Adsorption-induced active vanadium species facilitate excellent performance in low-temperature catalytic NO$_x$ abatement

Zhihua Lian[1], Jie Wei[2], Wenpo Shan[1], Yunbo Yu[1, 3, 4], Petar M. Radjenovic[2], Hua Zhang[2], Guangzhi He[3], Fudong Liu[5], Jian-Feng Li[2, *], Zhong-Qun Tian[2] and Hong He[1, 3, 4*]

1. Center for Excellence in Regional Atmospheric Environment and Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

2. State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, College of Materials, College of Energy, Xiamen University, Xiamen 361005, China

3. State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

4. University of Chinese Academy of Sciences, Beijing 100049, China.

5. 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, FL 32816, United States.
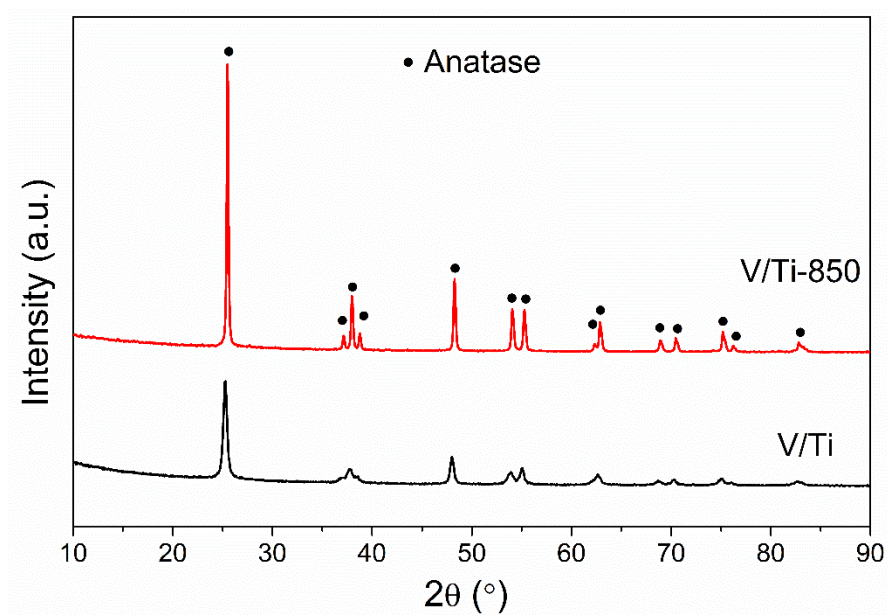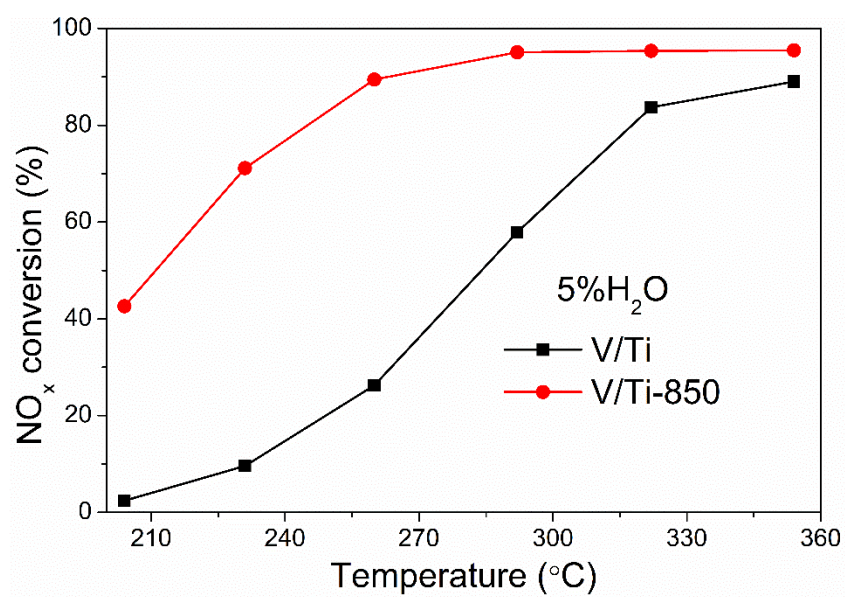
Fig. S1 XRD profiles of V/Ti and V/Ti-850.

