

Electronic Supplementary Information

**Time-resolved observation of V_2O_5/TiO_2 in NH_3 -SCR reveals
the equivalence of Brønsted and Lewis acid sites**

Experimental Details

Catalysts preparation

The supported V_2O_5/TiO_2 catalyst was prepared by conventional wet impregnation method. Specifically, ammonium metavanadate (0.116 g) was dissolved in 0.1M oxalic acid solution (150 mL). The resulting bluish aqueous solution was mixed with Degussa P-25 TiO_2 (3 g), and stirred under ambient conditions for 1 h. Then, the mixture was dried by using rotary evaporator at 80 °C, and subsequently dried overnight in oven at 100 °C. The resulting powder was calcined in static air at 500 °C for 4 h. For Li deposition, appropriate amount of LiOH was dissolved in water and deposited on V_2O_5/TiO_2 by wet impregnation with same procedure. The prepared catalysts were named as $xLi-V/TiO_2$, where x is an atomic ratio of Li to V.

Spectroscopy

In situ Raman spectra were measured on a BaySpecNomadic™ Raman spectrometer equipped with a confocal microscope (Olympus BX-51 upright microscope), a volume phase gratings, and a dichroic filter. The visible excitation (532nm) generated from a diode-pumped solid state continuous wave laser (max power 50 mW) was used. The scattered photons were focused onto a CCD detector (2048x64 pixels), with a spectral resolution of 4 cm^{-1} . A high temperature environmental cell (Linkam CCR1000) equipped with a quartz window was used for *in situ* Raman collection. The powdered samples, ~40 mg, were loosely spread onto a small ceramic sample holder inside the *in situ* cell. To remove the absorbed moisture and impurities, the environment cell was heated at 300 °C under 3% O_2/Ar (Airgas, certified, 2.977% O_2/Ar , 30 mL/min) for 30 min. Raman spectra of the dehydrated samples were then collected at the above condition. Spectral acquisition was done with 10 scans of 10s/scan, for a total acquisition time of ~2 min per spectrum.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were measured on a FTIR spectrometer (Nicolet 6700) equipped with a *in situ* cell (Praying Mantis™, Harrick's high temperature reaction chambers). All the gas lines at the inlet and outlet of the cell were heated to 140 °C, and the flow rate of the reaction gas was regulated with mass flow controllers. The powdered catalysts, ~80 mg, were rigidly packed onto the circular cell. Before NH_3 adsorption, the catalysts were pretreated under 5% O_2/N_2 for 1 h at 300 °C, and background spectrum was obtained after cooling down to 200 °C while purging with N_2 . After NH_3 pre-adsorption, cell was purged with N_2 for 30 min. During transient reaction experiments, the spectra were collected with the interval of 30 s at a resolution of 4 cm^{-1} .

Characterization methods and reaction system

Specific surface area of the prepared catalysts was measured by using BELSORP-mini II (BEL Japan) apparatus. Before N_2 adsorption, samples were evacuated at 200 °C for 6 h to remove

any impurities on surface. Ammonia temperature-programmed desorption (NH₃-TPD) and hydrogen temperature-programmed reduction (H₂-TPR) experiments were conducted on a BEL-CAT Basic instrument (BELJapan Inc.) equipped with thermal conductivity detector. About 0.05 g of catalysts were packed on a quartz-type U-shaped cell. Before NH₃-TPD measurement, catalysts were pretreated at 300 °C in O₂/N₂ for 1 h and cooled down to 200 °C in He gas. Then, the adsorption of NH₃ were conducted at this temperature by exposing catalyst to 5% NH₃/He for 1 h. After saturating catalyst surface with NH₃, furnace was heated at the rate of 10 °C/min under He flow. For H₂-TPR analysis, catalysts were pretreated at 400 °C in Ar gas for 1 h. Then, pre-treated samples were heated to 900 °C under 5% H₂/Ar. For the reaction experiments in the flow reactor, quartz type tubular reactor with the diameter of half inch was used in electric furnace. About 0.1 g of catalysts were placed inside reactor as sieved to particles sized between 180 to 250 μm. The reaction gas consisted of 500 ppm NO, 500 ppm NH₃, and 5% O₂ balanced with N₂, and the total flow rate was 200 mL/min. Steady-state NO_x concentration was monitored on NO_x chemiluminescence analyzer (42i High level, Thermo Scientific).

