Electronic Supplementary Information

Support Facet Effects on the Performance of V_2O_5-WO_3-CeO_2/TiO_2 Catalysts for Selective Catalytic Reduction of NO with NH_3

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Catalysts characterization

X-ray diffraction (XRD) patterns were acquired using a Shimadzu 6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å). The measurements were performed at a tube voltage of 40 kV and a current of 30 mA. Data were collected over a 2θ range of 10° to 60° with a scanning rate of 5° min^{-1} and a step size of 0.04°.

The microstructure and morphology of the supports were examined by transmission electron microscopy (TEM) using a JEM-2100 instrument operated at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) imaging was conducted to resolve atomic lattice fringes, with the instrument possessing a point resolution of 0.23 nm and a line resolution of 0.14 nm.

Specific surface areas were determined via nitrogen physisorption at −196 °C using a Micrometrics ASAP 2020 analyzer. Prior to analysis, approximately 0.15 g of each powder sample was degassed under a N_2/He mixture flow at 300 °C for 6 h to remove adsorbed moisture and contaminants.

Raman spectra were obtained using a LabRAM Aramis spectrometer with an excitation wavelength of 633 nm. Each spectrum was obtained by accumulating 20 scans.

H_2 temperature-programmed reduction (H_2-TPR) was conducted in a quartz U-tube reactor. 0.1 g of the catalyst was exposed to a 5 vol% H_2/Ar (20 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The H_2 consumption signal was recorded using a thermal conductivity detector (TCD).

NH_3 temperature-programmed desorption (NH_3-TPD) was performed in a quartz U-tube reactor. 0.25 g of the catalyst was first pretreated in a helium flow at 400 °C for 0.5 h, cooled to room temperature, and then saturated with liquid ammonia. The sample

was purged with helium (20 mL min^{-1}) for 0.5 h to remove physically adsorbed species. The temperature was ramped to 500 °C at 5 °C min^{-1}. The desorbed NH_3 was detected by a TCD.

NH_3 temperature-programmed oxidation (NH_3-TPO) was performed in a fix-bed quartz U-tube reactor. 0.2 g of the catalyst was pretreated in an argon flow at 400 °C for 0.5 h and then cooled to room temperature. The gas was switched to a mixture containing 2000 ppm NH_3 and 4 vol% O_2 balanced with Ar. The temperature was then increased from room temperature to 500 °C at a heating rate of 10 °C min^{-1}. The outlet gases, including NO (m/z=30), NH_3 (m/z = 17), N_2O (m/z = 44) and N_2 (m/z = 28), were analyzed in real-time using a quadrupole mass spectrometer.

The *quasi in situ* XPS measurements were carried out on a PHI 5000 VersaProbe system with a monochromatic Al Kα X-ray source (1486.6 eV, 25 W). Prior to analysis, the catalysts were subjected to the SCR reaction at 300 °C for 20 min in an attached reaction chamber. Subsequently, they were transferred under an inert atmosphere to an ultra-high vacuum (UHV) chamber (< 5×10^{-7} Pa) for outgassing. All binding energies were calibrated using contaminant carbon (C1s = 284.6 eV) as a reference.

The *in situ* DRIFTS was performed on a Bruker Tensor II spectrometer equipped with a liquid nitrogen-cooled MCT detector. The catalyst powder was loaded into the Harrick IR cell and pretreated under an argon flow at 400 °C for 0.5 h to obtain a clean surface. Background spectra were collected at desired temperatures during cooling under argon and were subtracted from the corresponding sample spectra. All spectra were recorded by accumulating 64 scans at a resolution of 4 cm^{-1}. For NH_3 adsorption studies, the pretreated sample was cooled to room temperature and exposed to liquid NH_3 until saturation. After purging with argon for 1 h, spectra were collected at specific temperatures. To probe the reactivity of adsorbed ammonia species, the catalyst was

first saturated with NH_3 at 150 °C, purged with argon for 1 h, and then exposed to a flow of (NO + O_2) gas balanced with Ar. The temporal evolution of the IR bands corresponding to surface-adsorbed species was recorded.