Fig. S2 NH$_3$-SCR activity over V/Ti and V/Ti-850 in humid conditions. Reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 5 vol.% O$_2$, 5 vol.% H$_2$O, total gas flow rate of 500 mL min^{-1}, space velocity of 100 000 h^{-1}, and balanced by N$_2$ gas.
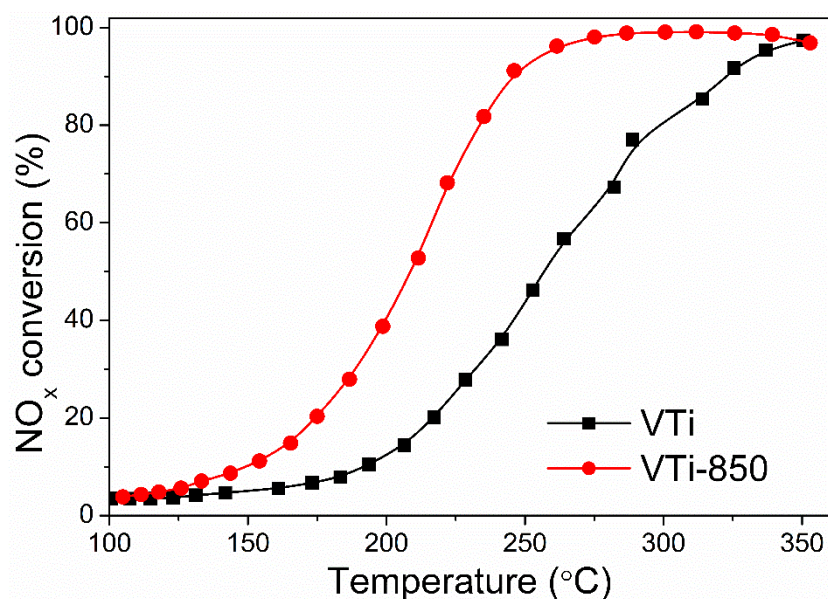
Fig. S3 NO_x conversion over vanadia-based catalysts while heating from 100 to 350 °C at the rate of 10 °C min^{-1}. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, 5 vol.% H_2O, total gas flow rate of 500 mL min^{-1}, space velocity of 100 000 h^{-1}, and balanced by N_2 gas.
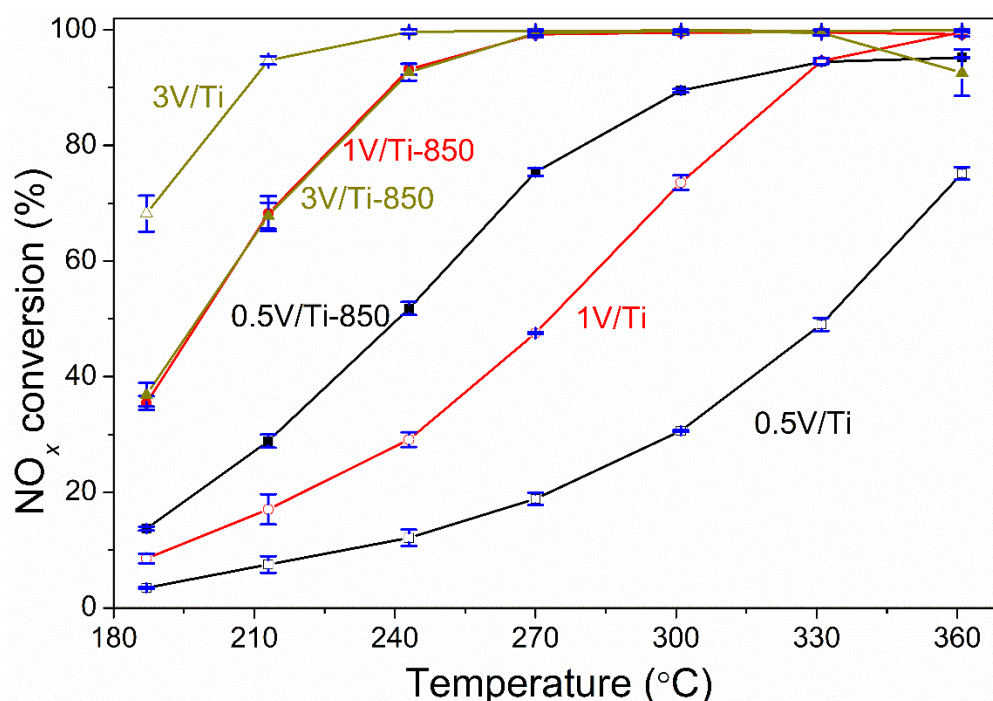

