃ adsorption were observed. The bands at 3361, 3245, and 3163 cm⁻¹ are attributed to the stretching vibration of N-

H bonds in coordinated NH₃ linked to Lewis acid sites, while the bands at 1597 and 1230, 1178 cm⁻¹ are ascribed to asymmetric and symmetric bending vibrations of the coordinated NH₃, respectively.¹⁰⁻¹² It is evident that more NH₃ adsorbed on V/Ti-2 than that on V/Ti-1. More acid sites on V/Ti-2 can facilitate the adsorption and activation of NH₃ during the catalytic reaction and thus promote the catalytic activity in NH₃-SCR.

References

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