Results and discussion

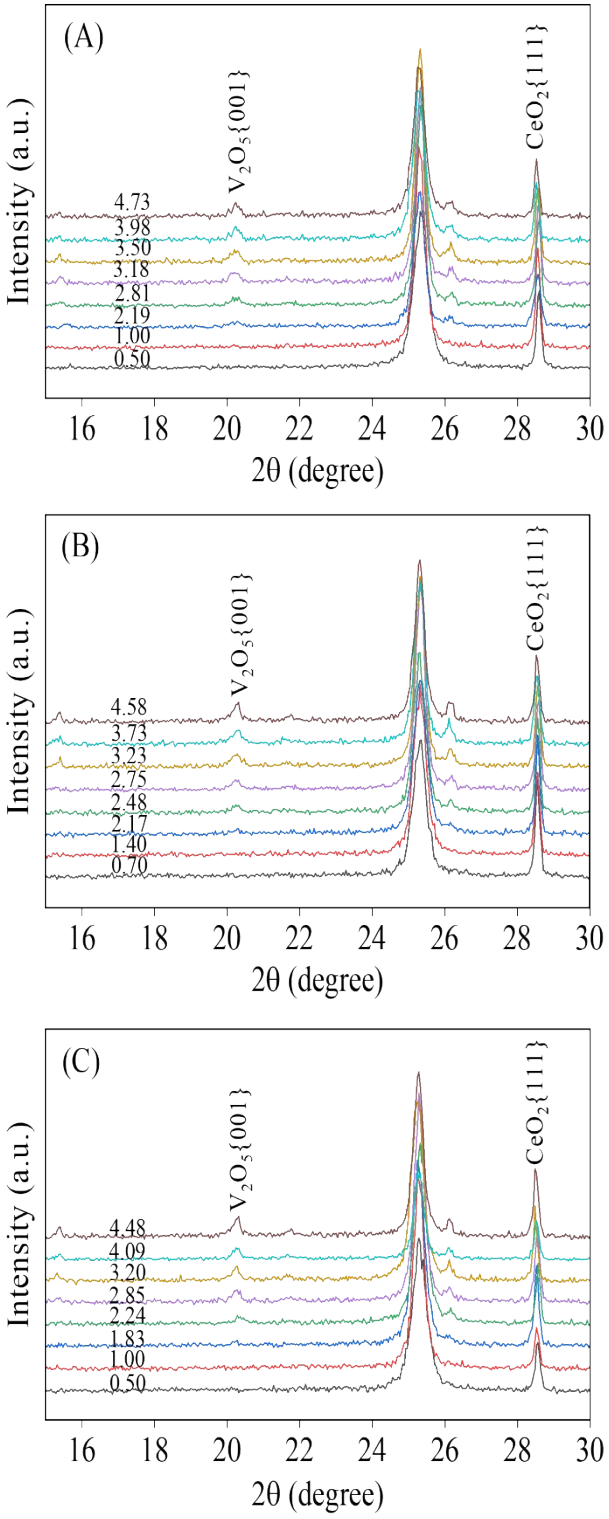

Fig. S1. XRD spectra of (A) V_2O_5/TiO_2-NS{001}, (B) V_2O_5/TiO_2-NP{101} and (C) V_2O_5/TiO_2-NL{111} catalysts with different V_2O_5 loading amounts (mmol VO_x/100 m^2 TiO_2).