Supplementary Tables and Figures

Table S1 Linear fitting results of the consumption rate of surface NH₃ for the prepared catalysts.

Reaction	Catalysts	Acid sites speciation	R-Square	Slope (10 ⁻² mmol/g·min)		y-intercept (10 ⁻² mmol/g)	^a Deviation of surface NH ₃	
				Value	Standard Error			
Standard SCR (NO+O ₂)	V/TiO ₂	L-NH ₃	0.9949	-0.2537	0.0049	4.196	0.096	
		B-NH ₃	0.9993	-0.2551	0.0018	5.907	0.707	
	0.05Li-V/TiO ₂	L-NH ₃	0.9902	-0.2325	0.0062	3.800	0.100	
		B-NH ₃	0.9974	-0.2943	0.0040	5.735	0.335	
	0.2Li-V/TiO ₂	L-NH ₃	0.9871	-0.0958	0.0029	2.267	0.033	
		B-NH ₃	0.9967	-0.1798	0.0028	4.204	0.404	
	0.5Li-V/TiO ₂	L-NH ₃	0.9499	-0.0913	0.0056	2.449	0.051	
		B-NH ₃	0.9722	-0.0474	0.0021	1.338	0.338	
	Slow SCR (NO)	V/TiO ₂	L-NH ₃	0.9533	-0.0736	0.0030	3.591	0.509
			B-NH ₃	0.9834	-0.0955	0.0023	5.263	0.063
		0.05Li-V/TiO ₂	L-NH ₃	0.9527	-0.0518	0.0021	3.159	0.541
			B-NH ₃	0.9937	-0.0884	0.0013	4.989	0.411
0.2Li-V/TiO ₂		L-NH ₃	0.8978	-0.0386	0.0024	1.987	0.313	
		B-NH ₃	0.9889	-0.0806	0.0016	3.542	0.258	
0.5Li-V/TiO ₂		L-NH ₃	0.9341	-0.0307	0.0015	2.375	0.125	
		B-NH ₃	0.9857	-0.0184	0.0004	1.199	0.199	

^aDeviation = |Calculated amount of acid sites from TPD - y-intercept|

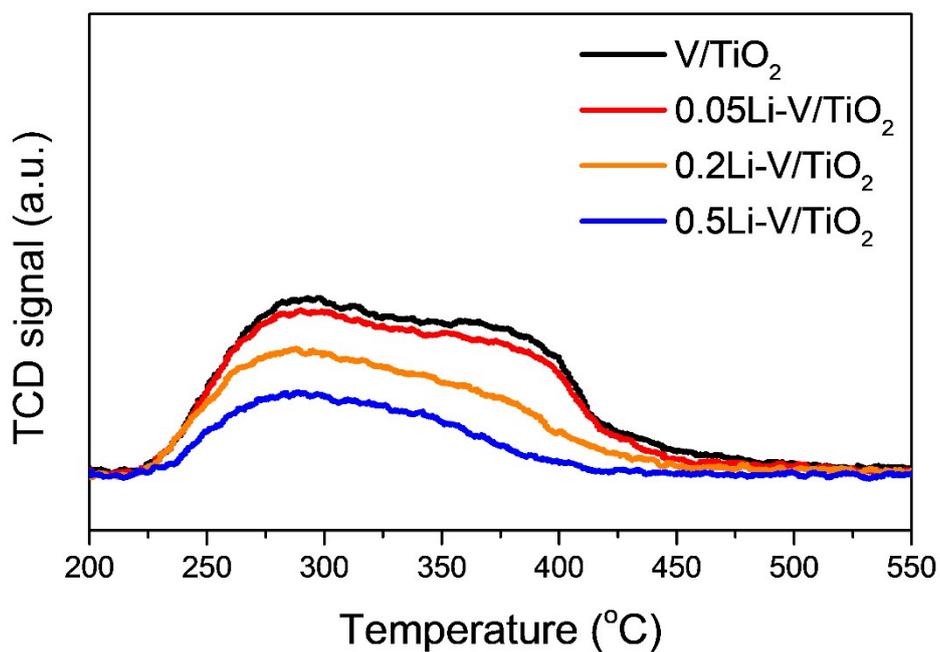


Fig. S1 Temperature-programmed desorption of ammonia (NH₃-TPD) profiles of V/TiO₂ and xLi-V/TiO₂ (x=0.05, 0.2, and 0.5) catalysts. Before measurements, samples were heated at 500 °C under 20% O₂/N₂ for 30 min to remove moisture and impurities. The adsorption of NH₃ was conducted at 200 °C, and subsequent desorption of NH₃ was detected from 200 to 550 °C.