Fig. S4 The NH_3-SCR activity over vanadia-based catalysts with different vanadia loadings before and after thermal treatment. Reaction conditions: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, total gas flow rate of 500 mL min^{-1}, space velocity of 100 000
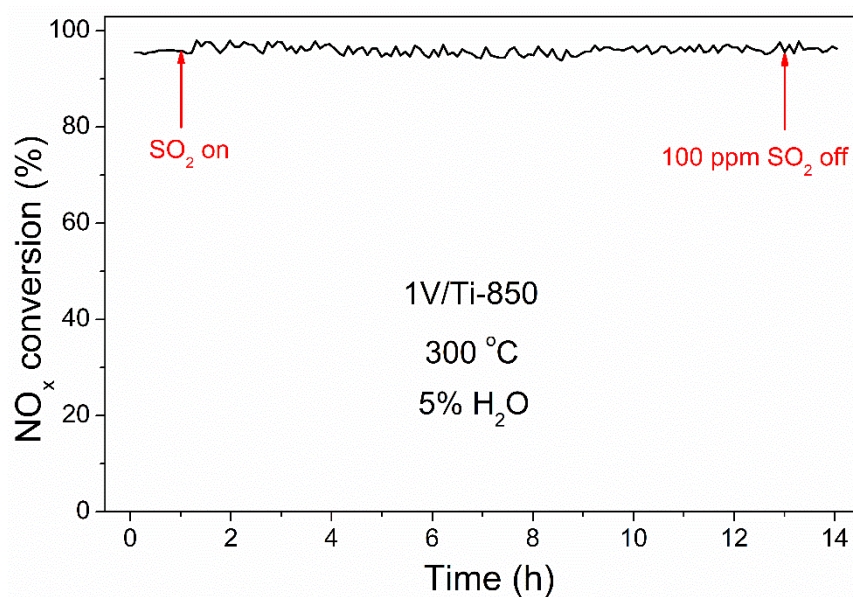
Fig. S5 Effect of SO$_2$ on NO$_x$ conversion over the V/Ti-850 catalyst at 300 °C.
Reaction conditions: 500 ppm NO, 500 ppm NH$_3$, 5 vol.% O$_2$, 5 vol.% H$_2$O, 100 ppm
SO$_2$ (when used), total flow rate of 500 mL min^{-1}, space velocity of 100 000 h^{-1} and
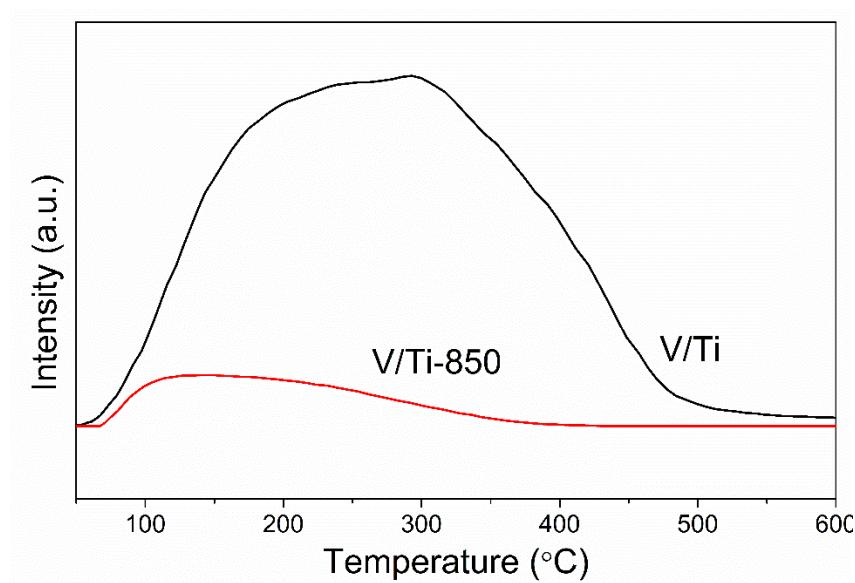balanced by N$_2$ gas.