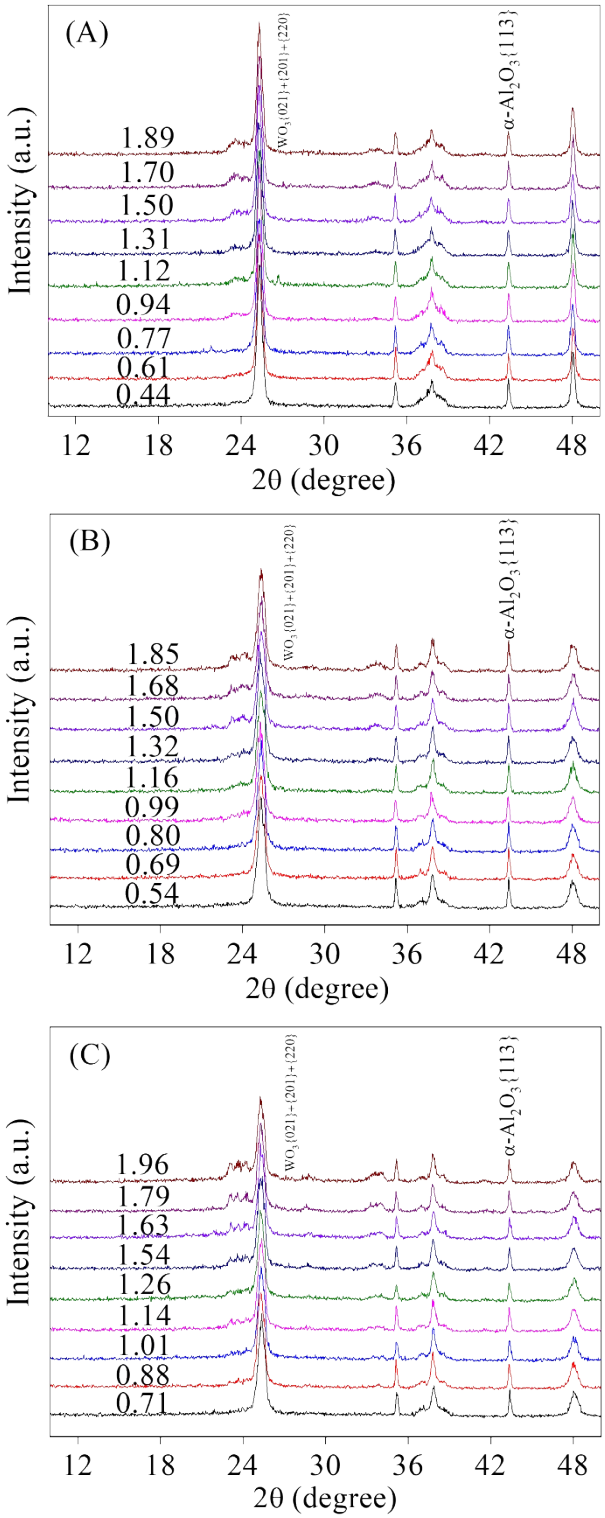

Fig. S2. XRD spectra of (A) WO_3/TiO_2-NS{001}, (B) WO_3/TiO_2-NP{101} and (C) WO_3/TiO_2-NL{111} samples with different WO_3 loading amounts (mmol WO_x/100 m^2 TiO_2).