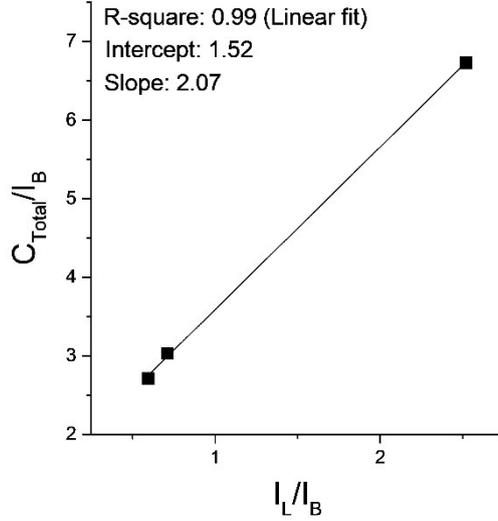


Fig. S2 Estimation of the extinction coefficient ratio by correlating the specific band intensities of L-NH₃ (I_L , 1220 cm⁻¹), B-NH₃ (I_B , 1423 cm⁻¹) from DRIFT spectra (Fig. 1b) and the total concentration of adsorbed NH₃ species (C_{Total}) from NH₃-TPD results (Fig. S1).

Fig. S2 was shown to quantify relative populations of NH₃ adsorbed on Lewis acid sites (L-NH₃) and that on Brønsted acid sites (B-NH₃) from IR spectra over V/TiO₂ and Li-V/TiO₂ catalysts in Fig. 1b. For quantification, we have to calculate the extinction coefficients of NH₃ species, ϵ , that relate the specific band intensities I with the corresponding concentrations C . The band intensities (I_{KM}) of Kubelka-Munk transformation of diffuse-reflectance data have following relations.

$$I_{KM} = \epsilon C$$

$$C_{Total} = C_B + C_L = I_B/\epsilon_B + I_L/\epsilon_L$$

$$C_{Total}/I_B = (I_L/I_B)/\epsilon_L + 1/\epsilon_B$$

Based on Fig. S2, the extinction coefficient ratio of L-NH₃ and B-NH₃ can be obtained as follows:

$$\epsilon_L/\epsilon_B = (\text{Intercept})/(\text{Slope}) = 1.52/2.07 = 0.73 \approx 1$$