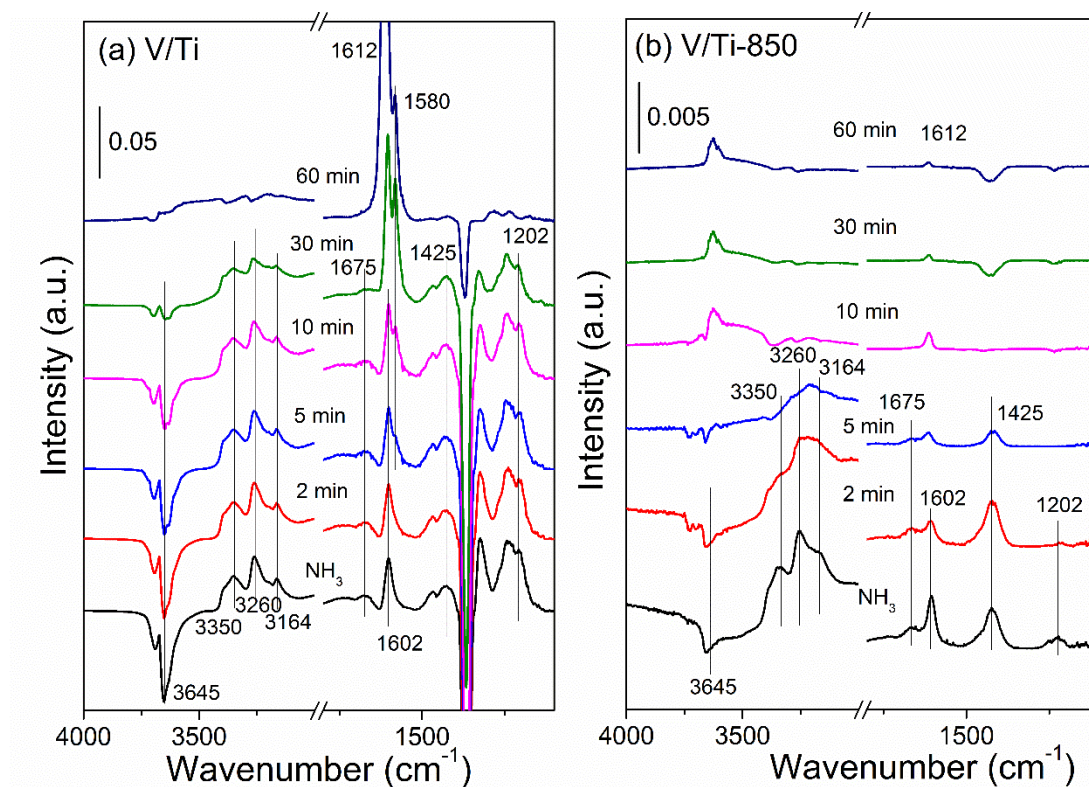Fig. S6 NH$_3$-TPD results of V/Ti and V/Ti-850.