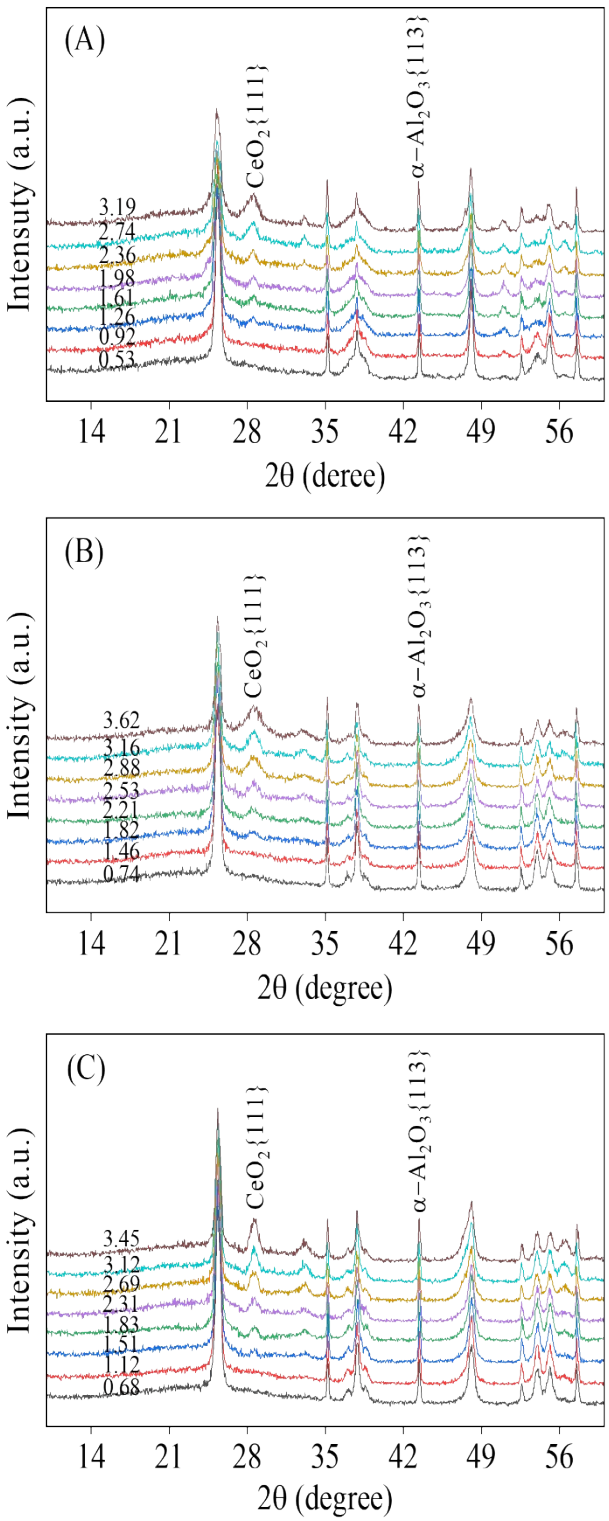

Fig. S3. XRD spectra of (A) CeO_2/TiO_2-NS{001}, (B) CeO_2/TiO_2-NP{101} and (C) CeO_2/TiO_2-NL{111} samples with different CeO_2 loading amounts (mmol CeO_x/100 m^2 TiO_2).

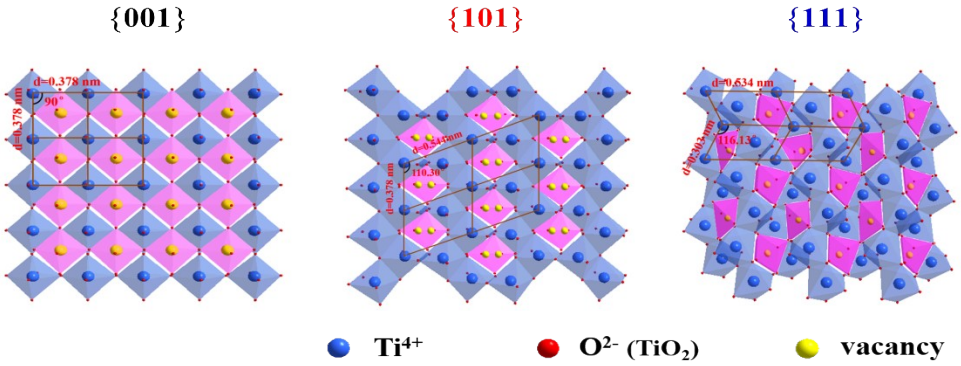

Fig. S4. Sizes of different facet structures of anatase TiO_2 supports.

The calculation of surface vacancy density of anatase TiO_2 supports

The vacancy sites without considering the exposed surface facet composition were calculated as follows:

Octahedral vacancy capacity for exposed TiO_2{001} facet = 1 vacancy site/(0.378 nm × 0.378 nm) = 6.92×10^{20} vacancy sites/100 m^2 = 1.1 mmol sites/100 m^2 TiO_2

Tetrahedral vacancy capacity for exposed TiO_2{101} facet = 2 vacancy sites/(0.378 nm × 0.544 nm × sin110.30°) = 10.3×10^{20} vacancy sites/100 m^2 = 1.7 mmol sites/100 m^2 TiO_2

Octahedral vacancy capacity for exposed TiO_2{111} facet = 1 vacancy site/(0.303 nm × 0.534 nm × sin116.13°) = 6.89×10^{20} vacancy sites/100 m^2 = 1.2 mmol sites/100 m^2 TiO_2