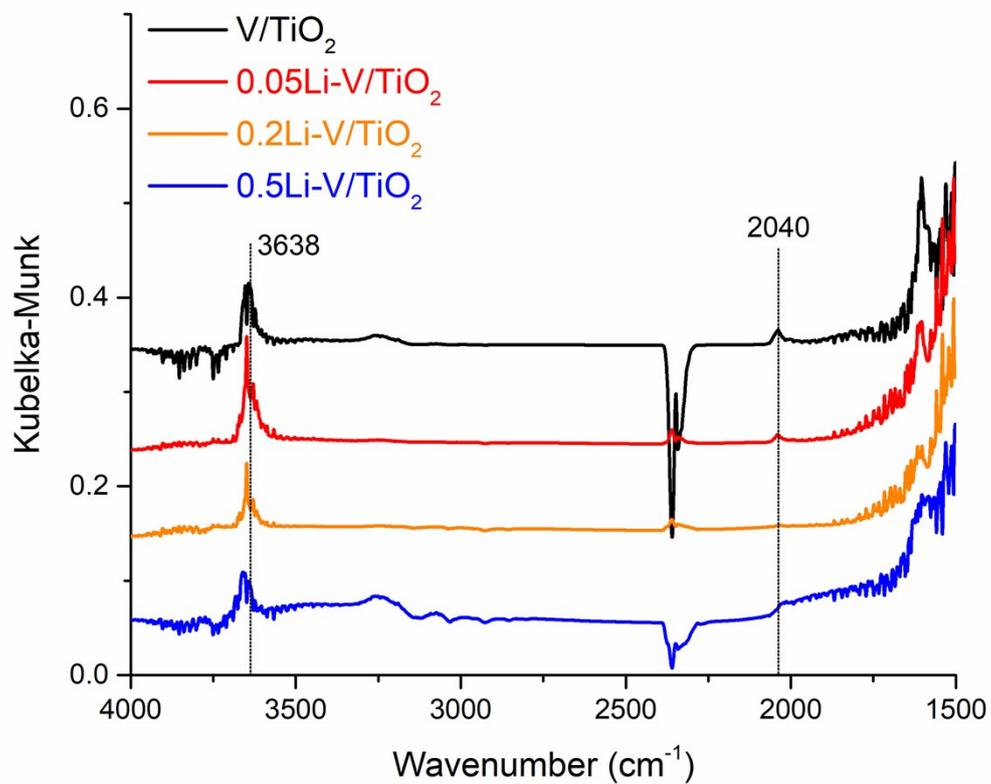


Fig. S3 *In situ* DRIFT spectra of V/TiO₂ and Li-V/TiO₂ catalysts at 200 °C. KBr background collected at 200 °C was used for all measurement. Before measurements, the cell was heated at 500 °C under 10% O₂/N₂ (100mL/min) for 30 mins. Spectra were then collected at 200 °C in the range of 500-4000 cm⁻¹.

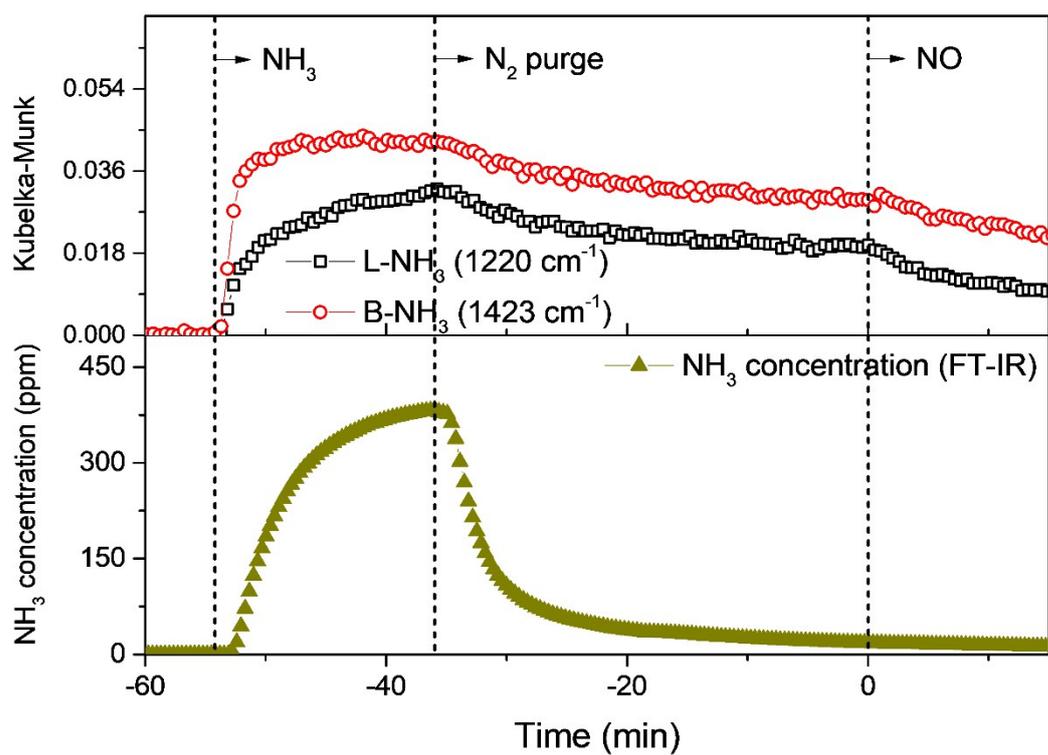


Fig. S4. Procedure of NH_3 pre-adsorption over V/TiO_2 catalyst before starting transient reaction under NO or $\text{NO}+\text{O}_2$ conditions at $200\text{ }^\circ\text{C}$. While observing surface NH_3 species (1220 and 1423 cm^{-1}) in the DRIFT spectra, the NH_3 concentration at the rear end of the DRIFT cell was monitored with an FT-IR gas cell analyzer.