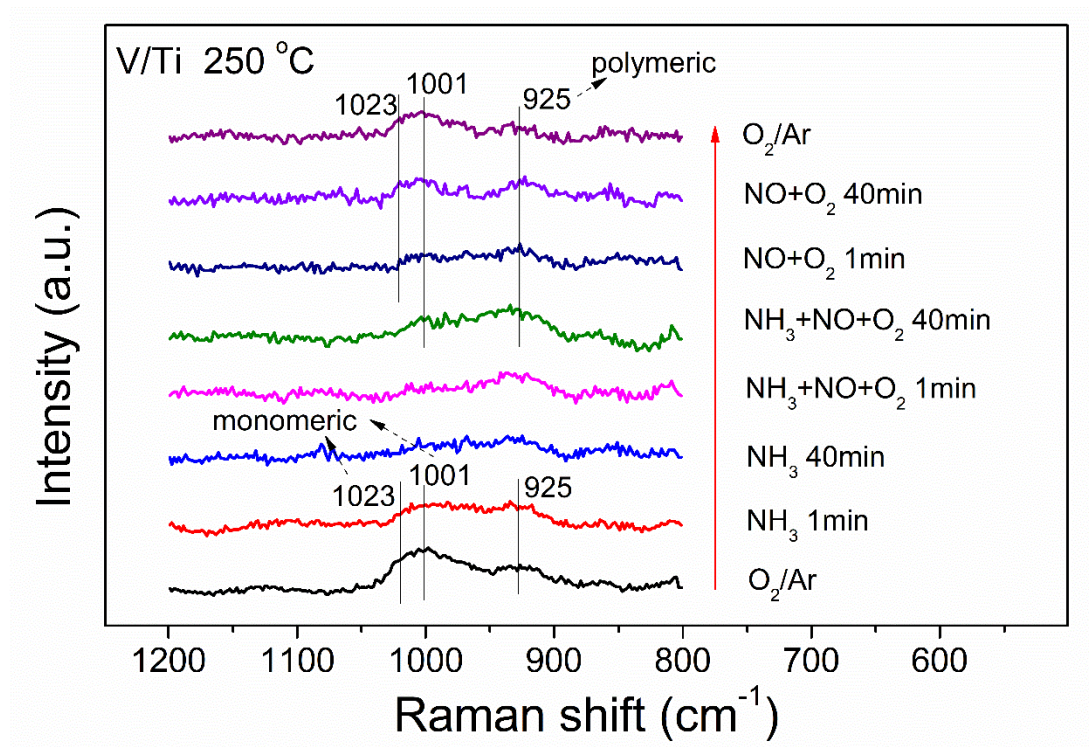Fig. S7 *In situ* DRIFTS of NO + O_2 reacted with pre-adsorbed NH_3 species at 200 °C on (a) V/Ti, and (b) V/Ti-850.

Fig. S8 *In situ* Raman spectra of V/Ti under different NH_3-SCR conditions at 250 °C.

DFT calculation.

The formation energy of NH₃-adsorbed on monomeric, dimeric, and crystalline vanadia loaded on TiO$_2$ surfaces ($E^f_{mono/di/cryst\ VOx}$) was calculated, which is defined as[1]:

$$E^f_{mono/di/cryst\ VOx} = E_{mono/di/cryst\ VOx} - E_{TiO2} - E_V - \frac{x}{2}E_{O2}$$

Where $E_{mon/di/cryst\ VOx}$, E_{TiO2}, E_V, and E_{O2} are the energies of NH₃-adsorbed monomeric, dimeric, and crystalline vanadia species loaded on TiO$_2$, the TiO$_2$ surface, bulk vanadium metal, and gas-phase O$_2$, respectively. The negative formation energy represents the stabilization of VO$_x$ species on TiO$_2$ surfaces. The formation energies are -6.00 eV, -6.88 eV, and -5.86 eV for NH₃-adsorbed monomeric, dimeric, and crystalline vanadia on TiO$_2$, respectively, indicating that the adsorption of NH₃ is beneficial to the formation of polymeric vanadia on TiO$_2$.