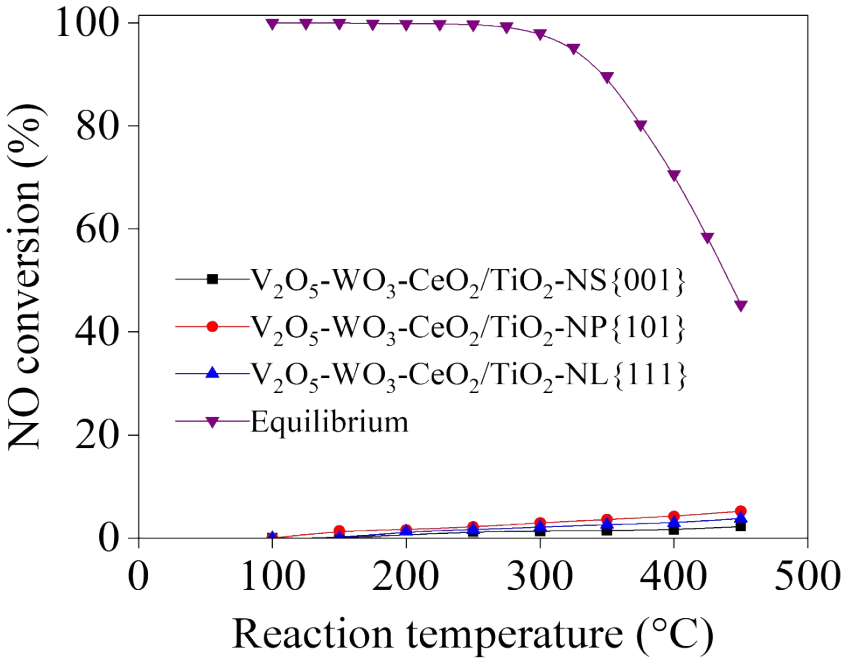

Fig. S5. Catalytic performance of supported V_2O_5-WO_3-CeO_2/TiO_2 catalysts for NO oxidation.