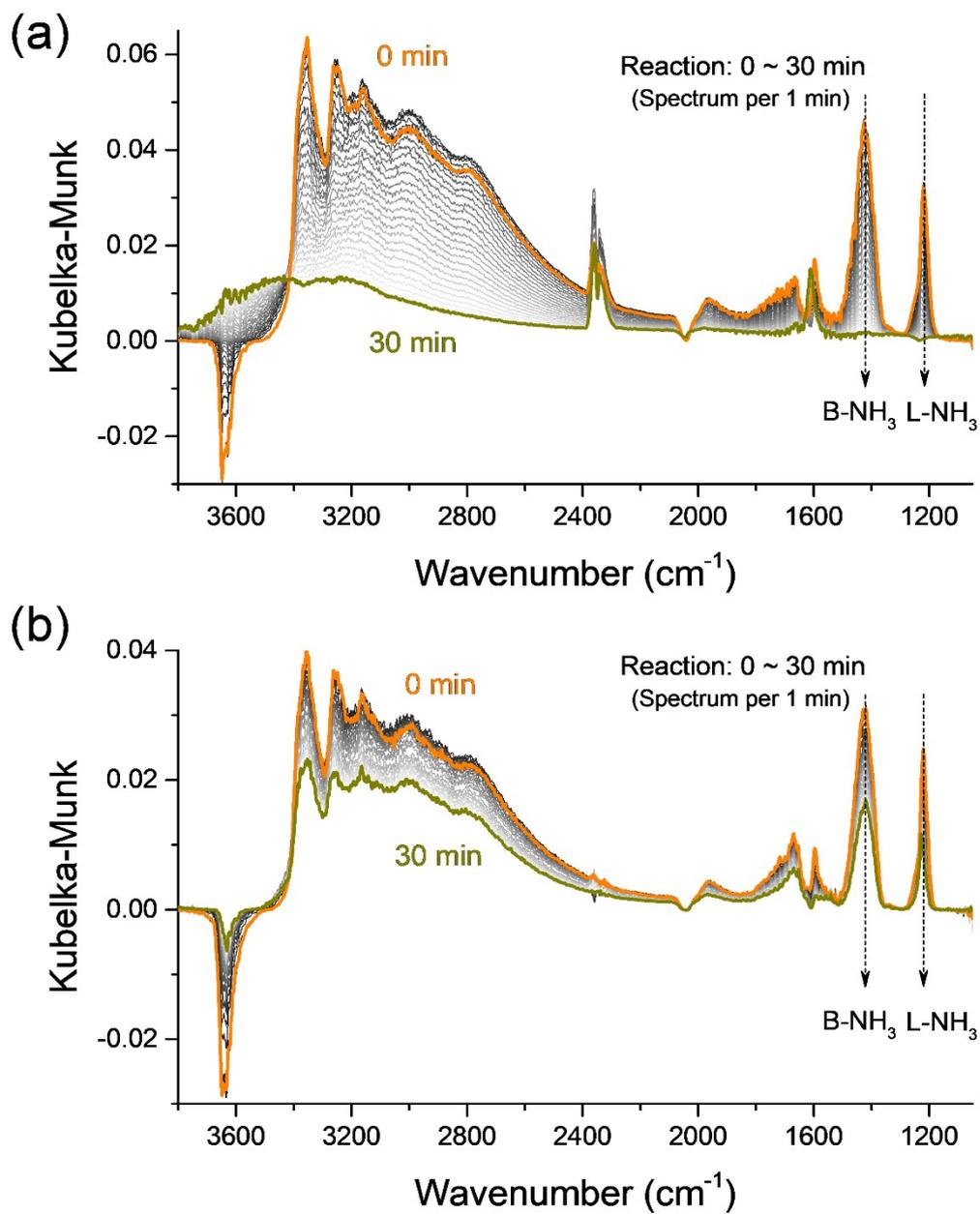


Fig. S5 Series of DRIFT spectra for the reaction of surface pre-adsorbed NH₃ with (a) NO+O₂ (b) NO on V/TiO₂ catalyst at 200 °C.