Table S1 The formation energy (E^f) of NH₃-adsorbed monomeric, dimeric, and crystalline vanadia on TiO$_2$ surfaces.

Species	Monomeric VO$_x$	Dimeric VO$_x$	Crystalline VO$_x$
E^f (eV)*	-6.00	-6.88	-5.86

* The formation energies of dimeric, and crystalline vanadia have been normalized to the values of individual VO$_x$ species.
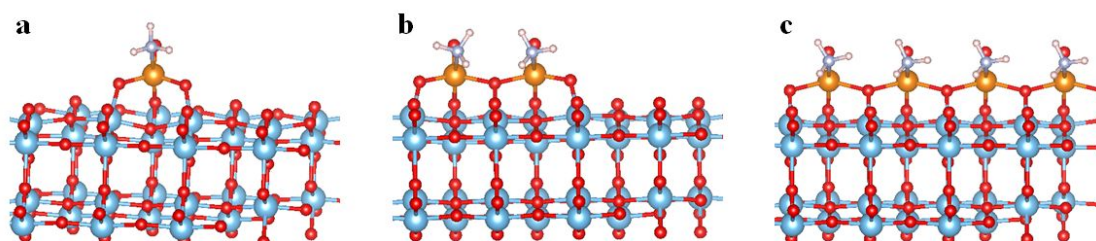

Fig. S9 Optimized geometries of NH₃-adsorbed on (a) monomeric, (b) dimeric, and (c) crystalline vanadia loaded on TiO$_2$ surfaces for formation energy calculations. Large blue, red, orange, small blue, and white circles denote Ti, O, V, N, and H atoms, respectively.
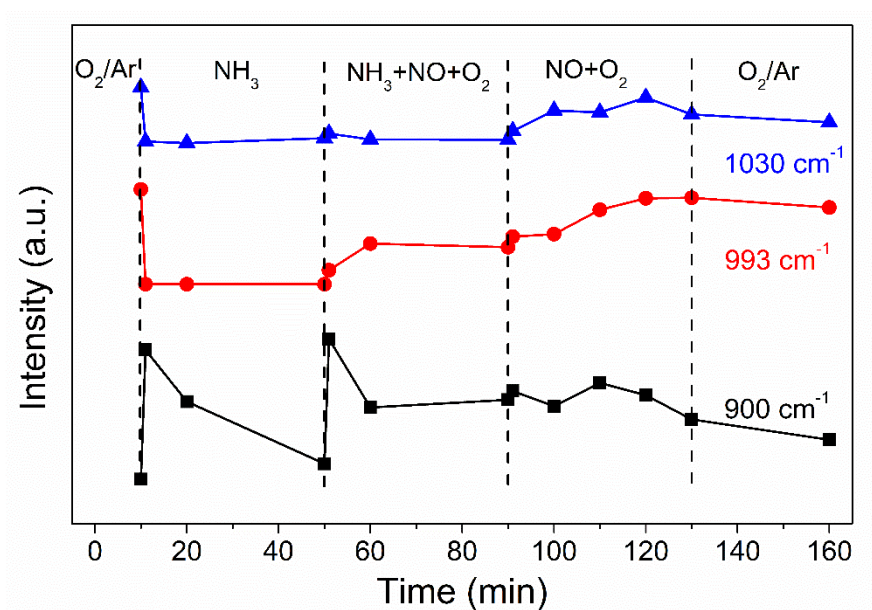
Fig. S10 Plot of the change in integral areas of various Raman peaks of vanadium species under different atmospheres with time.

References

1. Song, I.; Lee, J.; Lee, G.; Han, J. W.; Kim, D. H., Chemisorption of NH_3 on Monomeric Vanadium Oxide Supported on Anatase TiO_2: A Combined DRIFT and DFT Study. *J. Phys. Chem. C* **2018,** *122* (29), 16674-16682.