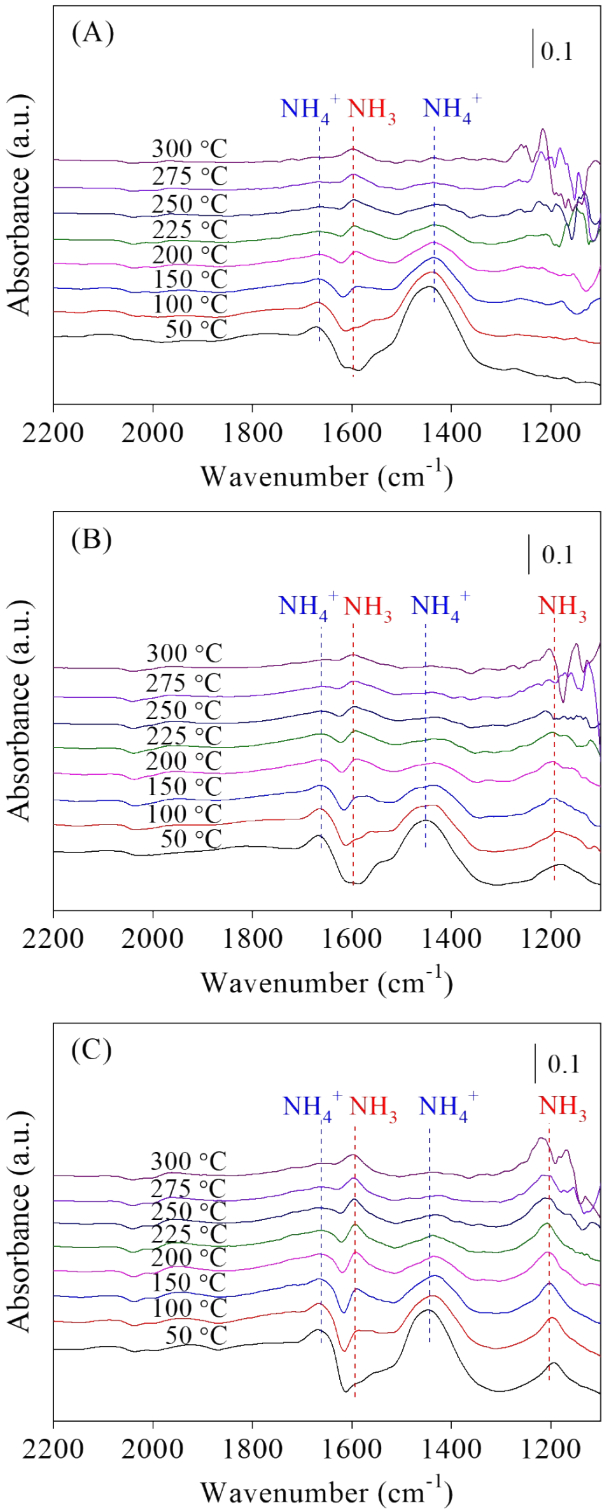

Fig. S6. NH_3-IR spectra of (A) V_2O_5-WO_3-CeO_2/TiO_2-NS{001}, (B) V_2O_5-WO_3-CeO_2/TiO_2-NP{101} and (C) V_2O_5-WO_3-CeO_2/TiO_2-NL{111} catalysts.

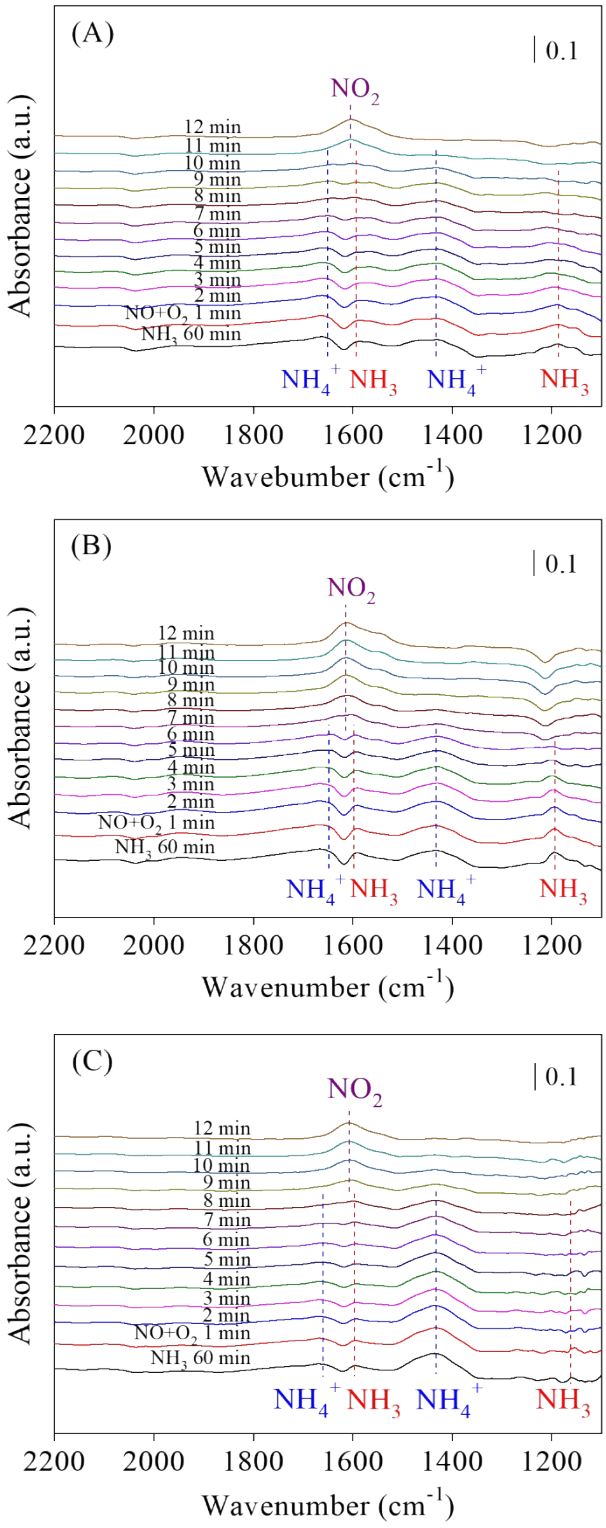

Fig. S7. Reactivity of pre-adsorption NH_3-IR spectra of (A) V_2O_5-WO_3-CeO_2/TiO_2-NS{001}, (B) V_2O_5-WO_3-CeO_2/TiO_2-NP{101} and (C) V_2O_5-WO_3-CeO_2/TiO_2-NL{111} catalysts with NO + O_2 at 200 °C.