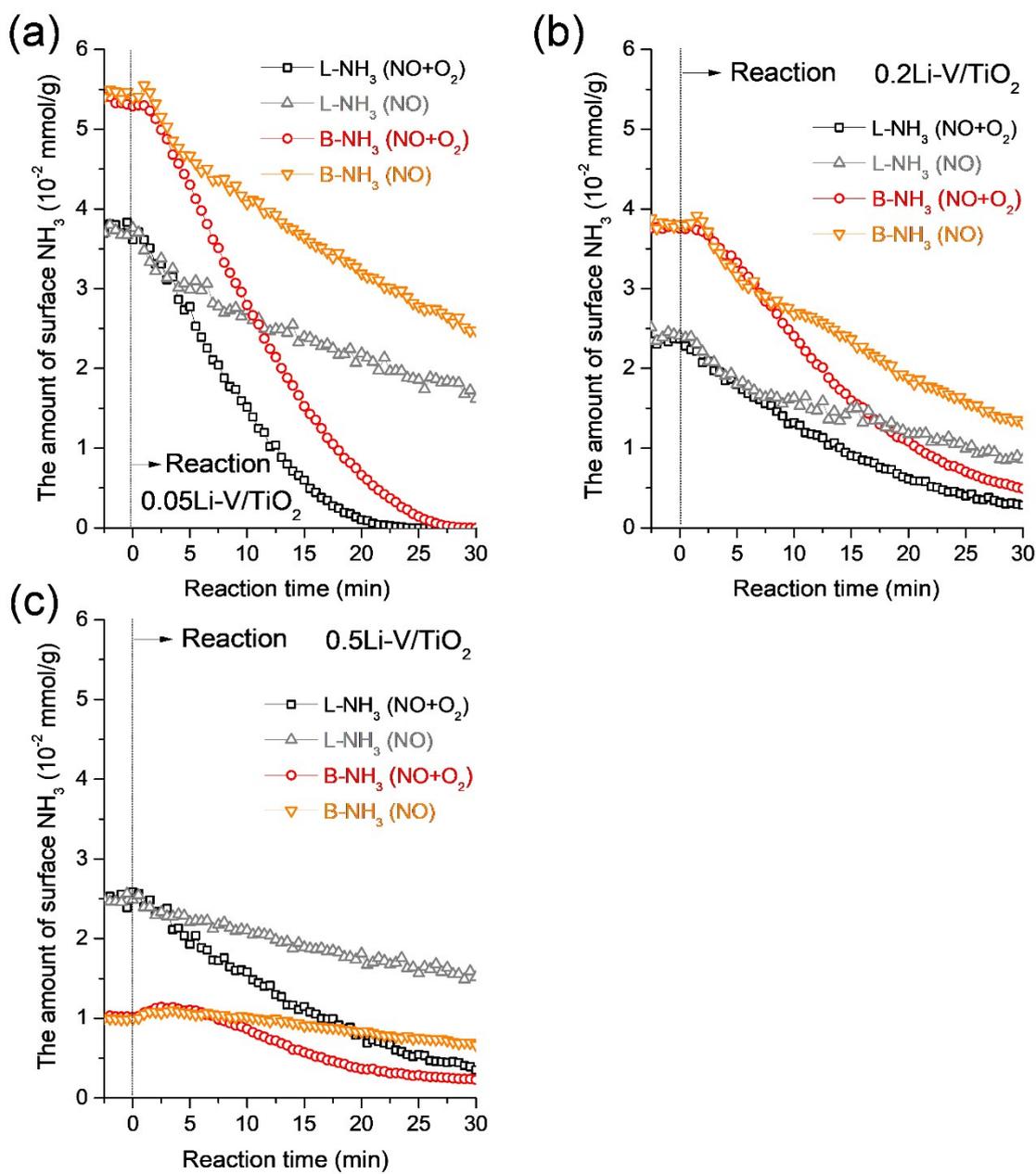


Fig. S6 Time resolved data for the amount of surface L- NH_3 (1220 cm^{-1}) and B- NH_3 (1423 cm^{-1}) species from DRIFT spectra measured during transient reaction under NO or $\text{NO}+\text{O}_2$ conditions at $200\text{ }^\circ\text{C}$ for (a) 0.05Li-V/TiO_2 , (b) 0.2Li-V/TiO_2 , and (c) 0.5Li-V/TiO_2 catalysts. IR signals were converted to the amount of surface NH_3 based on TPD results.

