

**Effect of treatment atmosphere on vanadium species of  
V/TiO<sub>2</sub> catalyst for the selective catalytic reduction of NO<sub>x</sub>  
with NH<sub>3</sub>**

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## 1. Experimental

### 1.1 Catalyst synthesis and activity tests

All catalysts used anatase TiO<sub>2</sub> powder (DT-51 Millenium Chemicals) as support. The impregnation method was used to synthesize the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts. The calculated amount of NH<sub>4</sub>VO<sub>3</sub> (V<sub>2</sub>O<sub>5</sub> loading 2.5%) was dissolved in oxalic acid solution. After TiO<sub>2</sub> was added, the mixture was agitated for 1h, and then the moisture was evaporated at 60 °C using a rotary vacuum evaporator before drying overnight at 100 °C and calcining in static air for 3 h at 500 °C. The obtained sample was denoted as V/Ti. Before aftertreatment, the samples were pressed, crushed and sieved to 40-60 mesh. Then these samples were treated under different atmospheres in a flow of 50 000 h<sup>-1</sup> at 480 °C for 2 h (10%O<sub>2</sub> in N<sub>2</sub>, pure N<sub>2</sub> and 1000 ppm NH<sub>3</sub> in N<sub>2</sub>), and denoted as V/Ti-O<sub>2</sub>, V/Ti-N<sub>2</sub> and V/Ti-NH<sub>3</sub>, respectively.

The SCR activity tests conditions were 200 000 h<sup>-1</sup> gas hourly space velocity, 500 ppm NH<sub>3</sub>, 500 ppm NO, 5 vol.% O<sub>2</sub>, and N<sub>2</sub> balance at atmospheric pressure. The effluent gases, including NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>, were continuously analyzed by an FTIR gas analyzer (Thermo Fisher IGS) equipped with a heated, low-volume multiple-path gas cell (2 m).

### 1.2 Characterization of the catalysts

Nitrogen adsorption/desorption isotherms at -196 °C were measured on a Quantachrome Autosorb iQ2 automatic adsorption instrument. The samples were degassed at 300 °C for 5 h before N<sub>2</sub> physisorption. Surface area and average pore diameter and pore volume were calculated from the BET equation in the 0.05-0.30 partial pressure range and the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the isotherms, respectively.

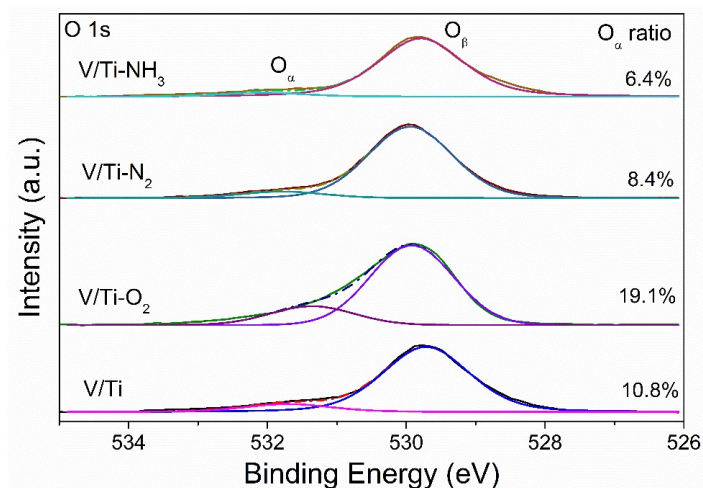
Powder XRD patterns were recorded by an X'Pert Pro XRD diffractometer (PANalytical B.V., Holland) using Cu K $\alpha$  radiation at 40 kV and 40 mA. The data of  $2\theta$  from 10 to 90° were collected at 8° min<sup>-1</sup> with the step size of 0.07°.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 Scanning ESCA Microprobe with a monochromatized micro-focused Al X-ray source. All the binding energies were calibrated using C1s as the reference energy (C1s = 284.6 eV).

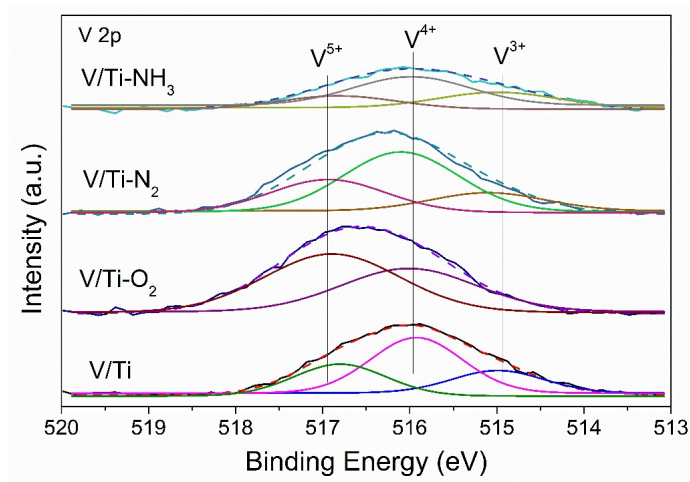
The <sup>51</sup>V NMR experiments were performed on a Bruker Avance III 500 spectrometer. The corresponding <sup>51</sup>V Larmor frequency was 131.6 MHz, using a 1.9-mm HX double-resonance probe at a spinning rate of 40 kHz. The single pulse NMR spectra of <sup>51</sup>V were acquired with a rf field strength of 166.7 kHz and a recycle delay of 0.3 s. Typically, 42,000 scans were collected for each <sup>51</sup>V MAS NMR spectrum. The <sup>51</sup>V chemical shift was referenced to V<sub>2</sub>O<sub>5</sub> at -610 ppm.