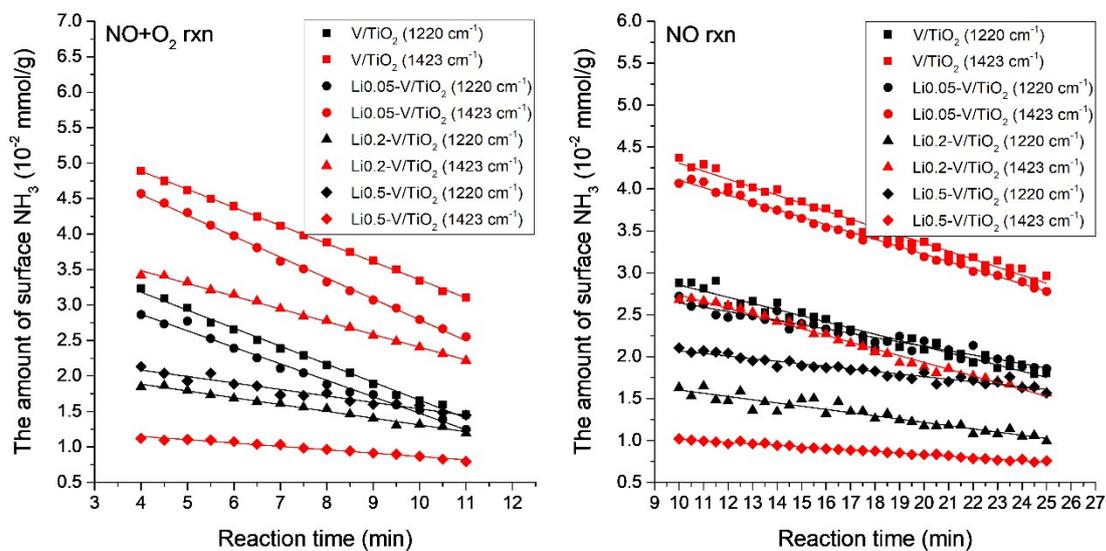


Fig. S7 Determination of the NH_3 consumption rate from time-resolved DRIFT data in Fig. 2 and Fig. S6 for V/TiO_2 and $\text{Li-V}/\text{TiO}_2$ catalysts. For the reaction with $\text{NO}+\text{O}_2$, the data from 4 to 11 min was selected for linear fitting. For the reaction with NO , the data from 10 to 25 min was selected for linear fitting. Fitting results were summarized in Table S1.

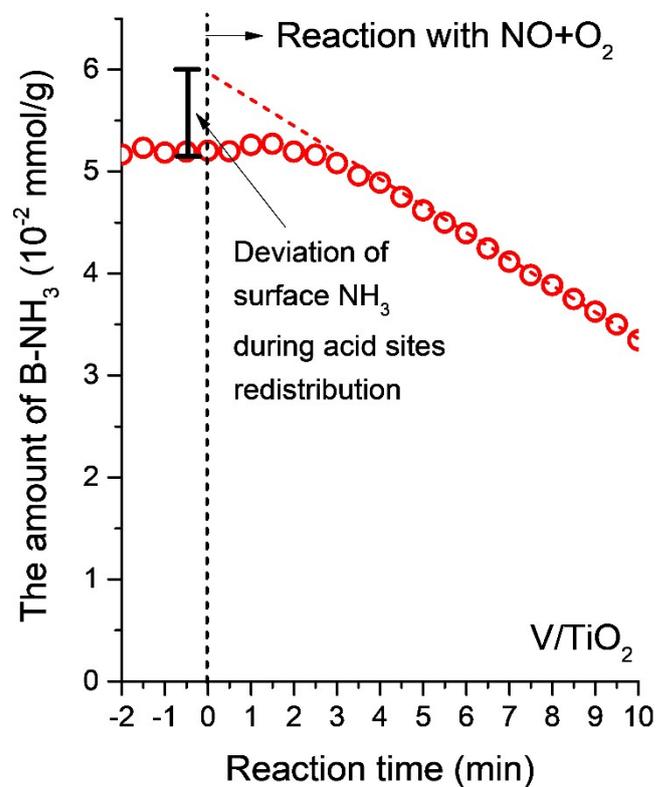


Fig. S8 Instantaneous deviation of the number of Brønsted acid sites in the initial stage of the transient reaction. Transformation of Lewis acid sites to Brønsted acid sites under oxidative condition can underestimate the initial NH_3 consumption rate on Brønsted acid sites.