DRIFTS experiments were conducted on a Thermo Fisher Nicolet iS50 FTIR spectrometer equipped with a Smart Collector and an MCT/A detector cooled by liquid nitrogen. The sample was pretreated at 300 °C for 0.5 h in a flow of 20 vol.%

O<sub>2</sub>/N<sub>2</sub>, cooled down to 200 °C, and subsequently purged with N<sub>2</sub> for 30 min for background collection. The reaction conditions were as follows: 300 ml/min total flow rate, 500 ppm NH<sub>3</sub>, and N<sub>2</sub> balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm<sup>-1</sup>.



**Fig. S1** XPS for O 1s of V/TiO<sub>2</sub> catalysts.



**Fig. S2** XPS for V 2p of V/TiO<sub>2</sub> catalysts.

Table S1 the XPS results of different V/TiO<sub>2</sub> samples.

Catalysts	V atomic %	S atomic %	Ti atomic %	V 2p		
				V <sup>3+</sup> /V	V <sup>4+</sup> /V	V <sup>5+</sup> /V
V/Ti	1.43	1.77	26.60	0.20	0.51	0.29

V/Ti-O <sub>2</sub>	1.60	1.22	27.31	--	0.43	0.57
V/Ti-N <sub>2</sub>	1.70	1.16	27.38	0.16	0.54	0.30
V/Ti-NH <sub>3</sub>	1.18	0	26.41	0.27	0.50	0.23

H<sub>2</sub>-TPR results of V/TiO<sub>2</sub> catalysts are shown in Fig. S3. There was only one broad peak of H<sub>2</sub> consumption for the four samples. According to the literature [1, 2], surface vanadium species can be reduced at 400-500 °C. The H<sub>2</sub> consumption of V/Ti-NH<sub>3</sub> was the lowest among the four samples, which may be due to this sample having the lowest content of surface V based on XPS results. V/Ti, V/Ti-O<sub>2</sub> and V/Ti-N<sub>2</sub> presented similar H<sub>2</sub> reduction peaks and redox capability.

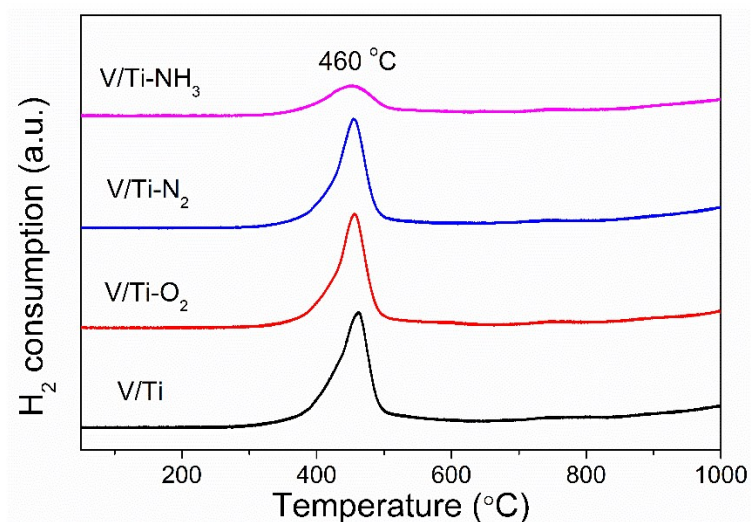


Fig. S3 H<sub>2</sub>-TPR results of V/TiO<sub>2</sub> catalysts.

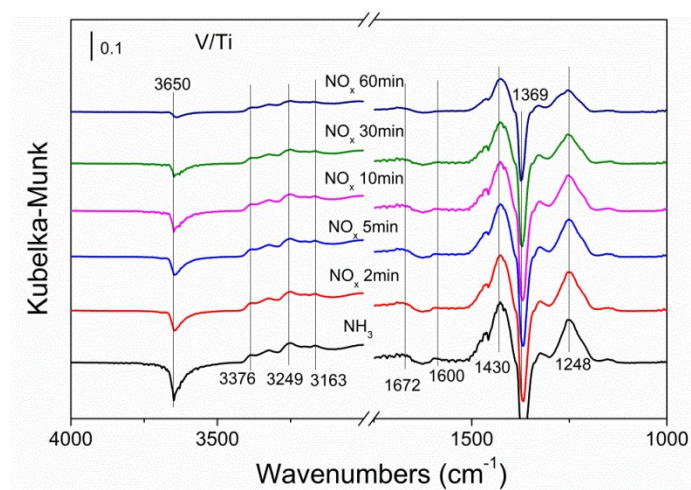


Fig. S4 *In situ* DRIFT spectra of V/Ti pretreated by NH<sub>3</sub> followed by exposure to NO  
+ O<sub>2</sub> at 200 °C.

### Reference

- [1] I. Song, H. Lee, D.H. Kim, Rotation-Assisted Hydrothermal Synthesis of Thermally Stable Multiwalled Titanate Nanotubes and Their Application to Selective Catalytic Reduction of NO with NH<sub>3</sub>, *Acs Appl. Mater. Inter.*, 10 (2018) 42249-42257.
- [2] Z. Lian, F. Liu, H. He, Effect of preparation methods on the activity of VO<sub>x</sub>/CeO<sub>2</sub> catalysts for the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>, *Catal. Sci. Technol.*, 5 (2015) 389-396.