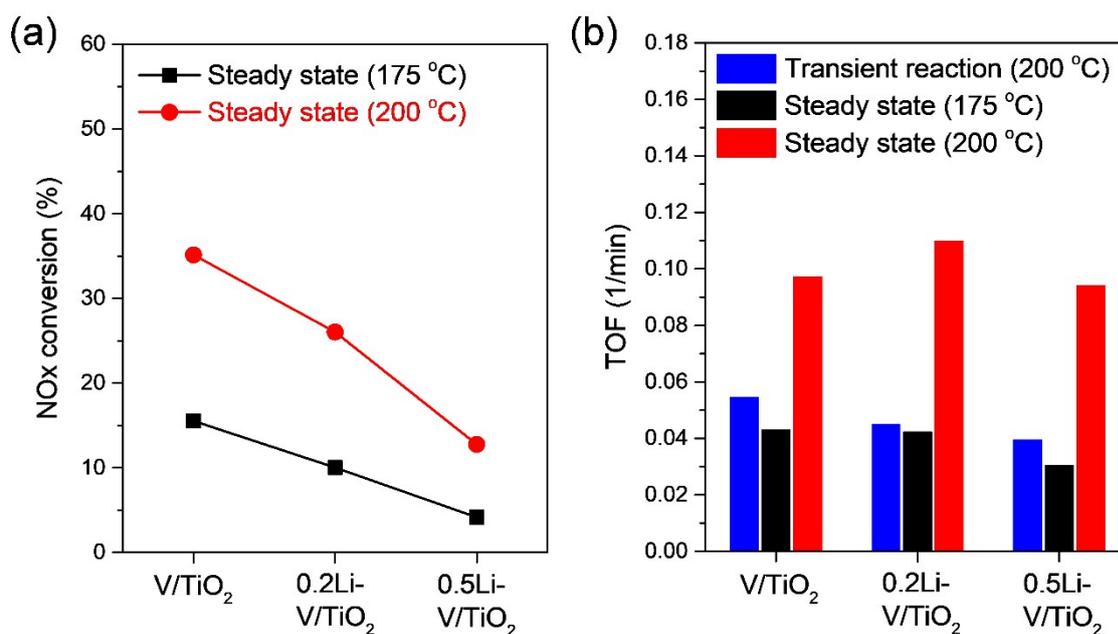


Fig. S9 (a) Steady state NO_x conversions in the plug flow reactor measured at 175 and 200 °C for V/TiO₂ and xLi-V/TiO₂ catalysts. The reaction gas contains 500 ppm NO, 500 ppm NH₃, 10% O₂ balanced with N₂. GHSV: 120,000 h⁻¹. (b) Comparison of catalytic turnovers (TOF) in NH₃-SCR reaction measured under transient reaction condition in the DRIFT cell with values measured under steady state reaction condition in the flow reactor.

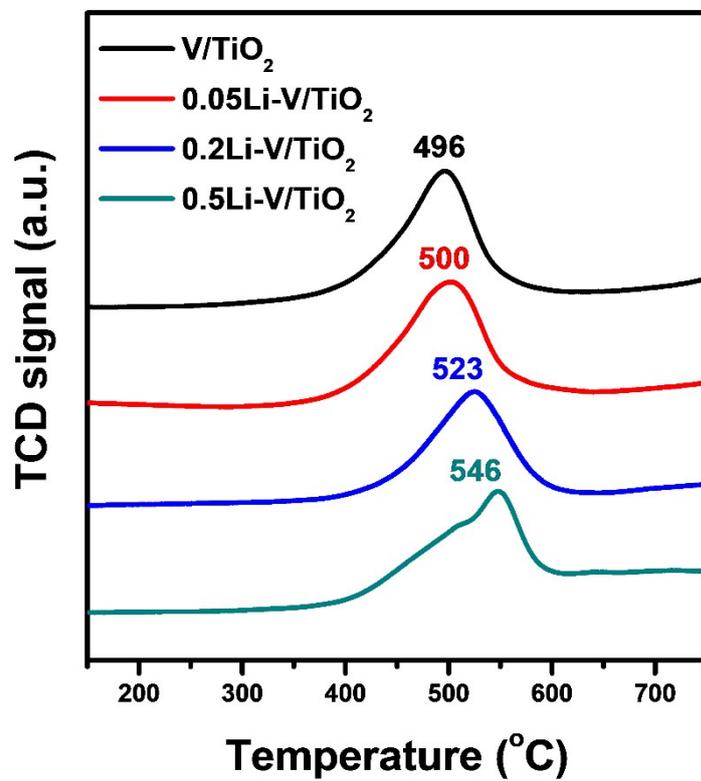


Fig. S10 Hydrogen-TPR results for V/TiO₂ and Li-V/TiO₂ with different Li loading.